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Theoretical Bond Energies: A Critical Evaluation

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The recently proposed scheme of Grimme (BE scheme) (*J. Am. Chem. Soc.* **1996**, *118*, 1529) to calculate intrinsic bond energies (BE's) of hydrocarbons, which define seminal *equilibrium* quantities of chemical structures, is evaluated critically. CH and regular CC bonds are treated well; the corresponding BE's are reliable and self-consistent. In contrast, the performance of the method is markedly reduced for bonds of unusual length, if the bond length is not determined by bond bending or by conjugation. Differences between BE's for CH bonds, which lie within the remarkably narrow range from ca. 103 to 110 kcal mol^{-1}, and CH bond dissociation energies (BDE's, ca. 86−132 kcal mol^{-1}, linear correlation, $R_c = 0.9291$) give a measure of radical (de)stabilization. BE's of sp^x−sp^y CC single bonds correlate linearly with the respective BDE's ($R_c = 0.9987$) and can be used for a reliable prediction of BDE's at almost no computational cost. Individual intrinsic bond energies are used to establish CC and CH bond length−bond energy−bond order correlations. In extension of Grimme's original report, the performance of the model is tested thoroughly for anions, cations, and radicals of hydrocarbons and it is shown that these species are treated less satisfactorily. Attempts to treat non-hydrocarbon compounds by the same procedure are also less successful with the exception of saturated silicon hydrides. Results of this work show that the relationships between bond length−bond order−bond energy as described by established models of the chemical bond can be related to the properties of the electron density at bond critical points. Despite the much greater angle distortion, cyclopropane has a strain energy only slightly larger than cyclobutane. This problem of the nearly equivalent strain energies is readdressed, leading to new estimates for the stabilization of cyclopropane due to CH bond strengthening (11.7 kcal mol^{-1}) and to σ-aromaticity (11.3 kcal mol^{-1}).

I. Introduction

The chemical bond is a fundamental concept in chemistry.[2] Chemical bonds determine the ground state (equilibrium) properties of molecules as well as their reactivity. A fundamental characteristic of a chemical bond is its strength, which usually is evaluated in terms of its bond dissociation energy (BDE).[3] However, BDE's entail two contributions, the intrinsic bond energy (BE), an equilibrium property, and the total (i.e., both geometrical and electronic) reorganization energy (R) of the fragments formed after the dissociation of the bond. While there is little doubt that CH homolysis of a methyl CH bond in propene to yield the resonance-stabilized allyl radical and a hydrogen atom is facilitated by this reorganization (BDE = 88.2 kcal mol^{-1} vs BDE(CH in methane) = 104.9 kcal mol^{-1}),[4] the situation in isobutane is less obvious. The tertiary CH bond is often described as being "weak", but is this intrinsically so (low BE) or to what extent is its comparatively low BDE (96.5 kcal mol^{-1})[4] due to stabilization of the *tert*-butyl radical? BE's are experimentally accessible only for diatomics and highly symmetrical molecules with one type of bond (e.g., methane where the BE is one-fourth of the atomization energy (AE)); they are not directly measurable for other systems due to the reorganization contribution, R. Although this complication renders the separation of BDE's into two nonobservable contributions, BE and R, difficult, the assessment of BE's as an equilibrium property of chemical bonds is highly desirable to understand molecular structures more fully; also, BE's would offer new insights and methods to define and to analyze inter alia molecular strain, aromaticity, and bond length−bond energy relationships. Once a reliable method for the determination of BE's is available, R's can be deduced; these will improve our understanding of bond dissociation processes.

Obviously a theoretical scheme is necessary to separate and to quantify the different contributions to the BDE's. Such a scheme should fulfill several requirements. It must be self-consistent and should be applicable to a broad range of molecules. The method recently suggested by Grimme seems to meet these requirements for hydrocarbons.[1] We report our attempts to improve and to evaluate this model through performance and self-consistency checks. After reevaluation of parameters for the description of CC and CH bonds, calculated BE's are used to examine bond length−bond energy−bond order relationships. These studies provide new insights into the properties of the electron density at bond critical points of CC single, double, and triple bonds. Extensions of the method to ionic and open-shell molecules and to non-hydrocarbons (nitrogen-containing compounds and silicon hydrides) are explored. While limitations are apparent, it is possible to readdress the problem of strain energy in small carbon and silicon rings.

II. Background

Of the several approaches to calculate BE's in the literature,[1,5−10] those of Bader et al.[6] and by Grimme[1] are the most

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appealing. Both are derived from Bader's theory of atoms in molecules, AIM, and thus can be applied to a broad variety of molecules.[11] The approaches are based on the analysis of the electron density, an observable quantity. Bader used the hypervirial theorem to derive an integral over the interaction surface of two bonded atoms as defined by AIM. This integral is proportional to the bond energy when there is minimal charge transfer between the atoms.[12] Bader reported several CC and CH bond energies for hydrocarbons.[6] Cremer and Gauss applied this method to evaluate the strain energies of cyclopropane and cyclobutane.[9] To circumvent the time-consuming numerical integration necessary for this approach, Grimme recently presented an ansatz for the calculation of BE's from the properties of bond critical points (BCP's), which also are derived from the AIM theory.[1] The BCP properties in terms of energy ($E(r_{\mathrm{BCP}})$) and of charge density ($\rho(r_{\mathrm{BCP}})$) characterize a chemical bond.[11] Grimme assumed a relation between BE's and the properties of the corresponding BCP's in the form

$$\mathrm{BE}_i = c_1^{\mathrm{AB}} E_i(r_{\mathrm{BCP}})/(c_2^{\mathrm{AB}} + \rho_i(r_{\mathrm{BCP}})) - c_3^{\mathrm{AB}} \Delta R \qquad (1)$$

where ΔR is the difference in length between the path of maximal electron density between the two atoms and the internuclear distance.[13] Hence, the last term in eq 1 is associated with molecular strain in terms of "bent bonds". The division of an energy density by a charge density (first term in eq 1) yields an energy per charge, which is taken as the energy per electron in a given bond. Remarkably, in this ansatz only the empirical correction of the electron density by a constant c_2^{AB} and by the proportionality constants c_1^{AB} and c_3^{AB} are needed to describe the bond energy of a bond between the atoms A and B. The parameters c_i^{AB} for each type of bond (e.g., CC, CH) are obtained by fitting the atomization energies of a set of molecules to eq 2. Since equilibrium properties are to be determined, AE's for the vibrationless molecules should be used.

$$\mathrm{AE}_j = \Sigma \mathrm{BE}_{ij} \qquad (2)$$

Although the BE's for hydrocarbons reported by Grimme are often reasonable, a few shortcomings are apparent: (1) Grimme only employed a set of eight compounds for the parameter fit. (2) Vibrationless atomization energies were derived from atomization energies at 298 K, corrected by using experimental or PM3 frequencies. (3) Parameter c_2^{CH} (eq 1) was set equal to c_2^{CC}. (4) Parameter c_3^{CC} was determined solely by fitting the atomization energy of cyclopropane; in other words, no rigorous validation for the performance of the model with respect to the treatment of strained molecules was undertaken. (5) Only a few checks were made on the self-consistency and plausibility of the evaluated bond energies. (6) Only bond energies for the methyl ions were given to demonstrate the extension of the method to charged species. No information is available for other charged systems or open-shell compounds. (7) No attempt was reported to expand the scheme to compounds including elements other than carbon and hydrogen.

III. Methods

All structures were optimized at the B3LYP/6-311+G** level using GAUSSIAN 98.[14] The analysis of the electron density was done with the EXTREME program from Bader's AIMPAC package.[15] No spurious maxima in the electron density in the vicinity of triple bonds were detected at the DFT level employed.[1] AE's were determined from G2[16] and G2(MP2)[17] calculations for the vibrationless states of the molecules (i.e., zero-point energy corrections were not applied). For the AE of 2-butyne the value from a CBS-QB3[18] calculation was used, as the G2 methods are not able to treat the rotational profile of the methyl groups correctly (cf. Table 1). BDE's of CH and CC bonds were determined from G2,[16] G2MP2,[17] and CBS-QB3[18] calculations for the parent molecules and the resulting fragments. For the nonlinear least-squares fitting of the AE's MATHCAD 6.0 (MathSoft Inc.) was used.

IV. Results and Discussion

A. Evaluation of the Parameters. The test set we employed to evaluate the parameters of eq 1 is shown in Table 1 together with the AE's from the G2/G2MP2 methods (columns 2 and 3) and with the AE's calculated as the sum of BE's using eq 1 with our final set of parameters (column 4). Although most of the AE's used for the fit agree reasonably well with the data Grimme employed, deviations up to 6 kcal mol^{-1} from his values are found for highly strained molecules like cyclopropene or tetrahedrane. The least-squares fitting proved to be tedious: a spectrum of solutions is obtained due to the flatness of the surface spanned by the variables around the minima. Moreover, the c_1 and c_2 parameters are not fully independent. Our best set of parameters was determined to be

$$c_1^{\mathrm{CC}} = 0.2480 \qquad c_1^{\mathrm{CH}} = 0.2909$$
$$c_2^{\mathrm{CC}} = 0.0982 \qquad c_2^{\mathrm{CH}} = 0.1993$$
$$c_3^{\mathrm{CC}} = 2.2023 \qquad c_3^{\mathrm{CH}} = 0.1711$$

The units of c_1 are e, of c_2 are e bohr^{-3}, and of c_3 are hartree bohr^{-1}. The overall fit has a correlation coefficient of $R_c = 0.9999_6$ (cf. Grimme's 0.9995) and the standard deviation from the reference AE's (cf. Table 1) is 4.57 kcal mol^{-1} (Grimme: 4.90 kcal mol^{-1}). This corresponds to an average error of 0.45 kcal mol^{-1} per bond. Parameter c_3^{CH} proved to be rather insignificant for the fit; when it was omitted, the standard deviation did not change. This is due to the small ΔR values of CH bonds. However, c_3^{CH} becomes significant when, for example, the bending of CH bonds is involved. Attempts to include molecules in the fit that are less satisfactorily described by the method were futile. Better performance with such molecules was not achieved (see discussion below). This provides the first indication of the limitations of the ansatz.

B. Performance of the Model and Limitations. The excellent performance of the model is obvious from the data in Table 1. The agreement between the calculated AE's of aromatic hydrocarbons compared to the G2/G2MP2 values have improved as compared to Grimme's results (e.g.: naphthalene, error −4.2 vs −7.0 kcal mol^{-1}; anthracene, estimated from the AE given by Grimme, −12.9 vs −17.4 kcal mol^{-1}). Nevertheless, the tendency to underestimate the AE's of molecules as the size increases remains. Note that the deviations of the AE's calculated from BE's exceed the deviations of G2MP2 from G2 data. This justifies the use of the computationally less expensive G2MP2 method for larger systems.

Severe overestimations of AE's of up to 30 kcal mol^{-1} are obtained for allene and for molecules containing cyclopropene or polycondensated cyclopropane units; these are not included in the fitting set. As mentioned in the Introduction, attempts to include these compounds in the fit did not improve the overall performance of the ansatz.

Because of the limitations mentioned, neither qualitative nor significant quantitative improvements are expected if, for

TABLE 1: Test Set for the Fitting of Atomization Energies (AE's, kcal mol^{-1} Hypothetical Vibrationless State) from G2MP2, G2, and CBS-QB3 Calculations[a]

	AE				error	
compd	G2MP2	G2	CBS-QB3	ΣBE's	ΣBE's	ΣBE's (%)
methane	419.45	**419.96**	420.11	415.53	−4.43	−1.07
ethane	710.57	**711.28**		711.05	−0.23	−0.03
ethene	561.89	**562.40**		562.94	0.55	0.10
ethyne	403.23	**403.75**	404.04	402.09	−1.67	−0.41
propane	**1004.11**			1005.16	1.06	0.11
propene, rotamer I	857.94	**858.74**		859.11	0.38	0.04
propene, rotamer II	856.05	**856.83**		857.63	0.80	0.09
propyne	702.01	**702.76**	705.19	705.41	2.65	0.38
n-butane	**1297.78**			1299.72	1.94	0.15
isobutane	**1299.54**			1297.61	−1.92	−0.15
trans-butene	**1153.61**			1154.68	1.07	0.09
2-butyne, D_{3h}	999.77	1000.76	**1003.90**[b]	1004.664	0.76	0.08
2-butyne, D_{3d}	981.88	983.68	1003.85	1004.656	0.81	0.08
neopentane	**1596.04**			1588.18	−7.86	−0.49
2,3-dimethybutane	**1887.04**			1881.86	−5.18	−0.28
cyclopropane	850.34	**851.00**		854.33	3.33	0.39
cyclobutane	1145.80	**1146.75**		1150.78	4.03	0.35
cyclohexane	**1759.50**			1766.01	6.51	0.37
tetrahedrane	**789.66**		790.74	795.02	5.36	0.67
prismane	**1247.84**			1239.28	−8.56	−0.69
methylenecyclopropane	989.01	**989.82**		993.05	3.23	0.32
cyclobutene	**996.78**			995.55	−1.23	−0.12
cyclobutadiene	**816.34**			815.89	−0.45	−0.06
trans-butadiene	**1008.69**			1010.93	2.24	0.22
cyclopentadiene	**1170.93**			1180.04	9.11	0.77
benzene	**1361.11**		1367.12	1361.40	0.29	0.02
naphthalene	2152.85	**2154.24**[c]		2150.09	−4.15	−0.19

[a] Values in boldface are the AE's used for the parameter fitting. AE's computed by eq 1 as sums of calculated bond energies (ΣBE's) are given together with errors compared to the reference energies. [b] The CBS-QB3 value was used, as the G2 methods obviously describe the rotational barrier of 2-butyne incorrectly. [c] Value taken from ref 67.

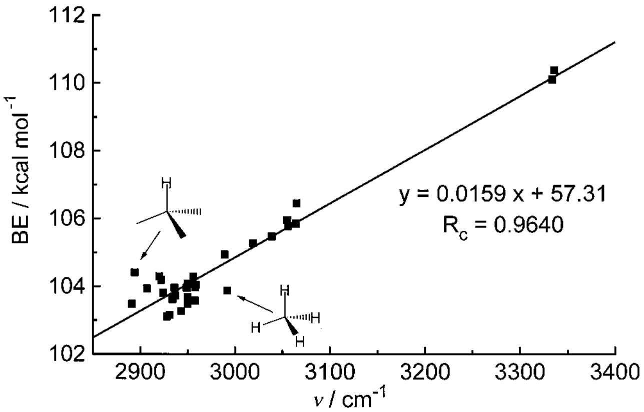

Figure 1. Correlation of isolated CH stretching frequencies[24] with calculated BE's (cf. Supporting Information).

example, G3 or CBS-QB3 AE's are used instead of the AE's from G2 and G2MP2 calculations.

C. Bond Length−Bond Energy−Bond Order Correlations. *(a) CH Bonds.* The correlation of bond lengths with bond orders,[19,20] with dissociation energies,[21] and with bond stretching frequencies[22] has a long history.[23] Equilibrium bond energies offer the possibility of overcoming the disadvantage that (close to) equilibrium quantities have to be compared with energies that are influenced by relaxation effects during bond dissociation. Furthermore, correlations with vibrational frequencies, bond lengths, and bond order schemes can be used to evaluate the consistency of the bond energies derived from Grimme's ansatz.

As a first test, we plotted BE's for a set of CH bonds against isolated CH stretching frequencies (Figure 1), which, as determined by McKean,[24] provide an alternative measure of bond strength.

The correlation coefficient of $R_c = 0.9640$ is satisfactory. With the exception of the bond energy for the tertiary CH bond of isobutane (deviation 1.1 kcal mol^{-1}), all CH energies lie within a range of ±0.75 kcal mol^{-1} from the correlation line. The standard deviation of the CH BE's from the correlation line (0.47 kcal mol^{-1}) gives a measure of the reliability of the calculated BE's.[25] Note that this error mainly stems from the scattering of the alkyl CH data (Figure 1). The correlation of CH BE's with isolated CH stretching frequencies is complemented by an equally good linear correlation between bond length and bond energy for the same set of molecules ($R_c = 0.9671$). Although not quite as good as the excellent correlation of our calculated CH bond lengths (B3LYP/6-311+G**) with the isolated CH stretching frequencies ($d = -8.485 \times 10^{-5}\ \nu$ Å cm + 1.344 Å; $R_c = 0.9960$),[26] they demonstrate the consistency of the calculated CH bond energies.

How are these equilibrium bond energies related to bond dissociation energies? A direct comparison of BE's with D^0_{298} data[4,27] gives a reasonably linear relationship with $R_c = 0.9291$ (Figure 2). However, the slope of 6.12 is far from unity, demonstrating that bond dissociation is facilitated if it leads to stabilized radicals (BE > BDE due to gain of stabilization energy during the dissociation, $R < 0$; BE + R = BDE) and hampered if the radicals are destabilized (BE < BDE, $R > 0$). This emphasizes that the (de)stabilization energies of the dissociated radicals due to steric and electronic effects are reflected—but to a much reduced extent—by the BE values (Table 2); in other words, they are already reflected in the ground state.

Reorganization energies, R's, defined by the difference between CH BE's and D^0_{298} values are a measure of the stabilization of the corresponding carbon radicals.[28] The values of R agree with expectations for simple alkyl, unstrained

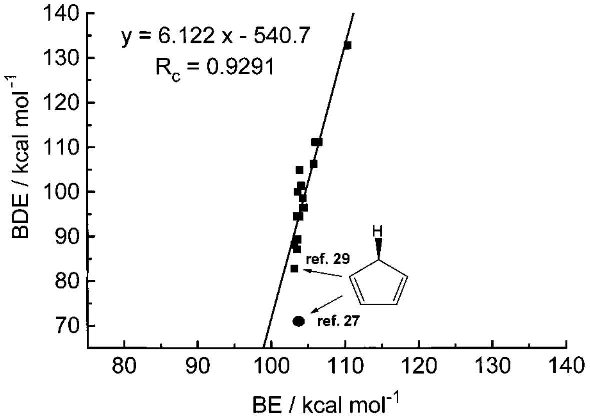

Figure 2. Correlation of BE's with bond dissociation energies (cf. Table 2). The dot indicates the erroneous BDE value for the CH bond of cyclopentadiene (71.1 kcal mol^{-1}) as given in ref 27.

TABLE 2: Reorganization Energies (*R*) for the Dissociation of Several CH Bonds As Defined by the Difference between Experimental D^0_{298} Values and BE's[a]

compd	D^0_{298}(exp)	D^0_{298}(G2/G2MP2)	BE	*R*
methane	**104.9 ± 0.1**[b]	**105.8**	103.9	1.0
	105.1 ± 0.2[c]	105.8		
ethane	**101.4 ± 0.4**[b]	**102.6**	104.1	−2.7
	98.2 ± 1.0[c]	102.7		
propane, CH$_2$	**98.6 ± 0.4**[b]	**100.3**	104.3	−5.7
	97.9 ± 1.0[c]	100.4		
iso-butane, CH	**96.5 ± 0.4**[b]	**98.8**	104.4	−7.9
	93.2 ± 2.0[c]	99.7		
neopentane	*100.0 ± 2.0*[c]		103.6	−3.6
cyclopropane	*106.3 ± 0.3*[c]	**113.0**	105.8	0.5
		113.1		
cyclobutane	*96.5 ± 1.0*[c]	102.1	104.3	−7.8
cyclopentane	*94.5 ± 1.0*[c]		103.9	−9.4
cyclohexane	*94.5 ± 1.0*[c]		103.5	−9.0
ethene	**111.2 ± 0.8**[b]	**112.0**	106.0	5.2
	110.0 ± 2.0[c]	112.2		
ethyne	**132.8 ± 0.7**[b]	**135.0**	110.4	22.4
	132.0 ± 5.0[c]	135.2		
propene, CH$_3$	**88.2 ± 2.1**[b]	**88.7**	103.2	−15.0
	86.3 ± 1.5[c]	89.0		
cyclopentadiene, CH$_2$	*71.1 ± 1.5*[c]	85.5	103.2	−20.3
	82.9 ± 2.2[d]			
propyne, CH$_3$	*89.4 ± 2.0*[c]	**93.2**	103.6	−14.2
		93.4		
2-butyne	*87.2 ± 2.0*[c]		103.5	−16.3
benzene	**111.2 ± 0.8**[b]		106.5	4.7
	110.9 ± 2.0[c]			

[a] If available, D^0_{298} Values from ref 4 (boldface) were used. All energies in kcal mol^{-1}. As reference D^0_{298} from G2 (boldface) and G2MP2 calculations are given. [b] Values taken from ref 4. [c] Values taken from ref 27. [d] Value from ref 29.

cycloalkyl, alkenyl, arenyl, allyl, and propargyl radicals (radical stabilizations around 3−9 kcal mol^{-1} by methyl and ethyl groups and around 14−18 kcal mol^{-1} for cases with allylic and propargylic resonance. However, a significant (ca. 5 kcal mol^{-1}) *destabilization* for ethene and benzene and a large electronic *destabilization*, $R = 21.6$ kcal mol^{-1}, for the ethynyl radical is predicted by the BE method. An analogous situation is reported by Sanderson[5] for the dissociation of HCN into H$^•$ and CN$^•$; *R* values of 4.0, 5.9, and 13.0 kcal mol^{-1} were reported by Zhixing[8] for ethene, benzene, and ethyne, respectively.

The relevance of the BE concept is illustrated by the CH BDE of cyclopentadiene. While the D^0_{298} value of 71.1 kcal mol^{-1} reported by McMillen and Golden[27] deviates considerably from the BE/BDE correlation line, the calculated G2MP2 value (85.5 kcal mol^{-1}) fits within the expected accuracy. The latter agrees with the experimental results of Hehre et al. (D^0_{298} = 82.9 ± 2.2 kcal mol^{-1}).[29] Thus, the BE's and the BE/BDE correlation can help identify erroneous experimental D^0_{298} values.

TABLE 3: CC BE's (kcal mol^{-1}) of Selected Hydrocarbons

compd	BE	compd	BE	compd	BE
ethane	86.6	cyclopropane	73.2	benzene	120.5
ethene	139.1	cyclobutane	79.1	butadiene, C═C	136.2
				C—C	104.2
ethyne	181.3	cyclohexane	87.3	butadiyne, C≡C	178.0
				C—C	125.0

A lesson can be learned from this section: While the experimental CH D^0_{298} values vary considerably, ca. 80−135 kcal mol^{-1} in the set used here, the corresponding calculated BE's only range from ca. 103−110 kcal mol^{-1}.[30] Thus, differences in CH D^0_{298} values are not due mainly to changes in the intrinsic bond strengths but are determined mostly by geometric and electronic reorganizations during bond dissociation. For example, the BDE of the tertiary CH bond in isobutane is 11.9 kcal mol^{-1} lower than that for a CH bond in methane, but the BE's (104.4 and 103.9 kcal mol^{-1}, respectively) are nearly the same and even follow the opposite order. While Rüchardt discussed this problem in 1970 in terms of ground-state destabilization and product stabilization,[31] it is now clear that the "weakness" of a bond (toward dissociation) need not be a property of the bond itself! The correlation between BE's and BDE's implies that the factors determining the *R* in the course of the bond dissociation—although to a lower extent—operate in the ground state as well.

(b) CC Bonds. As has already been pointed out by Grimme,[1] the calculated CC bond energies are in line with expectations (Table 3). The CC bond energies rise with increasing bond order, the relative energies of CC single, double, and triple bonds follow the 1:1.6:2.1 order, demonstrating the lower BE of π vs σ CC bonds. That BE's are reduced by strain is obvious in the homologous series cyclopropane, cyclobutane, and cyclohexane with CC BE's of 73.2, 79.1, and 87.3 kcal mol^{-1}, respectively. The BE of a CC bond in benzene (120.5 kcal mol^{-1}) is 7.7 kcal mol^{-1} higher than the average of the BE's of the CC double bond in ethene (139.1 kcal mol^{-1}) and the CC single bond in ethane (86.6 kcal mol^{-1}). Conjugation in polyenes/polyynes leads to stronger (formal) single bonds and weakens the multiple bonds.

While the self-consistent nature of the theoretical CH BE's is demonstrated convincingly by the correlation with isolated CH vibration frequencies, no such straightforward test exists for CC BE's. Therefore, resort was made to correlations of CC BE's with CC BDE's, with energy data from VB calculations for CC bonds of polycyclic aromatic hydrocarbons (PAH's),[32] with bond indices of CC bonds in PAH's,[33] and with bond lengths of a large set of CC single, double, and triple bonds.

The use of CC BDE's to check a possible correlation with the CC BE's seems straightforward. Unfortunately, accurate experimental data are scarce;[34] the often cited values compiled by McMillen and Golden[27] are outdated (see below). We therefore decided to use set of small hydrocarbons for the correlation (Table 4). For this set, accurate CC single bond BDE's can be deduced from the well established heats of formation of the precursor and of the resulting radicals as given for the G2 test set[35] or can be calculated from G2MP2, G2, or CBS-QB3 data.

If BE's of the test set are compared with the experimental and the three sets of calculated BDE's, (very) good linear correlations are obtained ($R_c \geq 0.9970$, Table 4, Figure 3). As

TABLE 4: Experimental and Calculated (G2MP2, G2, CBS-QB3) CC BDE's and CC BE's for Small Hydrocarbons (kcal mol^{-1})[a]

	BDE						error BDE predicted[d]			
compd	exp I[b]	exp II[c]	G2MP2	G2	CBS-QB3	BE	exp II	G2MP2	G2	CBS-QB3
ethane	90.4 ± 0.3	**90.1 ± 0.3**	91.1	90.8	90.7	**86.6**	−1.8	−1.1	−1.1	−1.7
propane	85.8 ± 1.0	**88.9 ± 0.6**	90.8	90.5	89.8	**87.0**	0.2	0.0	0.0	0.0
butane,										
CH_2-CH_3	86.5 ± 1.0		91.5	91.3	91.0	**86.9**		−0.8	−0.9	−1.3
CH_2-CH_2	82.2 ± 1.0	**87.8 ± 1.0**	90.6	90.3	89.4	**87.2**	1.7	0.6	0.6	0.9
isobutane	85.7 ± 1.0	**88.6 ± 0.7**	90.7	90.3	89.4	**86.9**	0.3	−0.1	−0.1	0.3
neopentane	84.1 ± 1.0	**87.9 ± 0.7**			89.4	**86.2**	−0.3	−1.2		−1.1
propene,										
$C-CH_3$	100.6 ± 2.0	**101.8 ± 1.1**	102.9	102.5	101.5	**93.8**	0.1	1.0	1.0	1.6
propyne,										
$C-CH_3$	125.7 ± 1.0	**125.9 ± 1.0**	128.6	128.1	128.3	**104.3**	−4.4	−4.5	−4.6	−5.0
butadiene										
$=C-C=$		**116.9 ± 1.8**	118.0	117.4	115.6	**104.2**	4.4	5.9	6.0	7.5
butenyne,										
$\equiv C-C=$			140.6	140.0	139.0	**112.9**		−0.1	0.0	0.9
butadiyne,										
$\equiv C-C\equiv$			164.6	164.0	165.5	**125.0**		−0.7	−0.8	−2.1
correlation										
BE vs BDE	**0.9836**	**0.9857**	**0.9987**	**0.9987**	**0.9970**					
RMSE[e]							**2.4**	**2.3**	**2.5**	**3.0**

[a] Errors (kcal mol^{-1}) of BDE's predicted from BE's and the linear correlations between BDE's and BE's. [b] Values taken from ref 27. [c] Values calculated from data given in ref 35. [d] Difference between the BDE (experimental, calculated) and the value predicted from the corresponding BE and the linear correlation between the BDE's and the BE's. Equations used: BDE(exp II) = 1.874BE − 73.99; BDE(G2MP2) = 1.917BE − 75.84; BDE(G2) = 1.916BE − 76.25; BDE(CBS-QB3) = 1.936BE − 78.60. [e] Root-mean-square error of the predicted BDE's (kcal mol^{-1}).

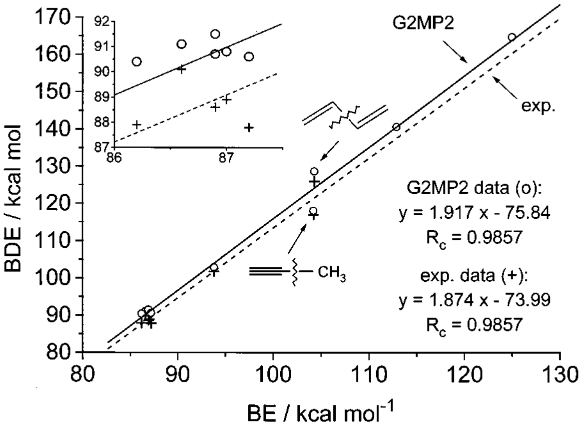

Figure 3. Correlation of BE's for CC single bonds (Table 4) with experimental BDE's and BDE's from G2MP2 calculations.

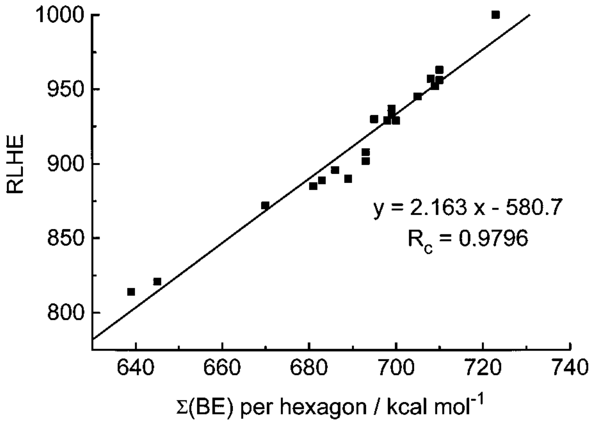

Figure 4. Correlation of BE's with relative local hexagon energies (RLHE) from VB calculations by Li and Jiang[32] (cf. Supporting Information).

we have found in the analysis of CH bonds, the BDE's are significantly higher than the BE's if alkenyl or alkynyl radicals are generated by the bond dissociation process. As before, the factors that determine the radical stability are reflected—although to a much lesser extent—in the ground state. The linear correlations between the BE's and the BDE's reveal the consistency of the calculated BE's convincingly. In addition, the very good correlation of the BDE's and BE's allows the prediction of BDE's from BE's with the accuracy reflected by the low root-mean-square deviation of the BDE's from the correlation lines (<3.0 kcal mol^{-1}, Table 4). On the basis of the experimental (data set II), G2MP2, and G2 BDE's, significant deviations of 4−6 kcal mol^{-1} are only observed for butadiene and propyne. Note that BE's are available at almost no computational costs compared to G2(MP2) or CBS-QB3 calculations. Furthermore, this BE scheme based procedure is conceptually simpler than other treatments that have been proposed recently.[34]

As an alternative approach intended to expand the analysis to aromatic systems, we correlated BE's with the CC bond energies calculated by Li and Jiang for individual benzene rings in PAH's.[32] These energies were used by Li and Jiang to define a measure for local aromaticity and reactivity and were given as relative local hexagon energies (RLHE's) relative to benzene (RLHE = 1000). RLHE's should correlate with the sum of BE's for the individual carbon rings. Indeed, for a set of 10 PAH's (cf. Supporting Information), a satisfactory linear correlation with $R_c = 0.9795$ was established (Figure 4).

Linear relationships of even somewhat better quality emerged when BE's for a series of [*n*]acenes ($n = 1-5$, $R_c = 0.9917$) and [*n*]phenacenes ($n = 3-5$, $R_c = 0.9877$) were plotted against the Fulton CC bond indices[36] of the CC bonds, reported by Wiberg (Figure 5).[33] The Fulton indices are derived from the sharing of electrons between nuclear basins as defined by Bader's AIM theory and are obtained from an analysis of the electron density.[36]

Two conclusions can be drawn: (1) As with the CH BE's, the CC BE's calculated with the BE ansatz are self-consistent. (2) Within the (limited) range of the CC bonds discussed here and within the methodological framework, the bond energies and bond orders not only correlate but do so linearly. Since

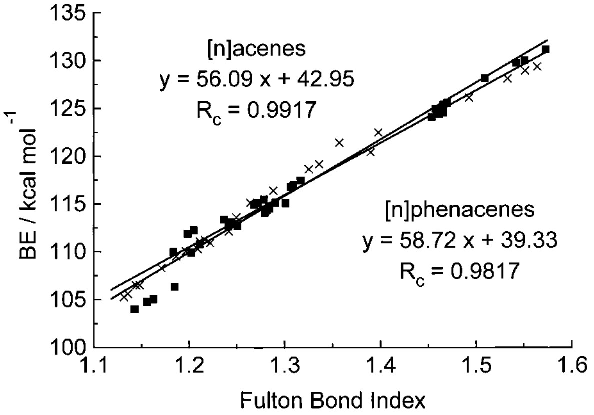

Figure 5. Correlation of BE's with Fulton bond indices[33,36] for [*n*]-acenes (×) and [*n*]phenacenes (squares) (cf. Supporting Information).

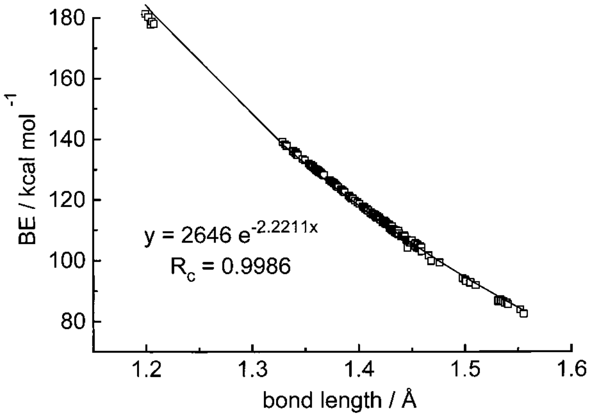

Figure 6. Correlation of BE's with bond lengths of 202 CC single, aromatic, double, and triple bonds. Data are given in the Supporting Information.

Wiberg found that Fulton bond indices correlate with the bond lengths of PAH's, a relationship between CC bond energies and CC bond lengths must also exist. Such relationships might have quite general validity.

A study including over 200 single, aromatic, double, and triple CC bonds revealed a general BE-bond length relation for CC bonds (Figure 6, data are given in the Supporting Information). Although the data fit a linear model with excellent quality ($y = -276.2x + 507.1$; $R_c = 0.9954$), it is tempting to apply an exponential model ($y = 2646 \exp(-2.221x)$; $R_c = 0.9986$; Figure 6) because it is equivalent to Krygowski's exponential relationship (eq 3) between the bond energy $E(n)$ of a CC bond of order n and its bond length, $d(n)$. In this model, $E(1)$ and $d(1)$ define the energy and length of a prototype CC single bond.[37] The Krygowski model was deduced from Pauling's bond length−bond order relationship[19] (eq 4) and the Johnston−Parr dependence of bond energy on bond order[21] (eq 5).

Grimme's idea to establish a link between the properties of bond critical points and bond energies therefore points out a connection between the topology of the electron density and the older intuitive concepts of chemical bonding. However, this has its drawbacks; for example, the BE ansatz suffers from the same limitations that characterize the models defined by eqs 3−5: The underlying philosophy of all these treatments is a continuous transformation of single into double into triple bonds with decreasing bond length. While this holds for a set of aromatic and conjugated molecules where bond length changes are due to changes in π bond orders, problems can be expected when bond length variations are not due to the effects of conjugation, in other words, are due to strain.

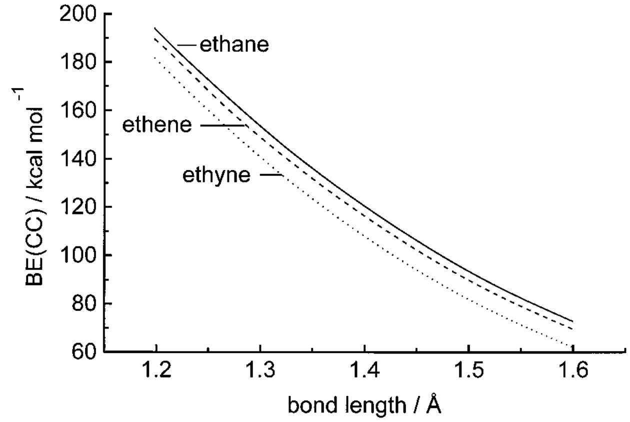

Figure 7. Dependence of the CC BE's of ethane, ethene, and ethyne on the CC bond length. CH distances, HCH and CCH angles were optimized at each point.

D. Bond Energies of Strained Bonds. Strain is explicitly treated by the BE ansatz if it is caused by bent bonds, a prototypical example being cyclopropane. How does the model perform when strain is induced by compression/elongation of a bond? How do the charge and energy densities at the bond critical points respond? The seminal studies of Bader et al.[11] and Cremer et al.[38] do not deal with this problem.

To gain more insight, we evaluated BE's for the single, double, and triple CC bonds in ethane, ethene, and ethyne, respectively, with imposed CC bond lengths between 1.20 and 1.60 Å in each case (Figure 7). CH bond lengths and bond angles were optimized at each point.

Contrary to the expectations evoked by Bader's statement that the electron density at bond critical points of double and triple bonds is increased due to the presence of π electrons,[39] the CC BE's calculated with the BE ansatz are determined mainly by the CC bond length, as is obvious from Figure 7. The CC BE's thus reflect largely a property of the σ electron density. The π electron density plays a minor, only slightly modifying role; counterintuitively, at a constant CC bond length, calculated BE's are lower if π electrons are present (cf. the curves for ethane, ethene, and ethyne). Qualitatively identical graphs were obtained when the charge or energy density was plotted against the CC bond length; therefore, these two quantities, as well as their combination in terms of Grimme's BE's (eq 1) are not able to distinguish between bonds of different order if "nonequilibrium" bond lengths are imposed. If π conjugation is present, cf., for example, the central CC bond in butadiene, changes in the calculated bond orders and energies probably are largely determined by the concomitant change in the σ electron density due to the modified bond length and are nearly independent of the change in π densities.

While the observed increase of bond energy in the course of bond "compression" (Figure 7) is physically unreasonable, the decrease of the BE with increasing bond length seems meaningful. Yet, if the sum of CH and CC BE's for, for example, ethane is plotted against the CC bond length in order to describe the potential for the CC bond stretch, the loss in bond energy caused by bond stretching is overestimated if the corresponding B3LYP/6-311+G** energy at each point is taken as reference (Figure 8). Further, the analytical form of the dissociation curve deduced from the sum of BE's does not reflect the required profile for CC bond homolysis. According to the BE method no equilibrium geometry exists!

To an appreciable extent, such failures of the ansatz are due to the simplicity of the model, inter alia, due to the neglect of

TABLE 5: Compilation of AE's (kcal mol^{-1}) Obtained from G2 (Boldface) or G2MP2 Calculation and from the Sums of BE's, Respectively, of Several Ions and Radicals[a]

	cation			radical			anion		
	AE (G2/G2MP2)	ΣBE	error (%)	AE (G2/G2MP2)	ΣBE	error (%)	AE (G2/G2MP2)	ΣBE	error (%)
methyl	**340.26**	333.78	−6.49 (−1.91)	**306.50**	318.11	11.62 (3.79)	**279.22**	297.01	17.80 (6.37)
ethynyl				**262.19**	289.10	26.90 (10.26)	**306.43**	284.63	−21.80 (−7.12)
allyl	834.36	794.54	−39.83 (−4.77)	**762.46**	775.10	12.64 (1.66)	747.20	755.77	8.57 (1.15)
pentadienyl	1303.22	1249.43	−53.79 (−4.13)	1212.67	1227.53	14.85 (1.22)	1209.37	1205.37	−4.01 (−0.33)
3-cyclopentenyl	1321.46	1270.92	−50.54 (−3.82)	1222.22	1239.24	17.03 (1.39)	1201.33	1205.68	4.35 (0.36)
4-cyclopentenyl	1296.65	1257.56	−39.08 (−3.01)	1210.09	1228.54	18.44 (1.52)	1181.43	1189.73	8.30 (0.70)
cyclopentadienyl				1084.52 ($^2A_2$)	1101.012	16.50 (1.52)	1101.26	1081.22	−20.04 (−1.82)
cyclopentadienyl				1083.92 ($^2B_1$)	1101.007	17.09 (1.58)			
cyclopropenyl	**690.68**	636.20	−54.48 (−7.89)	**570.92**	595.36	24.44 (4.28)	**537.59**	564.55	26.95 (5.01)
ethene	**575.39**	550.76	−24.63 (−4.28)	-			**488.85**	539.79	50.94 (10.42)

[a] Errors (kcal mol^{-1}, in parenthesis: error in %) relative to the G2/G2MP2 reference values. The parameter set obtained from fitting neutral closed-shell species was used.

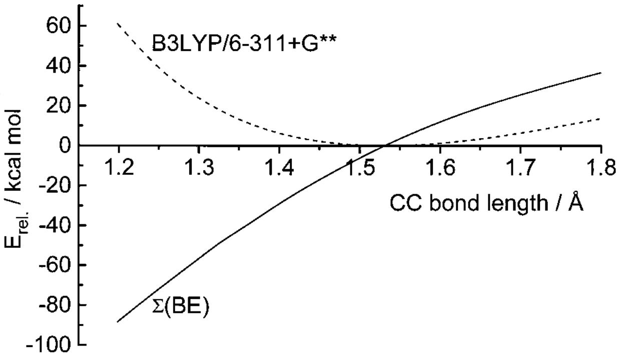

Figure 8. Deformed ethane: variation of the sum of BE's (CC + CH) and absolute energy (B3LYP/6-311+G**) of ethane relative to the equilibrium energies as a function of the CC bond length. CH distances, HCH and CCH angles were optimized at each point.

nuclear−nuclear repulsion. Hence, the simple inclusion of more and more molecules in the fitting set to attain a better parametrization will not lead to an increase in overall performance of the model (as pointed out above). The poor results in the case of allene, cyclopropene, and methylenecyclopropene can be traced back to this problem.

E. Treatment of Charged and Open Shell Species. An obvious extension of the BE method is its application to charged species and to open shell systems. Grimme reported promising results for the methyl cation and anion.[40] However, no further data are available for other ions, radical ions, and neutral radicals.

Table 5 shows a compilation of our results. The G2 and G2MP2 data serve as references, and the same parameters derived for the hydrocarbons were employed in eq 1. Some general conclusions can be drawn: AE's of cationic systems are generally underestimated by the BE method by ca. 3−5%, the bond energies of neutral radicals are overestimated by ca. 1.5%. AE's of anionic species deviate by ±2% from the reference values. As with parent cyclopropene, the description of the cyclopropenyl ions and the cyclopropenyl radical is less accurate.

There are unexpectedly large deviations of AE's calculated from individual bond energies with respect to the G2 reference values. The methyl anion error is 17.8 kcal mol^{-1} (6.4%). This appears to be due to the different geometries used in these calculations. If the electron densities from B3LYP/6-311+G**//MP2/6-31G* or B3LYP/6-311+G**//B3LYP/6-311G(2d,d,p) single point calculations are used, the sum of individual bond energies deviate from the G2 reference by only 5.4 (2.0%) and 1.4 kcal mol^{-1} (0.5%), respectively. Note that the MP2/6-31G* and B3LYP/6-311G(2d,d,p) geometries are used for the evaluation of the G2 and CBS-QB3 reference energies, which are in close agreement with each other (AE(G2) = 279.2 kcal mol^{-1}; AE(CBS-QB3) = 278.3 kcal mol^{-1}).[40] Concerning the problem that the use of different geometries to obtain BE's and G2 reference data may be a general source of error, it has to be emphasized that the methyl anion is a special case since it is only weakly bound.[41]

A similar problem is observed for the radical anion of ethene, where the B3LYP/6-311+G** geometry is much less twisted (φ_{HCCH} = 10.1°, $a(^{13}C)$ = 0.63 mT) than that given by MP2/6-31G* (φ_{HCCH} = 50.3°) or B3LYP/6-311G(2d,d,p) (φ_{HCCH} = 48.2°, $a(^{13}C)$ = 3.07 mT). Correspondingly, the initial error of 50.9 kcal mol^{-1} (10.4%, B3LYP/6-311+G** geometry) compared to the G2 reference is reduced to 10.3 kcal mol^{-1} (2.1%) if the electron density from a B3LYP/6-311+G**//B3LYP/6-311G(2d,d,p) calculation is used. Again, AE's calculated from G2 and CBS-QB3 data agree well (488.9 vs 490.4 kcal mol^{-1}).

Finally, unusually large deviations from the reference data are encountered for the AE's of the ethynyl radical (26.9 kcal mol^{-1}, 10.3%) and of the ethynyl anion (−21.8 kcal mol^{-1}, −7.1%). As with all nonconjugated radicals and anions, problems might be due to the presence of electrons that formally do not participate is the formation of a chemical bond and are thus not included in the evaluation of AE's according to eq 1.

Although the accuracy of the BE method is much less for the charged and the open shell systems, the general order of AE's within the series AE(cation) > AE(radical) > AE(anion) is well reproduced. The only exceptions are found for the pairs ethynyl radical/anion and cyclopentadienyl radical/anion. Here, G2/G2MP2 data indicate a stabilization of the anions relative to the radicals in contrast to the BE method that gives the opposite energetic order.

Further improvements might be achieved if BE parameters for cations, anions, and radicals were evaluated separately.

F. Treatment of Non-Hydrocarbons. *(a) Nitrogen-Containing Compounds.* The approaches of Bader,[6] Cremer,[9] and Grimme[1] have not been extended to compounds other than hydrocarbons. Our trials revealed this to be far from trivial. Attempts to include, for example, nitrogen containing compounds were futile: after the fitting procedure, no matter whether bond curvature was taken into account (by fitting c_3^{AB}-parameters) or whether the c_2^{AB} parameters were assumed to be equal to c_1^{AB},[1] the resulting atomization energies had errors up to 50%. No improvement was achieved by dividing the fitting set into subsets comprising (a) only pure nitrogen compounds (nitrogen, tetraazatetrahedrane, hexaazabenzene, hexaazaprismane), (b) compounds with only NH and NN bonds (ammonia, hydrazine, *cis*- and *trans*-diimide), (c) compounds with CH, CC, and CN bonds (trimethylamine, acetonitrile, methylisonitrile, *cis*- and *trans*-dimethyldiimide, pyridine, pyridazine, pyrimidine, pyrazine). Two reasons for these failures are apparent, namely the effect of charge transfer and the neglect of the electron densities of the lone pairs. Efforts to include the lone pair densities explicitly by modified versions of eqs 1 and 2 were hampered by the failure of the AIM program to identify the nitrogen lone pairs as (3, −3) critical points in $-\nabla^2\rho$ (cf. ref 11) in several cases.

(b) Silicon Hydrides. Extension to silicon hydrides was more successful. However, problems arose due to the topology of the electron density of compounds with SiSi double bonds. Instead of a single (3,−1) BCP for the SiSi bond of disilaethene, a (3,−3) maximum accompanied by two (3,−1) BCP's was found. Curiously, this not only was a feature of the bent C_{2h} conformer but also of the planar D_{2h} saddle point.

AE's of SiH_4 ... n-Si_4H_{10} and of cyclo-Si_3H_6 from G2 calculations were fitted by means of a simplified approach. The parameters below

$$c_1^{SiSi} = 0.8475 \qquad c_1^{SiH} = 2.5077$$
$$c_2^{SiSi} = 0.3159 \qquad c_2^{SiH} = 1.3049$$
$$c_3^{SiSi} = 0.6161$$

gave a linear correlation between the AE's (G2) and the sum of BE's of the individual compounds with a standard deviation of 0.51 kcal mol^{-1} and a correlation coefficient of 0.9999$_{97}$. The AE of tetrasilacyclobutane, which was not included in the fitting set, is reproduced with an error of −2.5 kcal mol^{-1} (−0.3%). Trial calculations including trisilapropene (+46.5 kcal mol^{-1}/7.9% vs G2) and hexasilabenzene (D_{3d}) (+38.4 kcal mol^{-1}/4.7% vs G2MP2) showed that the parameters only are suitable for the treatment of SiSi single bonds; efforts to include such unsaturated compounds in the fitting procedure also were futile. SiH and SiSi BE's for some acyclic silicon hydrides can be found in the Supporting Information; data for cyclic silicon hydrides are shown in Figure 9.

V. Applications

Strain Energies of Cyclopropane and Cyclobutane and Their All-Sila Analogues—An Old Controversy. According to Baeyer's classical definition given in 1885,[42] strain in three-membered rings should be significantly higher than in their four-membered homologues due to the smaller CCC bond angles. The unexpected similarity of the strain energies of cyclopropane (27.5 kcal mol^{-1})[43] and of cyclobutane (26.5 kcal mol^{-1})[43] must be due to additional effects.[9,43−45,47] Is cyclopropane stabilized by some mechanism or is the strain of cyclobutane unusually high? Besides torsional effects and nonbonded interactions the Dunitz-Schomaker 1,3-CC repulsion in cyclobutane, different rehybridization, and σ-aromaticity might contribute. Rehybridization, which could reduce the strain energy of cyclopropane by CH bond strengthening, was discussed quite early, for example, in 1964 in the textbook by Roberts and Caserio.[44] Dewar and McKee suggested in 1980[45] that σ-aromaticity due to the delocalization of the six electrons in the CC bonds might stabilize cyclopropane. The most sophisticated analysis of strain in small rings by Cremer and Gauss[9] considered all these effects.

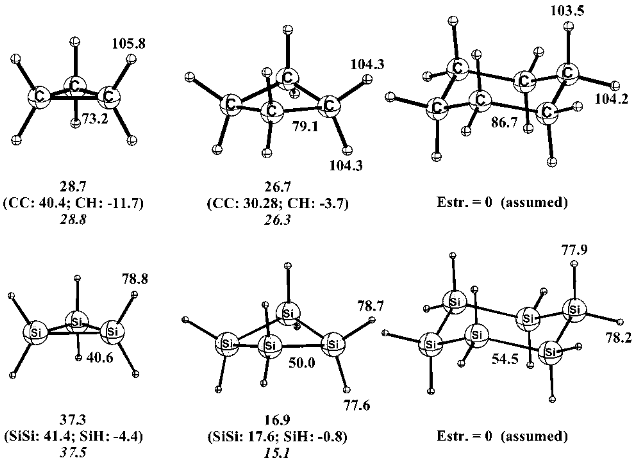

Figure 9. Evaluation of strain energies of small carbon and silicon rings relative to cyclohexane and hexasilacyclohexane. Individual bond energies are indicated at the bonds. Values below the molecules are: strain energies derived from BE's, total strain energies for individual types of bonds (in parentheses), strain energies derived from G2 calculations for the small ring compounds and G2MP2 calculations for the six membered reference system. All energies are in kcal mol^{-1}.

Although BE's cannot be divided into individual contributions, CH bond energies from a BE analysis can be used to evaluate the extent of CH bond strengthening in small rings. Closely related is the problem of rehybridization in the silicon analogues, trisilacyclopropane and tetrasilacylobutane. Unlike their carbon counterparts, three-membered silicon rings have much higher strain energies than the homologous four-membered rings.[45−47] As pointed out by Schleyer[47] and by Sax,[48] silicon is less prone toward rehybridization than carbon; thus, no significant stabilization of trisilacyclopropane due to stronger SiH bonds can be expected. As saturated three- and four-membered rings are treated well by the BE method, insight concerning the strain in small rings should result from the analysis of BE's. Hence, we applied our modified version of the BE method to the three- and four-membered carbon and silicon rings; cyclohexane and its hexasila analogue were chosen as the "strainless" references.[49]

The cyclopropane and cyclobutane strain energies evaluated by comparison of the BE's per CH_2 group for the small ring compounds with that of cyclohexane were 28.7 and 26.7 kcal mol^{-1}, respectively. These values agree excellently with the strain energies for the vibrationless molecules, 28.8 and 26.3 kcal mol^{-1}, respectively, based on G2 calculations for cyclopropane/cyclobutane and G2MP2 calculations for cyclohexane. A decomposition of the total strain into the CC and CH bond contributions shows that the total CC bond strain of cyclopropane (40.4 kcal mol^{-1}) is 10.1 kcal mol^{-1} higher than that of cyclobutane (30.3 kcal mol^{-1}). This difference is largely compensated by the 8.0 kcal mol^{-1} greater increase of CH bond strength in cyclopropane. Relative to cyclohexane, the total CH bond energy increase in cyclopropane is 11.7 kcal mol^{-1} (1.95

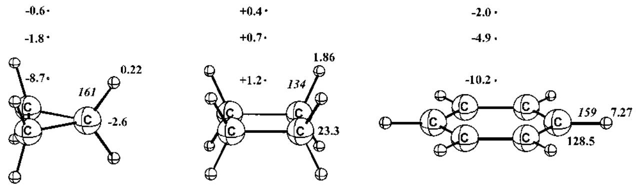

Figure 10. Nucleus independent chemical shifts (NICS, B3LYP/6-311+G**) and experimental[68] ^{1}H, ^{13}C chemical shifts as well as ^{1}H−^{13}C coupling constants (in italics) for cyclopropane, cyclobutane, and benzene. NICS values were calculated points 1.0, 2.0, and 3.0 Å above the centers of each molecule. Chemical shifts in ppm relative to TMS, coupling constants in Hz.

kcal mol^{-1} per bond), compared to only 3.7 kcal mol^{-1} total increase (0.46 kcal mol^{-1} bond^{-1}) in cyclobutane.[50]

A number of unusual magnetic properties of cyclopropane are noteworthy. Its large diamagnetic susceptibility (-39.2×10^{-6} cm^3 mol^{-1}),[51] which is accompanied by a considerable magnetic susceptibility anisotropy (-11.6×10^{-5} J T^{-2} mol^{-1}),[52,53] was attributed to the existence of a diamagnetic ring current in the three-membered ring.[54,55] While doubt has been expressed concerning this interpretation,[56] further support for cyclic electron delocalization in cyclopropane and its derivatives comes from the upfield shift of cyclopropane ^{1}H NMR signals[57,58] and the shielding of protons located above the plane of cyclopropane rings.[59−62] The long range shielding/deshielding effects of cyclopropane rings have recently been analyzed by Sauers using ab initio methods and NICS calculations (negative nucleus-independent chemical shift).[63,64] NICS values above the molecular plane of cyclopropane (Figure 10) indicate the existence of a diatropic ring current in the σ-plane of the molecule.[65] This supports the possible stabilization due to σ-aromaticity discussed by Dewar[45a,b] and by Cremer and Kraka.[45c] As pointed out by Cremer and Gauss, the extent of CH bond strengthening in cyclopropane can be used to define a lower bound for the total energy due to this effect.[9] On the basis of their estimates for Pitzer strain, CC bond stretch strain, and Bayer strain in cyclopropane, earlier estimations of the increased CH bond strength in cyclopropane (Cremer and Gauss:[9] 6.4 kcal mol^{-1}; Schleyer:[47] 10.0 kcal mol^{-1}; Roberts and Caserio:[44] 18.0 kcal mol^{-1}) correspond to a stabilization of cyclopropane by 17.0, 13.0, and 5.0 kcal mol^{-1}, respectively, due to electron delocalization.[9,66] Using our new estimate of the CH bond energies, a value of 11.3 kcal mol^{-1} is deduced for the "σ-aromaticity" of cyclopropane.

On the basis of BE's the strain energy of trisilacyclopropane (37.0 kcal mol^{-1}) is twice as large as that of tetrasilacyclobutane (16.8 kcal mol^{-1}). As for the carbon analogues, the strain energies from BE's agree well with earlier estimates[43] and with reference data evaluated from G2 calculations for trisilacyclopropane/tetrasilacyclobutane and G2MP2 calculations for hexasilacyclohexane ($E_{\mathrm{str}} = 37.5/15.1$ kcal mol^{-1}). The energy decomposition gives contributions to the total strain of 41.4 kcal mol^{-1} from the SiSi bonds of the three-membered, and of 17.6 kcal mol^{-1} from the SiSi bonds of the four-membered ring. In line with earlier predictions,[47,48] the SiH bonds of the small silicon rings are not strengthened appreciably relative to hexasilacyclohexane. These stabilizations amount to only 4.4 kcal mol^{-1} (0.73 kcal mol^{-1} per bond) for trisilacyclopropane and to 0.8 kcal mol^{-1} (0.10 kcal mol^{-1} per bond) for tetrasilacyclobutane.

VI. Conclusions

The model proposed by Grimme to calculate intrinsic bond energies from the properties of bond critical points is very appealing. The methodology is simple and relies only on the widely employed Gaussian[14] and AIMPAC[15] programs.

Calculated CH and CC bond energies are self-consistent and plausible. Compared to CH bond dissociation energies (ca. 86 to 132 kcal mol^{-1}), the intrinsic CH bond energies are located in the surprisingly narrow range between ca. 103 and 110 kcal mol^{-1}. Differences between CH BE's and CH BDE's reflect the reorganization energies in the course of bond dissociation. The correlation of the BE's and the BDE's for CH bonds shows that the factors determining radical stabilities operate in the ground states as well − although to a much lesser extent. According to the BE scheme, alkenyl and alkynyl radicals are *destabilized* by 5 and by 22 kcal mol^{-1}, respectively. The DBE's and BE's of sp^{x}sp^y CC bonds are highly correlated and thus allow a reliable prediction of BDE's at little computational cost, establishing an attractive alternative to other schemes that have been proposed.[34]

The present work demonstrates a correlation between intrinsic CC bond energies and CC bond lengths for a set of 202 CC single and (conjugated) double and triple bonds. This correlation is equivalent to the models of chemical bonds introduced long ago by Pauling[19] and by Johnston and Parr.[21] Grimme's ansatz therefore suffers from the same limitations as those earlier models in that changes in bond length due to strain, rather than conjugation, lead to unreliable bond energies. While this deficiency can be compensated by the introduction of an energy correction for bond curvature in some small ring compounds (e.g., in cyclopropane, cyclobutane, and even cyclobutene as well as cyclobutadiene), allene, cyclopropene, methylenecyclopropene, [1.1.0]bicyclobutane, [1.1.1]propellane, etc. are not described adequately by the model. The analysis of CC bond energies in ethane, ethene, and ethyne as a function of the CC bond length shows that the Grimme method is not able to model these potentials correctly. Further modifications of the model, mainly the inclusion of a term for nuclear−nuclear repulsion, have to be made to overcome this shortcoming.

The BE method does not describe anions, cations or open shell species with chemical accuracy; and detailed analyses of their BE's are not reasonable.[1] Likewise, we could not extend the method to treat nitrogen-containing systems satisfactorily. On the other hand, parameters for saturated silicon hydrides were obtained and inter alia used for an analysis of BE's in small carbon and silicon rings. The BE method confirms the earlier arguments that only cyclopropane profits energetically from CH bond rehybridization[47]−SiH BE's are insensitive to SiSi angle strain compared to the BE's of their CH counterparts. Our Grimme-based cyclopropane CH bond energies in combination with the estimates of Cremer and Gauss[9] for the Pitzer strain, CC bond stretch strain, and Bayer strain in cyclopropane result in an estimate of 11.3 kcal mol^{-1} of the σ-aromaticity of cyclopropane. NICS values above the cyclopropane ring (Figure 10) clearly reveal the existence of a ring current in cyclopropane.

Acknowledgment. Dedicated to Prof. Dr. Rolf Huisgen with warmth and esteem on the occasion of his 80th birthday. K.E. thanks the Fonds der Chemischen Industrie, Germany, for a postdoctoral fellowship.

Supporting Information Available: BE's for acyclic silicon hydrides and data plotted in Figures 1, 3, 4, and 5 are available in tabulated form. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Grimme, S. *J. Am. Chem. Soc.* **1996**, *118*, 1529.

(2) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(3) A recent example cf.: Bauschlicher, C. W., Jr.; Langhoff, S. R. *Mol. Phys.* **1999**, *96*, 471.

(4) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(5) Sanderson, R. T. *J. Org. Chem.* **1982**, *47*, 3835.

(6) Bader, R. F. W.; Tang, T.-H.; Tal, Y.; Biegler-König, F. W *J. Am. Chem. Soc.* **1982**, *104*, 946.

(7) Ehrhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* **1985**, *68*, 231.

(8) Zhixing, C. *Theor. Chim. Acta (Berlin)* **1985**, *66*, 365.

(9) Cremer, D.; Gauss, J. *J. Am. Chem. Soc.* **1986**, *108*, 7467.

(10) Barone, V.; Fliszár, S. *Int. J. Quantum. Chem.* **1995**, *55*, 469.

(11) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Calderon Press: Oxford, 1994, reprinted 1995.

(12) Bader, R. F. W. *J. Chem. Phys.* **1980**, *73*, 2871. Bader, R. F. W.; Nguyen-Dang, T. T. *Adv. Quantum Chem.* **1981**, *14*, 63.

(13) Values of ΔR are obtained from an AIM analysis using the EXTREME program from Bader's AIMPAC package; cf. ref 15.

(14) 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.; Baboul, A. G.; 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.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A.; *Gaussian 98*, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(15) http://www.chemistry.mcmaster.ca/aimpac/.

(16) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(17) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.

(18) Ochterski, J. W.; Petersson, G. A.; Montgomery, J. A., Jr. *J. Chem. Phys.* **1996**, *104*, 2598. Montgomery, J. A., Jr.; Frisch, M. J.; Ochterski, J. W.; Petersson, G. A. *J. Chem. Phys.* **1999**, *110*, 2822.

(19) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542.

(20) Bader, R. F. W.; Slee, T. S.; Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1983**, *105*, 5061.

(21) Johnston, H. S.; Parr, Ch. *J. Am. Chem. Soc.* **1963**, *85*, 2544.

(22) Swanton, D. J.; Henry, B. R. *J. Chem. Phys.* **1987**, *86*, 4801; and cit. lit.

(23) For bond order−bond energy correlations cf.: Politzer, P.; Ranganathan, S. *Chemical Physics Lett.* **1986**, *124*, 527; and cit. lit.

(24) McKean, D. C. *Chem. Soc. Rev.* **1978**, *7*, 399.

(25) Note that this error margin is equal to the one estimated for Bader's integration method; cf. ref 9.

(26) Excellent correlations of even HF/4-21G* calculated CH bond length with isolated stretching frequencies have been reported: Snyder, R. G.; Aljibury, A. L.; Strauss, H. L.; Casal, H. L.; Gough, K. M.; Murphy, W. F. *J. Chem. Phys.* **1984**, *81*, 5352. Schäfer, L.; Siam, K. *J. Chem. Phys.* **1988**, *88*, 7255.

(27) Data taken from: McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1982**, *33*, 493.

(28) A compilation of reorganization energies has recently been given by: Larsson, J. A.; Kremer, D. *J. Mol. Struct.* **1999**, 385−407. It should be noted, however, that their data were derived under the assumption that $R = 0$ for ethene, benzene, and ethyne which is in contradiction with our findings.

(29) DeFrees, D. J.; McIver, R. T., Jr.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3334.

(30) Note that the CH BE's calculated by the independent method of Zhixing (ref 8) also are in a rather small range, from 96.3 kcal mol^{-1} (isobutane) to 115.0 kcal mol^{-1} (ethyne).

(31) Rüchardt, Ch. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 830.

(32) Li, S.; Jiang, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8401.

(33) Wiberg, K. B. *J. Org. Chem.* **1997**, *62*, 5720.

(34) DiLabio, G. A.; Pratt, D. A. *J. Phys. Chem. A* **2000**, *104*, 1938. Vreven, T.; Morokuma, K. *J. Chem. Phys.* **1999**, *111*, 8799−8803. Froese, D. J.; Morokuma, K. *J. Phys. Chem. A* **1999**, *103*, 4580.

(35) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(36) Fulton, R. L. *J. Am. Chem. Soc.* **1993**, *97*, 7516−7529. Fulton, R. L.; Mixon, S. T. *J. Phys. Chem.* **1993**, *97*, 7530.

(37) Krygowski, T. M.; Ciesielki, A.; Bird, C. W.; Kotschy, A. *J. Chem. Inf. Sci.* **1995**, *35*, 203.

(38) Cf. Cremer, D.; Kraka, E. *Croat. Chim. Acta* **1984**, *57*, 1259; and cit. lit.

(39) Cf. ref 11, Chapter 3.2.4.

(40) The sum of BE's for the methyl anion according to our implementation (297.1 kcal mol^{-1}) is close to Grimme's value of 299.3 kcal mol^{-1}. However, the AE for the methyl anion given by Grimme (303.2 kcal mol^{-1}) deviates markedly from our G2 and CBS-QB3 data (279.2 and 278.3 kcal mol^{-1}). Evidently, Grimme calculated the energy for the process $CH_3^- \rightarrow C + 3H + e^-$ instead of $CH_3^- \rightarrow C^- + 3H$. The G2 and CBS-QB3 energies for the former process are 306.7 and 305.5 kcal mol^{-1}, respectively.

(41) Salzner, U.; Schleyer, P. v. R. *Chem. Physics Lett.* **1992**, *199*, 267.

(42) Baeyer, A. *Chem. Ber.* **1885**, *18*, 2269.

(43) Greenberg, A.; Liebman, J. *Strained Organic Molecules*; Academic Press: New York, 1978 and references cited.

(44) Roberts, J. D.; Caserio, M. C. *Basic Principles of Organic Chemistry*; Benjamin Press: New York, 1964; p 113.

(45) (a) Dewar, M. J. S.; McKee, M. L. *Pure Appl. Chem.* **1980**, *52*, 1431. For a more detailed discussion of σ-conjugation and the σ-aromaticity of cyclopropane(s): (b) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 699. A discussion of the topology of the cyclopropane electron density with respect to the effect of planar delocalization is given in: (c) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

(46) Nagase, S.; Kobayashi, K.; Nagashima, M. *J. Chem. Soc., Chem. Commun.* **1992**, 1302. Nagase, S.; Nakano, M.; Kudo, T. *J. Chem. Soc., Chem. Commun.* **1987**, 60.

(47) Schleyer, P. v. R. In *Proceedings of the NATO Advanced Research Workshop on "Substituent Effects in Radical Chemistry"*; Viehe, H. G., Janousek, Z., Merényi, R.,Eds.; Louvain-la-Neuve, 1986; p 69.

(48) Sax, A. *Chem. Phys. Lett.* **1986**, *127*, 163.

(49) AE's per CH_2 fragment of cyclohexane for the vibrationless molecule are 293.3 kcal mol^{-1} (G2MP2) In good agreement with the AE of 293.7 kcal mol^{-1} from the energy difference *n*-butane(G2MP2) − propane(G2). For the SiH_2 fragment AE's of 210.7 kcal mol^{-1} (hexasilacyclohexane(G2MP2)) and 211.1 kcal mol^{-1} (*n*-tetrasilabutane(G2) − trisilapropane(G2) are found. Note the good agreement with the XH_2 BE's of 294.3 kcal mol^{-1} (cyclohexane) and 210.5 kcal mol^{-1} (hexasilacyclohexane).

(50) The contribution of the CH bonds to the stabilization of cyclopropane is also obvious from the shortening of the CH bond length in cyclopropane compared to ethane, cf.: Gauss, J.; Cremer, D.; Stanton, J. F. *J. Phys. Chem. A* **2000**, *104*, 1319.

(51) Lacher, J. R.; Pollack, J. W.; Park, J. D. *J. Chem. Phys.* **1951**, *20*, 1047.

(52) Aldrich, P. D.; Kukolich, S. G.; Campbell, E. J.; Read, W. G. *J. Am. Chem. Soc.* **1983**, *103*, 5569.

(53) Lukins, P. B.; Laver, D. R.; Buckingham, A. D.; Ritchie, G. L. D. *J. Phys. Chem.* **1985**, *89*, 1309.

(54) Patel, D. J.; Howden, M. E. H.; Roberts, J. D. *J. Am. Chem. Soc.* **1963**, *85*, 3218.

(55) For the diamagnetic susceptibility exaltation as criterion for cyclic electron delocalization cf.: Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. *J. Am. Chem. Soc.* **1968**, *90*, 811; also see Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209. For the anisotropy of the magnetic susceptibility as a criterion for cyclic electron delocalization cf.: Fleischer, U.; Kutzelnigg, W.; Lazzeretti, P.; Mühlenkamp, V. *J. Am. Chem. Soc.* **1994**, *116*, 5298.

(56) Dauben, H. J., Jr.; Wilson, J. D.; Laity, J. L. In *Nonbenzenoid Aromatics*; Snyder, J. P., Ed.; Academic Press: New York, 1971; Chapter 3.

(57) Wiberg, K. B.; Nist, B. J. *J. Am. Chem. Soc.* **1961**, *83*, 1226.

(58) Burke, J. J.; Lauterbur, P. C. *J. Am. Chem. Soc.* **1964**, *86*, 1870.

(59) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry*; Pergamon Press: New York, 1969; p 98.

(60) Poulter, C. D.; Boikess, R. S.; Brauman, J. I.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2291.

(61) Hahn, R. C.; Howard, Ph. H. *J. Am. Chem. Soc.* **1972**, *94*, 3143.

(62) Jason, M. E.; Kurzweil, P. R. *J. Org. Chem.* **1991**, *56*, 3664.

(63) NICS is a convenient probe for ring currents arising from cyclic electron delocalization: Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; van Eikema Hommes, N. J. R. *J. Am. Chem. Soc.* **1996**, *118*, 6317. For an extensive survey of NICS results, see: Patchkovskii, S.; Thiel, W. *J. Mol. Model.* **2000**, *6*, 67.

(64) Sauers, R. R. *Tetrahedron* **1998**, *54*, 337.

(65) The cumulative effect of the shielding by four cyclopropane rings was recently demonstrated by NICS = −14.6 at the center of the truncated tetrahedron, $C_{12}H_{12}$. A NICS value of −3.0 ppm is obtained at a point outside the cage located at the same distance from one of the cyclopropane rings: Bettinger, H. F.; Pak, Ch.; Xie, Y.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2377.

(66) These values are significantly lower than the earlier estimate by Cremer and Kraka of 48 kcal mol^{-1}: Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800. More recently, on the basis of a perturbational treatment of cyclopropane, Furusaki deduced a σ-aromatic stabilization energy of 77−79 kcal mol^{-1}, which is certainly too high: Furusaki, A. *J. Mol. Struct. (THEOCHEM)* **1996**, *362*, 365.

(67) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A., Jr.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 10570.

(68) Günter, H. *NMR−Spectroscopy*; John Wiley & Sons: New York, 1980.