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Theoretical Bond and Strain Energies of Molecules Derived from Properties of the Charge Density at Bond Critical Points

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Abstract: The atomization energy of a hypothetical vibrationless molecule in its ground state equilibrium nuclear configuration is partitioned into bonded contributions (bond energy, BE) with the use of properties of the electronic charge density at bond critical points. The method is applied in the framework of Kohn−Sham density functional theory (with a gradient-corrected exchange-correlation functional and a triple-ζ plus polarization AO basis) to various diatomics and strained and unstrained hydrocarbon molecules. A linear relation is established between the bond energies and a quantity termed bond electron energy which is the total energy density divided by a constant plus the charge density at the critical point. The use of one empirical parameter per atom pair and a bond path curvature term, which is the difference of the length of the curve of maximum electron density and the distance between the atoms, allows the determination of atomization and bond energies with errors below 0.5−1% in most cases. The bond energies of the CC (CH) bonds of ethane, ethene, benzene, and acetylene are found to be 86.1 (104.1), 140.5 (106.1), 120.3 (106.4), and 188.9 (111.4) kcal/mol, respectively. By comparison with the BE values of strainless reference compounds, the bond strain and total strain energies of some saturated and unsaturated hydrocarbons (cycloalkanes, cycloalkenes, tetrahedrane, cubane, benzocyclopropene, fenestrane) are calculated in good agreement with experimental data.

Introduction

The energetic contribution of a pair of neighboring atoms in a molecule to the atomization energy, E_{at}, is conveniently called bond energy (BE). Similarly to the case of diatomics, in which it equals the dissociation energy, it measures the atomic interactions by an energy criterion and is thus a quantity of fundamental interest in chemistry and physics.[1] In polyatomic systems, however, only the dissociation energies for distinct processes are experimentally well defined, but these contain contributions from structural and electronic relaxation in the products (reorganization energy). However, reliable information of the strengths of chemical bonds near the equilibrium nuclear configuration is important in several experimental areas (e.g., vibrational frequencies, spin−spin nuclear coupling constants, chemical reactivity).

The determination of BE values requires a meaningful partitioning of the total E_{at} to the contributions of individual bonds. In most chemistry textbooks (see, e.g., ref 2) estimates for BE values based on auxiliary assumptions are presented. For example, to determine the CC bond energy in ethane, the CH bond energy is assumed to be equal to those found in CH_4 (i.e., $E_{at}(CH_4)/4$) which then yields $BE(CC) = E_{at}(C_2H_6) - 6 \times BE(CH)$. For more complex molecules, this approach becomes impractical since too many unknowns are present so that the use of theoretical methods in the partitioning procedure seems necessary.

In 1980, Bader[3] introduced a theoretical approach based on his theory of atoms in molecules[4] in which all information of the system is extracted from the properties of the molecular electronic charge density ($\rho(r)$, $r \equiv x,y,z$).[5] From the hypervirial theorem, Bader derives an integral of $\rho(r)$ over the interatomic zero-flux surface which is proportional to the bond energies in cases of low charge transfer between the atoms. Using one empirical parameter, the BE values of saturated hydrocarbons could be determined with reasonable accuracy.[4,6] On the other hand, theoretical single CC bond energies determined by Barone and Fliszar[7] via the Hellman−Feynman theorem deviate by more than 10 kcal/mol from commonly accepted values (≈80−86 kcal/mol[8,9]). Finally, the method of Erhardt and Ahlrichs[10] which is based on a correlation of BE with shared electron numbers weighted by orbital energies should be mentioned here.

Obviously related to bond energies is the concept of strain energy (SE) which can be dated back to the beginning of organic chemistry (for reviews, see refs 11−13. The total SE of a molecule is usually defined (and calculated) as the energy difference of the molecule or parts of it and arbitrarily chosen (unstrained) reference systems. More information on the energetics in molecules may be obtained by comparing the individual bond energies of the strained system with those of similar bonds in unstrained molecules. The sum of all bond strain energies (BSE) obtained in this manner would then yield

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(1) Cottrell, T. L. *The Strengths of Chemical Bonds*; Butterworths: London, 1958.

(2) March, J. *Advanced Organic Chemistry,* 3rd ed.; J. Wiley: New York, 1985.

(3) Bader, R. F. W. *J. Chem. Phys.* **1980**, *73*, 2871.

(4) Bader, R. F. W. *Atoms in Molecules: A quantum Theory*; Clarendon Press: Oxford, 1994.

(5) Strictly speaking, the information is recovered from the first-order density matrix $\Gamma^1(r,r')$ which yields $\rho(r)$ as its diagonal element.

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

(7) Barone, V.; Fliszar, S. *J. Comput. Chem.* **1995**, *55*, 469.

(8) Cox, J. O.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: New York, 1970.

(9) Allen, T. L. *J. Chem. Phys.* **1959**, *31*, 1039.

(10) Erhardt, C.; Ahlrichs, R. *Theor. Chim. Acta* **1985**, *68*, 231. Since some unreliable BE data based on dissociation energies have been used in their work (e.g., ethene and acetylene), the reported low mean deviation of 6.4 kcal/mol seems questionable.

(11) Greenberg, A.; Liebman, J. F. *Chem. Rev.* **1976**, *76*, 311.

(12) Greenberg, A.; Liebman, J. F. *Strained Organic Compounds*; Academic Press: New York, 1978.

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the total SE value but providing more information at no additional effort.

The aim of this work is the partioning of the atomization energy of a molecule in its equilibrium nuclear configuration into the bond energies by using a quantity termed bond electron energy (BELE) which is derived from the properties of the charge density at the bond critical points. This approach avoids laborious computations (numerical integrations over complicated surfaces) and allows the analysis of the binding energy distribution in molecules on an absolute (BE values) and relative (SE and BSE values) scale even in large molecules.

Theory

According to Baders theory of atoms in molecules,[4] the properties of a molecular charge distribution are summarized in terms of its critical points. These are points where the charge density, $\rho(r)$, is a maximum, a minimum, or a saddle (the gradient vector field of the charge density, $\nabla\rho(r)$, vanishes). A critical point is characterized by the signs of the three principal curvatures of $\rho(r)$. A critical point with one positive and two negative curvatures is found between every pair of neighboring (bonded) nuclei and is called bond critical point ($r = r_b$). Ring and cage critical points with two and three positive curvatures are not considered here because they are not essential for a description of bonding, even in small rings if errors in predicted atomization energies of $\approx$1.0% are accepted. Extensive work of Bader et al. has shown that the interaction of two bonded atoms can be characterized qualitatively with properties of $\rho(r)$ at r_b, i.e., the density, $\rho(r_b)$, and the Laplacian of the density, $\nabla^2\rho(r_b)$, at the critical point (e.g., bond orders and qualitative classification of bonding).[4,6,14]

In 1980, Bader defined a local energy density, $E_d(r)$, as a functional of the first order density matrix[3]

$$E_d(r) = G(r) + V(r) \tag{1}$$

where $G(r)$ and $V(r)$ correspond to a local kinetic energy density and a local potential energy density.[15] If the forces in the system vanish, integration of $E_d(r)$ over an atomic basin yields the atomic energy in the molecule and the sum of these atomic energies equals the total energy. The sign of $E_d(r)$ reveals whether accumulation of charge at a given point r is stabilizing ($E_d(r) < 0$) or destabilizing ($E_d(r) > 0$). Cremer and Kraka[16] have analyzed the behavior of the $E_d(r)$ in the bond regions of a molecule. For a variety of different bonds with a significant covalent contribution, negative values of the energy density at the bond critical points were found.[17] They proposed that an integration of $E_d(r)$ over the interatomic surface, S(A,B), of two bonded atoms should yield quantities which are correlated with dissociation energies. Since such a (numerical) integration scheme (which is also necessary in the hypervirial partitioning procedure) is very time consuming in the case of larger molecules and reasonable (extended) AO basis sets, inspection of the $E_d(r)$ values solely at the bond critical points seems more promising. As will be shown below, the essentially new and most important aspect of this work is the finding that normalized $E_d(r_b)$ values are very effective in imaging the bond energies in a molecule.

Table 1. Calculated (DFT-BLYP/TZP; for details, see Outline of the Calculations) Bond Lengths (R_e), Charge Densities ($\rho(r_b)$), and Energy Densities ($-E_d(r_b)$) at the Bond Critical Points for the diatomics H_2^+, H_2, C_2, N_2, and F_2 and Simple Hydrocarbon Molecules[a]

compd[b]	bond	R_e (Å)	$\rho(r_b)$ (e·bohr^{-3})	$-E_d(r_b)$ (hartrees·bohr^{-3})	BE(exp) (kcal/mol)	BE/$-E_d(r_b)$ (bohr^{-3})
H_2^+	HH	1.047	0.998	0.0926	60.0	1.03
H_2	HH	0.748	0.2598	0.2618	109.5	0.67
C_2	CC	1.257	0.2924	0.3621	141.0	0.62
N_2	NN	1.105	0.6742	1.1544	228.5	0.32
F_2	FF	1.442	0.2476	0.0795	38.2	0.76
CH_4	CH	1.096	0.2708	0.2626	104.8	0.63
C_2H_6	CC	1.539	0.2330	0.1841	81.6[c]	0.70
C_2H_4	CC	1.335	0.3437	0.3820	142.9[c]	0.60
C_2H_2	CC	1.207	0.4117	0.5810	194.7[c]	0.53

[a] To compare experimental bond energies, BE, with the $-E_d(r_b)$ values, the quotient BE/$-E_d(r_b)$ is given in the last column. Experimental data from refs 8 and 25. [b] The total energies of the molecules are −0.6010, −1.1692, −109.5553, −199.5958, −40.2115, −79.7991, −78.5749 and −77.3317 hartrees. [c] Calculated from the experimental E_{at}^0 assuming a constant BE of the CH bonds of 104.8 kcal/mol (value of CH_4 from ref 25).

The data given in Table 1 for the diatomics H_2^+, H_2, C_2, N_2, and F_2 and simple prototype hydrocarbons methane, ethane (single bond), ethene (double bond), and acetylene (triple bond) have been obtained from Kohn−Sham density functional theory with a gradient-corrected exchange-correlation functional (BLYP) and a triple-ζ plus polarization AO basis (further details of the calculations are given in the following section). It is seen that the $-E_d(r_b)$ values increase with increasing bond energies. However, the correlation of $-E_d(r_b)$ with the BE data is strongly nonlinear in the hydrocarbon series and for H_2^+ and H_2. Furthermore, the proportionality constants are very different for different atom pairs (compare the data given in the last column of Table 1). For example, for triple-bonded N_2 and C_2H_2, the value of BE/$-E_d(r_b)$ differs by a factor of 2.

Obviously, no simple relationship exists between the BE and the $-\mathrm{E}_d(r_b)$ data. However, as will be shown in the following, a linear relation for the bond energies can be derived from a normalization of the $-E_d(r_b)$ values. First of all one should consider the dimensions of the energy density (energy per volume) and the charge density (elementary charge e per volume). Since we are interested in a quantity which is evaluated at one point in space only, the dimension volume has to be removed. Thus, division of $-E_d(r_b)$ by $\rho(r_b)$ leads to a new quantity which has now dimensions of energy per elementary charge (electron). We call this quantity bond electron energy and take it as measure that reflects the bond energies in molecules much better than any other property derived at the bond critical point. In order to linearize this relation for atom pairs which can form multiple bonds, a constant, c_2, is added in the denominator of eq 2

$$\mathrm{BELE}^{\mathrm{AB}} = \frac{-E_d(r_b)}{(c_2 + \varrho(r_b))} \tag{2}$$

which then yields the final definition of the bond electron energy.

The bond critical point is the source of two gradient paths (terminating at the atoms A and B) determining the line of maximum electron density (bond path) between A and B. The bond path does not necessarily coincide with the internuclear axis A−B, and hence its length, R_b, may exceed the geometrical bond length, R_e. Large differences, $\Delta R = R_b - R_e$, are observed

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

(15) $G(r) = 1/2\nabla\nabla'\Gamma^1(r,r')|_{r=r'}$; $V(r) = tr\, \overleftrightarrow{\sigma}(r)\, \overleftrightarrow{\sigma}(r) = 1/4(\nabla\nabla + \nabla'\nabla') - (\nabla\nabla' + \nabla'\nabla)\Gamma^1(r,r')|_{r=r'}$, $\Gamma^1(r,r')$ defines the first-order density matrix.[4]

(16) Cremer, D.; Kraka, E. *J. Am. Chem. Soc.* **1985**, *107*, 3800.

(17) Although the correct formulas for $G(r)$ and $V(r)$ are given in ref 16 (p 3802, footnote 21), the numerical values of $E_d(r_b)$ reported for ethene and cyclopropane are not reproduceable. Presumably, these authors have interchanged $G(r)$ with $K(r)$[28] so that their values correspond to $-G(r)$.

for the CC bonds in small rings (i.e., $\Delta R > 0.001$ Å[6,18]), indicating significant strain in these systems (the excess of the bond path angle to the geometric bond angle has been used by Wiberg et al.[4] to characterize the strain in cyclic hydrocarbons). To account for the low BE of such bent bonds, which is not reflected by the BELE value, an additional bond path curvature term (BPC) has been included. Thus, the final ansatz for the bond energy is the bond electron energy defined in eq 2 times a proprotionality constant, c_1, minus the BPC term $c_3\Delta R$.

$$\mathrm{BE} = c_1^{\mathrm{AB}}\mathrm{BELE}^{\mathrm{AB}} - c_3\Delta R \qquad (3)$$

First of all we assume the global parameters c_2 and c_3 to be independent of the atoms A and B (an approximation which is validated below) so that only one empirical parameter per atom pair remains to be determined. Summation of the BE values of all bonds in a molecule should then yield the theoretical atomization energy which allows the determination of the empirical parameters by comparison with the corresponding experimental value. Due to the nonadditivity of zero-point and thermal (heat-content) contributions, experimental atomization energies at 0 K for a molecule in its vibrationless gound electronic state (E_{at}^0) are used throughout.

Outline of the Calculations

All calculations have been carried out in the framework of Kohn−Sham density-functional theory[19] (DFT) with the nonlocal gradient-corrected exchange-corre-lation functional of Becke.[20] and Lee, Yang, and Parr (BLYP).[21] This method provides a much better description of the geometries, energies, and charge densities[22] of polyatomic molecules than the Hartree−Fock self-consistent field (HF-SCF) method. The density is expanded in a Gaussian AO basis set of triple-ζ quality (C, N, F, 10s6p → [6s3p]; H, 5s → [3s])[23] augmented with polarization functions (TZP, $\alpha_{\mathrm{d}} = 0.8$, 1.0, and 1.4 for C, N, and F, respectively; $\alpha_{\mathrm{p}} = 0.8$ for H). These AO basis sets give optimized nuclear geometries which are nearly converged within the selected functional and a significantly better description of the geometries (especially for the CH and multiple bonds) and the density than a DZP expansion. The standard 6-31G** basis sets have also been tested but cannot be recommended here due to the occurrence of spurious local maxima in $\rho(r)$ in the case of triple bonds.

All structures have been completely optimized at the DFT-BLYP/TZP level. The bond lengths and bond angles at this level of theory are clearly superior to HF-SCF results with the same basis set and slightly better than results reported at the local spin−density (DZP basis set) level.[24] Compared to experimental data,[25,26] the CC and CH bond lengths are generally too long by 0.003−0.005 Å for the unstrained hydrocarbons (0.007, 0.01, and 0.03 Å for H_2, N_2, and F_2, respectively). The optimized geometries of the strained systems are similar to those obtained from MP2 calculations. All calculations have been carried out with the TURBOMOLE program system[27] using a fine numerical grid (grid size = 3) for which the errors in the integrated number of electrons are below 10^{-4}. The topological electron density analysis was performed with EXTREME.[28] All molecules considered in this work can be described with a classical chemical valence formula in which each bond drawn (independent of its order) corresponds to one bond critical point.

Table 2. Calculated (DFT-BLYP/TZP) Bond Lengths (R_{e}, Å), BELE (hartrees e^{-1}), and BE (kcal/mol) and Comparison of Calculated and Experimental E_{at}^0 Values (kcal/mol) for the Unstrained Hydrocarbon Molecules

compd[a]		bond	R_{e}	BELE	BE	E_{at}^0 calcd	E_{at}^0 exp
CH_3^+	D_{3h}	CH	1.099	0.6391	112.9	338.6	341.1
CH_4	T_{d}	CH	1.096	0.5905	104.3	417.1	419.2
C_2H_6	D_{3d}	CH	1.099	0.5903	104.1	710.7	710.5
		CC	1.539	0.4526	86.1		
C_2H_4	D_{2h}	CH	1.090	0.6012	106.1	564.9	562.1
		CC	1.335	0.7382	140.5		
C_2H_2	$D_{\infty h}$	CH	1.068	0.6310	111.4	411.8	404.3
		CC	1.207	0.9923	188.9		
benzene	D_{6h}	CH	1.090	0.6027	106.4	1360.3	1365.3
		CC	1.402	0.6321	120.3		
neopentane	T_{d}	CH	1.100	0.5885	103.9	1586.3	1595.9
		CC	1.550	0.4499	85.6		
cyclohexane	D_{3d}	CH(ax)	1.103	0.5865	103.4	1762.7	1760.8
		CH(eq)	1.101	0.5905	104.1		
		CC	1.546	0.4538	86.3		

[a] The total energies of the molecules are −39.4681, −40.5001, −79.7991, −78.5749, −77.3317, −232.2208, −197.7020, and −235.8033 hartrees.

Results

Unstrained Molecules. The theoretical approach outlined above is at first applied to hydrocarbon molecules only. The empirical parameters c_1(CC), c_1(CH), and c_2 in eqs 2 and 3 are determined by a least-squares fitting procedure of the calculated (eq 4) with the corresponding experimental E_{at}^0 data.

$$\Delta E_{\mathrm{at}}^0(\mathrm{calcd}) = \sum^{\text{all bonds AB}} \mathrm{BE}^{\mathrm{AB}} \qquad (4)$$

As unstrained reference compounds, the prototype hydrocarbons listed in Table 2 were used. Since ΔR is near zero in these cases, c_3 is set to zero first. Due to the statistical insignificance of the parameter c_2(CH) (carbon and hydrogen form single bonds in the molecules studied here), the approximation $c_2(\mathrm{CC}) = c_2(\mathrm{CH}) = c_2$ is employed which allows a direct comparison of the c_1 values for the two different atom pairs. Experimental atomization enthalpies, $\Delta H_{\mathrm{at}}^{298}$, are taken from standard references[8,25] and corrected for zero-point and thermal contributions with experimental vibrational frequencies (if not available, semiempirical PM3[29] frequencies were used).

The results for the molecules included in the fitting procedure are given in table 2. The errors in the calculated atomization energies, E_{at}^0 range from −7.5 (acetylene) to 9.6 kcal/mol (neopentane[30]), which corresponds to an average error per bond of <1 kcal/mol in most cases (2.5 kcal/mol in the worst case of acetylene). The standard deviation of the fit is 4.9 kcal/mol with a correlation coefficient of 0.9995. Unstrained hydrocarbon

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(22) For most covalent bonds (with a dominant shared interaction), the charge density in the bonding regions is correctly reduced by the DFT method, i.e., $\rho(r_{\mathrm{b}})$ values are lower by ≈5% compared to HF-SCF data. Furthermore, the HF-SCF bond path curvatures in the strained molecules are larger by a factor of ≈1.5, which is partly attributed to the incorrect short bond lengths. For a comparison of HF-SCF, CI, and DFT charge densities, see: Wang, J.; Shi, Z.; Boyd, R. J.; Gonzalez, C. A. *J. Phys. Chem.* **1994**, *98*, 6988.

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(30) Large errors for neopentane are also found by other theoretical[4] and thermochemical group incremental schemes.[8]

Table 3. Calculated Total Energies (DFT-BLYP/TZP, hartrees), Calculated E_{at}^0 Values (kcal/mol), and Errors of the Calculated E_{at}^0 Values (kcal/mol) for the BELE Partitioning Method and the DFT/BLYP Method Itself[a] for Unstrained Hydrocarbons Not Included in the Fit

			error	
compd	E_{tot}	E_{at}^0(calcd)	BELE	DFT/BLYP
propane (C_{2v})	−119.1000	1004.2	−0.1	−3.3
isobutane (C_{3v})	−158.4014	1296.4	3.3	0.4
cis-2-butene (C_{2v})	−157.1850	1154.5	1.0	−2.3
trans-1,3-butadiene (C_{2h})	−155.9709	1013.4	−1.4	−5.8
adamantane (T_d)	−390.6079	2687.5	0.6	28.8
naphthalene (D_{2h})	−385.8492	2147.2	11.8	2.6
anthracene (D_{2h})	−539.4722	2932.2	17.4	7.1

[a] Calculated form the total DFT-BLYP/TZP energy and fitted atomic energies E(C) = −37.8455 hartrees and E(H) = −0.4948 hartrees (reference set of molecules given in Table 2).

molecules not included in the fit are also described with similar accuracy (see Table 3). In most cases the errors of the bond electron energy partitioning procedure for the atomization energies, are smaller than those derived from the total DFT energies and obivously, both data sets are not correlated with each other. Larger positive errors found for the aromatic hydorcarbons indicate a slight underestimation of the strengths of these bonds (≈1 kcal/mol per CC bond). However, a consistent description is also noted in these cases since the error increases linearly from benzene to naphthalene and anthracene (i.e., with the number of bonds).

The errors found here are slightly larger or similar to those reported by Bader[4] or Cremer and Gauss.[31] However, no unsaturated or large compounds as included here have been investigated in their work so that the hypervirial and the BELE partitioning methods can be classified as comparably accurate. A slight overestimation of the BE values for bonds with sp-hybridized carbon is noticed in C_2H_2 which is also found in the diatomic C_2 (E_{at}^0(exp) = 141 kcal/mol, E_{at}^0 (calcd) = 147.8 kcal/mol). Some of the errors may not only be explained with deficiencies of the theoretical approach but with the neglect of direct nonbonded interactions[32] or with failures in the DFT-BLYP electron density. However, it is apparent that a quantitative description of the individual bond energies in these molecules can be derived from *two* numerical values at a well-defined point in space and *one* empirical parameter per atom pair AB only. The optimal parameters c_1(CC) and c_1(CH) are found to be 0.3033 and 0.2814 e, respectively, with c_2 being 0.1738 e/bohr^3. The value of c_1 has the physical meaning of the amount of charge per bond (in a relative sense due to the presence of c_2 in eq 3) which contributes to covalent bonding. Hence, in heteronuclear systems for which charge transfer between the atoms gains dominance, c_1 decreases, i.e., the covalent portions decrease in favor of ionic attractions. For homonuclear bonds formed by atoms of the first and second row a constant value of $c_1(\mathrm{AA}) = c_1(\mathrm{CC})$ can be employed with reasonable accuracy (BE(calcd) is 64.4, 114.9, 259.1, and 35.9 for H_2^+, H_2, N_2, and F_2, respectively; the values are, with the exception of F_2,[33] consistently too high by 5−10%, compare with experimental data given in Table 1), indicating the physical significance of the empirical parameter c_1.

The approach (including a new fitting procedure) can be applied with minor loss of accuracy to strainless systems on the basis of HF-SCF calculations also. However, errors for strained molecules (see the following section) are larger at this theoretical level. For example, the errors in E_{at}^0 for tetrahedrane and cubane increase from −10 (DFT-BLYP) to −17 and −30 kcal/mol, respectively, at the HF-SCF level due to the neglect of electron correlation effects. This demonstrates that the approach requires a reliable electron density as input which can not fully be replaced by fitting empirical parameters.

The absolute BE values of CC single bonds (85−86 kcal/mol) are larger (≈70,[7] 79−83,[4] and 82[31] kcal/mol, while CH bond energies in saturated molecules (103−104 kcal/mol) are slightly lower (by 0.5−1.0 kcal/mol[4,31]) than previous theoretical estimates but are very similar to the values obtained empirically from thermochemical data (86.2 and 104.0 kcal/mol, respectively, for the CC and CH bonds in alkanes[8]). The values found for a CC double bond (140.5 kcal/mol) and an aromatic CC bond in benzene (120.3 kcal/mol) are also in good agreement with thermochemical data (140.6 and 119.2 kcal/mol,[8] respectively). The CC bond energies of ethene and acetylene are not 2 or 3 times as large as the CC single bond value in ethane. The first (second) π bond increases the BE by only 54 (48) kcal/mol, which reflects nicely the high chemical reactivity of acetylenic compounds.

Although the BE values of single bonds vary considerably less than those reported by Bader et al.,[4,6] trends in a series of hydrocarbons are comparable. For example, the equatorial CH bond in cyclohexane is stronger than the axial one, and the CC bonds in propane and butane are stronger than in cyclohexane. Furthermore, it is noted that accurate BE values are also obtained for the charged species CH_3^+ (see Table 2) and CH_3^- (C_{3v}) (E_{at}^0(calcd) = 299.3,[34] E_{at}^0(exp) = 303.2 kcal/mol), demonstrating the wide applicability of the method.

To test the numerical stability (which is a problem in numerical integration schemes, see ref 31) and accuracy of the method, the bond energies of the eclipsed conformer of ethane (D_{3h}) have been calculated. The DFT-BLYP/TZP rotational barrier of 2.6 kcal/mol is accurately obtained from the charge distribution via the partitioning method, i.e., the CC bond becomes less stable by 3.1 kcal/mol, while the BE values of the CH bonds increase by 0.1 kcal/mol relative to the D_{3d} minimum giving a total ΔE of 2.5 kcal/mol (exp = 2.9 kcal/mol[35]).

Strained Molecules. The application of the theoretical scheme to strained hydrocarbons is straightforward. Here, the bond path curvature (BPC) term in eq 3, $c_3\Delta R$, gains importance. As a consequence of the curvature of a bond path, the charge density is not distributed, so as to maximize the force of attraction, it exerts on the nuclei. This effect leads to a weakening of the bond, in spite of the fact that such bent bonds exhibit R_e values shorter than normal in some cases. It is important to mention here that c_1BELE and $c_3\Delta R$ are not correlated (ΔR may vanish due to symmetry) and only the inclusion of both terms provides a consistent measure of bonding within this model. The value of c_3 is set equal to 4.302 hartree Å^{-1} to obtain agreement between the calculated and experimental E_{at}^0 values for cyclopropane, i.e., no additional fitting procedure is applied.

The final results for some strained hydrocarbons including saturated, unsaturated, and aromatic systems are given in Table 4. The data of individual bonds are displayed in Figure 1. The

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

(32) Indirect effects of nonbonded interactions are included through the deformation of the charge density.

(33) The relative large error found for the calculated F_2 bond length indicates that the BLYP functional does not describe the electron correlation properly enough. Improvement of the AO basis (TZP2P + diffuse functions) does not change the results significantly (R_e = 1.437 Å, BE(calcd) = 37.2 kcal/mol).

(34) A set of diffuse sp-basis functions (α = 0.034) has been added to the TZP basis in this case.

(35) Hirota, E.; Saito, S.; Endo, Y. *J. Chem. Phys.* **1979**, *71*, 1183.

Table 4. Calculated Total Energies (DFT-BLYP/TZP, hartrees), Comparison of Calculated and Experimental $E_{at}{}^0$ Values (kcal/mol), and Comparison of Calculated[a] and Experimental[b] SE (kcal/mol)[c]

		$E_{at}{}^0$		SE		
compd	E_{tot}	calcd	exp	calcd	class	exp
cyclopropane (D_{3h})	−117.8635	850.5[d]	850.5	31.8	23.9	27.5
cyclopropene (C_{2v})	−116.6052	689.4	682.7	52.7	50.9	55.2
cyclobutane (D_{2d})	−157.1655	1149.3	1147.9	27.0	22.9	26.5
cyclobutene (C_{2v})	−155.9427	1006.1	1000.9	30.7	27.7	28.4
tetrahedrane (T_d)[e]	−154.6203	793.4	783.2	141.6	119.3	140
prismane (D_{3h})[f]	−232.0155	1245.2	1250.6	157.3	125.6	148.7
cubane (O_h)	−309.3997	1710.7	1701.6	159.3	138.8	154.7
[4.4.4.4]fenestrane (D_{2d})[g]	−349.8863	2107.2	2113.7	176.8	144.1	160[g]
benzocyclopropene (C_{2v})[h]	−270.2280	1473.2	1463.5	64.8	63.2	68[i]

[a] Unstrained reference BE values (bond type and unstrained reference molecule in parentheses) are 104.3 (CH, isobutane), 103.8 (CH_2, cyclohexane), 105.5 (CH on a double bond, *cis*-2-butene), 106.4 (CH on an aromatic ring, benzene), 86.3 (CC single bond, cyclohexane), 93.1 (C(sp^3)C(sp^2), *cis*-2-butene), 91.4 (C(sp^3)C(ar), *p*-xylene), 136.5 (CC double bond, *cis*-2-butene), and 120.3 (CC aromatic, benzene) kcal/mol. [b] Calculated from experimetal ΔH_f^{298} values and Franklins group increments.[36] [c] For comparison the SE values obtained in a classical manner from DFT-BLYP/TZP strainless group increments are also given. The strainless group increments are −39.3005 (CH_2), −38.7026 (CH), −77.3858 (*cis*-CH═CH), and −231.0284 (*o*-C_6H_4) hartrees. [d] Used to determine c_3 in eq 4. [e] ΔH_f^{298} from HF-SCF/6-31G* calculations.[41] [f] ΔH_f^{298} from homodesmic MP2/6-31G* calculations.[42] [g] ΔH_f^0 from homodesmic MP2/4-31G calculations.[43] [h] ΔH_f^{298} from a semiempirical PM3[29] calculation. [i] Reference 44.

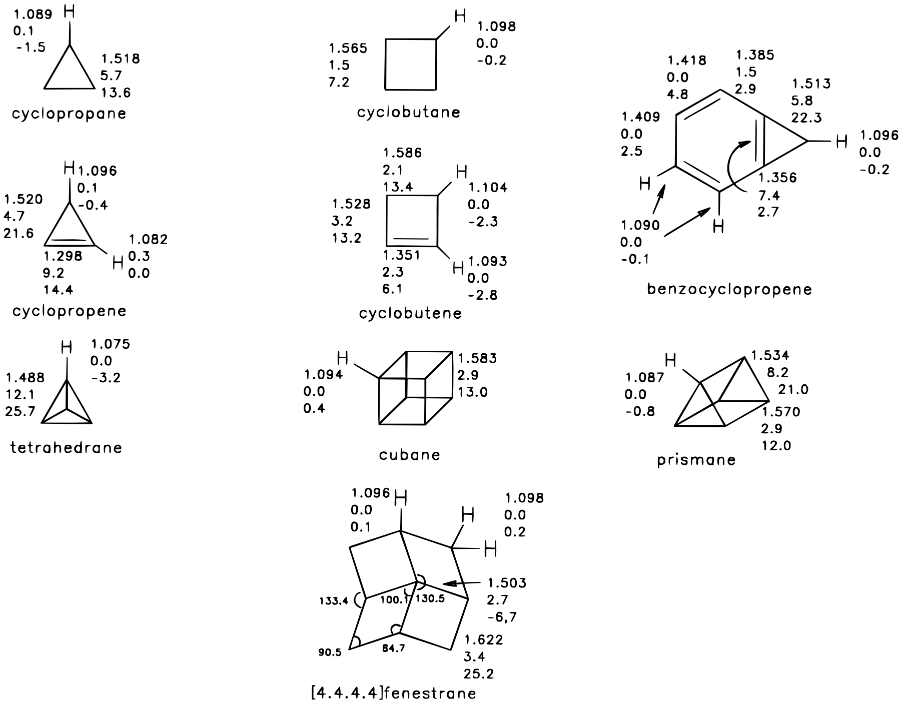

Figure 1. Schematic structures of the strained hydrocarbons (see also Table 4) and results of the bond energy calculations. The top number is the optimized bond length, R_e, in Å, the number in the middle is the bond path curvature term, $\Delta R = R_b - R_e$ ($\times 10^3$ Å), and the bottom value is the bond strain energy in kcal/mol derived from strainless reference bonds given in Table 4. All data given refer to DFT-BLYP/TZP calculations. For cyclobutane the average values of the two slightly different CH bonds are given. The bond angles indicated in the structure of [4.4.4.4]fenestrane are given in degrees.

BSE's are calculated from the difference of the corresponding BE value and an unstrained reference bond, i.e., BSE = BE(unstrained reference) − BE(strained).

The errors of the calculated atomization energies are generally not larger than in the strainless systems (the largest percentage error of 1.3% is found for tetrahedrane). The strain energies obtained as the sum of all bond strain energies compare also very well with the experimental data (i.e., to within 5−10% in most cases) derived classically from enthalpies and Franklins group increments.[36] The SE values obtained in a similar manner from the DFT-BLYP/TZP energies directly are also consistent with these data but systematically too low by 10%. Since strain energies are very sensitive to the computational approach applied for their evaluation and to the strainless reference system used (SE values reported in the literature often deviate by more than 10% from each other), the results presented here can be jugded as good enough for practical applications.

The striking similarity of the SE values of cyclopropane and cyclobutane is also rationalized with the theoretical approach. The BE values of the CC bonds are 72.7 and 79.1 kcal/mol, respectively, with BSE values of 13.6 and 7.2 kcal/mol. BSE(CC) data from the literature for these two molecules are 8.0 and 7.2 kcal/mol [4] or 9.3 and 6.8 kcal/mol.[37] These discrepancies, especially those observed for cyclopropane, are attributed to different descriptions of the CH bonds. For example, in ref 4, they are found incorrectly not to be stronger compared to strainless reference CH bonds (this topic is discussed in detail below). If the BPC term is neglected, the BE values of cyclopropane and cyclobutane are 88.2 and 83.2 kcal/mol, i.e., the former value is higher while the latter BE is

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(36) Franklin, J. L. *Ind. Eng. Chem.* **1949**, *10*, 1070.

(37) Pitzer, R. M. *J. Chem. Phys.* **1967**, *46*, 4871.

lower compared to a standard CC single bond (86.4 kcal/mol). This shows that the CC bonds in the three-membered ring are intrinsically strong but weakened due to the unfavorable accumulation of charge outside the internuclear axis. In unsaturated compounds such as cyclopropene or benzocyclopropene, this effect is also present, but a larger BPC term gives totally a nearly 2 times as large BSE value for the double bonds. Though not obvious from geometrical considerations, the formal double bonds in these systems are moderately or nearly unstrained. Thus, in benzocyclopropene, the aromatic ring contributes <30% to the total SE of 65 kcal/mol. Comparing the double bonds in cyclopropene and cyclobutene (the BE values are 126.1 and 130.4 kcal/mol, respectively), it is also obvious that changes in the bond distances are not necesserily related to BSE values since the shorter bond in cyclopropene (R_e = 1.298 Å) has the lower BE due to a larger BPC term. Hence, SE estimates often found in the literature based on optimized or experimental bond lengths may give misleading interpretations.

The strain energies and BSE values of CC bonds involved in two small rings are in some cases additive, a criterion which has been used for a classification of strained structural units.[12] For example, the CC bonds in cubane (tetrahedrane) show a BSE two times as large than in cyclobutane (cyclopropane) because one bond is involved in two rings. Although the three-membered ring bonds in prismane constitute two different rings, the BSE is the sum of the corresponding values of cylopropane and cyclobutane.

In most cases studied CH bonds connected to a strained carbon skeleton have a stabilizing effect (the BSE values are negative) on the total strain energy, i.e., the strain of the CC bond is partially compensated by stronger CH bonds (see Figure 1).[38] Coulson and Moffitt[39] were the first to show that the CH bonds of cyclopropane possess more s-orbital character than those of normal alkanes which seems to be a valid explanation for the CH bond strengthening in other cases also. Cremer and Gauss have estimated this stabilizing effect in the case of cyclopropane and cyclobutane with the hypervirial theorem partitioning method, and total values of −6 and −3 kcal/mol, similar to those reported here (−8.8 and −1.8 kcal/mol), were found.[31] The largest stabilizing BSE for a C(sp^3)−H bond is observed in tetrahedrane (−3.2 kcal/mol) which is in qualitative agreement with the large spin−spin coupling constant, $^1J_{CC}$ (i.e., large s-orbital character), found in a NMR study of the *tert*-butyl derivative.[40] Positive BSE values found previously[4] may be caused by the low-quality density (HF-SCF/STO-3G) employed.

An interesting example for the occurrence of negative BSE values in highly strained systems is the [4.4.4.4]fenestrane molecule (see Table 4 and Figure 1). The topology of this not yet synthesized compound forces the central carbon atom into a geometry which is not far away from a square planar coordination (the so-called anti-van't Hoff geometry). Unexpectedly however, the exceptional high strain energy of 177 kcal/mol is mainly concentrated in the outer CC bonds (BSE = 25.2 kcal/mol), while each central bond is stabilized by −6.7 kcal/mol. This is neither quantitatively nor qualitatively indicated by the central bond lengths which are quite similar to those of cyclopropane (BSE = 13.6 kcal/mol). The BPC term contributions (ΔR = 2.7 and 3.4 × 10^{-3} Å) are typical for four-membered rings, showing that the unusual distribution of strain is an inherent feature of this molecule. The small error of the calculated E_{at}^0 emphasizes these findings which explain partly the synthetic difficulties reported.[12] The outer CC bonds with BE values of 61 kcal/mol are assumed to be located near the corresponding transition states for bond cleavage resulting in a thermal (kinetic) instability. Negative BSE(CC) values are not very unusual and are often found in cases where the BPC term must be low or zero due to symmetry reasons (e.g., the double bond in bicyclo[2.2.0]hexene).

Finally, the limits of a bond energy partitioning scheme should also be mentioned. For example, the destabilization of planar CH_4 with respect to the tetrahedral form can be attributed to a charge transfer from the CH bonds to a nonbonding orbital at the carbon atom, i.e., there is a large atomic contribution to the total energy change. This can not fully be reflected by the BELE partioning scheme which emphasizes on properties of the charge density at bond critical points only. However, such a situation is actually not reached in the [4.4.4.4]fenestrane molecule, since, otherwise, the E_{at}^0 value should be large in error.

Conclusions

The understanding of chemical bonding requires a qualitative and quantitative description of the phenomenon. The approach outlined in this work has the capability for both by using a minimum of information of the system, i.e., two numerical values at the bond critical point ($\rho(r_b)$ and $E_d(r_b)$) and the difference of the bond path and geometric lengths between the two atoms. At first sight the good performance of such a simple scheme seems surprising. However, density functional theory tells us that there exists a functional between the total energy of a molecule and the total charge density. In this sense this study has empirically shown that there also exists a simple relation between the properties of the charge density at certain points in space and the energy which is released by the formation of the molecule. Therefore, it is concluded that the deformation of the atomic charge densities and its energetical consequences are very specifically reflected (imaged) in the topology of the charge density at the bond critical points.

Future work shall investigate as well theoretical aspects as further applications of the approach. First, the performance of charge densities of lower quality (semiempirical NDDO, HF-SCF with small basis sets) is of interest with respect to computational effort. Second, the dependence of c_1(AB) on the charge transfer character of the AB bond has to be investigated to expand the applicability to heteroatomic and inorganic molecular systems.

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[38] The term bond strain energy is somewhat misleading in this case (the strain originates from the topology of the carbon skeleton) but is used for consistency throughout.

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