5174 *J. Phys. Chem. A* **1997,** *101,* 5174−5182

Theoretical Evaluation of Strain, Bent Bonds, and Bonding Behavior of Strained Organic Molecules

Cun-Yuan Zhao,[†,‡] Yong Zhang,[‡] and Xiao-Zeng You*,[‡]

Department of Chemistry, Northwest Normal University, Lanzhou 730070, People's Republic of China, and
Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University,
Center for Advanced Studies in Science and Technology of Microstructures, Nanjing 210093,
People's Republic of China

Received: October 31, 1996; In Final Form: March 21, 1997[⊗]

A new approach is presented to evaluate the molecular strain and bonding behavior in strained organic molecules on the basis of the electrostatic theorem of Hellmann−Feynman through the *force concept* instead of *energetics*. Taking advantage of the physical simplicity, visuality, and quantification of this model, chemically meaningful definitions of equivalent point charge, overlap force angle, strain force, binding force, tension energy, and the bond force angle have been proposed to measure the molecular strain, bent bonds, and bonding behavior of strained organic molecules at the HF/6-31G* level of theory. The overlap force angles are consistent with the experiment and other *ab initio* molecular orbital calculations. Results reveal that the overlap force angle, strain force, tension energy, and bond force angle can be used to account for the relative stabilities of small propellanes. The magnitude of binding force suggests the existence of central bonds in small propellanes. The bond force angles in most strained organic molecules seem to prefer the tetrahedral angle 109.5°, while those in three-membered rings prefer the angle 120° over the angle 109.5°, though the geometrical angles can largely range from 60° to 132°. This indicates that, in most cases, the atomic orbitals have to be overlapped in the manner of the ideal or nearly ideal tetrahedral hybrid in order to relax the molecular strain. The largely shifted overlapping charge outside rings and bond force angles of nearly 120° for HCH, HCC, and CCC and the resultant increased s character of C−H bond for three-membered rings can rationalize the C−C bond's higher reactivity than the C−C bonds of other rings. In general, the departure ($\Delta\beta$) of the bond force angle from the tetrahedral angle provides a measure of the degree of relaxation of the charge density from the geometrical constraints imposed by the nuclear framework and may be used as a way of assessing the molecular strain, reactivity, and stability for strained organic molecules.

1. Introduction

The polycyclic and polyhedral hydrocarbons have been the interesting subject of theoretical and experimental studies[1−9] for a long time due to their distinctive structure and high reactivity. Several decades ago the "bent bond" model of bonding in cyclopropane were introduced by Coulson et al.[4,5] Both theoretical and experimental studies[6−9] have shown that the electron distribution in each C−C internuclear region in cyclopropane is not concentrated along the line between the nuclei, as is typical of covalent bond, but rather slightly outside this line. The "bent bond" model is often used to analyze energetics (strain energies) and electron density distribution of strained rings. According to the classical definition of strain introduced by Baeyer,[1] carbon atoms whose bond angles (as determined from interatomic vectors) depart markedly from the standard bond angles 109.5°, 120°, and 180° with respect to the sp^3, sp^2, and sp hybrid orbitals are said to be strained. From the viewpoint of thermochemistry, strain energy is defined as the deviation of heat of formation from that expected on the basis of additivity relationship[10] which holds for "standard" or "unstrained" molecules. This quantity is traditionally used to evaluate to what extent a molecule is strained as a whole. Bader and co-workers[8] have proposed that the bond between two atoms in a molecule can be characterized by means of a "bond path". The bond path consists of the two density gradient paths that originate at the electron density saddle point, which is located in the internuclear region, and terminate at the two nuclei. Along the bond path the electronic density is a maximum with respect to any displacement to either side of the path. For the ordinary C−C single bond, the bond path is simply the straight line connecting the two nuclei. The bond paths in cyclopropane and other strained organic molecules, on the other hand, are shifted away from this line and from rings. Wiberg and co-workers[2] proposed that the bond path angle, the angle subtended at a nucleus by two bond paths, when compared to the corresponding geometrical or bond angle, is important in quantifying the concept of bond strain in molecules. They also gave another related quantity, the bond path length. Politzer[9] introduced the bond deviation index to describe the strained bonds. The bond deviation index is defined as the difference between actual and reference bond paths, which are defined in terms of the superposed electronic densities of the free atoms. However, the problem of some definitions of strain and bent bonds is the use of an arbitary reference state, such as the "standard" or "unstrained" molecule in the definition of strain energy, or the reference bond path in the definition of bond deviation index. In addition, the strain energy can only assess the strain of a molecule in the whole manner. It cannot estimate the strain of a certain bent bond.

On the other hand, instead of the "bonding" concept in terms of the energy change, the chemical system can be interpreted with the "binding" concept in terms of the forces exerted on the nuclei. The force is just the classical electrostatic attraction acting upon the studied nucleus with the electric field formed by the other nuclei and all electrons. Then the chemical

---

[†] Department of Chemistry.
[‡] Coordination Chemistry Institute.
[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

S1089-5639(96)03426-3 CCC: $14.00

problems can be discussed on the basis of the well-defined physical model. However, this kind of investigation requires the charge distribution determined by quantum mechanics. In addition, there may be many possible distributions which could satisfy the requirement of zero forces on the nuclei. But not all of them can be the real nature. Thus both the ways to obtain electronic charge density and to classify the charge distribution are critical to the study of the characteristics of the chemical system. The charge density and its possible distribution may be used as the physical vehicle for the discussion of the nature of chemical bonding, as well as of binding.

To our knowledge, there is no systematic study in terms of force concept to characterize the bent bond, strain features, and the relationships among structure, strain, molecular stability, and reactivity of strained organic molecules. Therefore, the purpose of this work is to derive a general theoretical method to evaluate the bent bond and strain features of any arbitrary strained organic molecules by virtue of the Hellmann−Feynman theorem and to explore the relationships among structure, strain, stability, and reactivity by studying the bent bond and bonding behavior in strained organic molecules.

2. Theoretical Approach

(1) Partitioning of Electronic Force. From the electrostatic theorem due to Hellmann and Feynman,[11] the electronic force acting in the x direction on nucleus A in a molecule is given by

$$f_{A,x} = \langle \Psi | \hat{F}_{A,x} | \Psi \rangle \tag{1}$$

$\hat{F}_{A,x}$ is the force operator, which is expressed as follows:

$$\hat{F}_{A,x} = -\frac{\partial V_{\mathrm{en}}}{\partial X_A} \tag{2}$$

where V_{en} is the electron−nuclear potential energy operator and X_A is the x component of the Cartesian coordinate.

For the closed-shell system, the Slater single-determinant molecular wave function Ψ can be written as

$$\Psi = (N!)^{-1/2} |\psi_1(1)\bar{\psi}_1(2)\psi_2(3)\bar{\psi}_2(4)...\psi_m(N-1)\bar{\psi}_m(N)| \tag{3}$$

where N is the number of electrons of the system and m is the number of occupied orbital. For the closed-shell system, $N = 2m$. The MO ψ_k can be expressed as

$$\psi_k = \sum_{i=1}^{n} C_{ik}\phi_i \tag{4}$$

where n is the number of selected basis functions. Then the density matrix $\hat{P}$ and its elements P_{ij} are defined as

$$\hat{P} = \hat{C}\,\hat{C} \qquad \text{or} \qquad P_{ij} = \sum_{k=1}^{m} C_{ik}C_{jk} \tag{5}$$

where $\hat{C}$ is the eigenvalue of the molecular orbital. Then the electronic force acting on nucleus A in the x direction of the kth occupied orbital can be obtained by

$$\begin{aligned} f_{A,x}^{(k)} &= 2\langle \psi_k | \hat{F}_{A,x} | \psi_k \rangle \\ &= 2\sum_{i=1}^{n} C_{ik}C_{ik}\,\langle \phi_i | \hat{F}_{A,x} | \phi_i \rangle + 4\sum_{i>j}^{n} C_{ik}C_{jk}\langle \phi_j | \hat{F}_{A,x} | \phi_j \rangle \end{aligned} \tag{6}$$

The total electronic force is summed by the force acting on nucleus A in the x direction with all occupied orbitals:

$$\begin{aligned} f_{A,x} = 2\sum_{k=1}^{m}\sum_{i=1}^{n} C_{ik}C_{ik}\langle \phi_i | \hat{F}_{A,x} | \phi_i \rangle + 4\sum_{k=1}^{m}\sum_{i>j}^{n} C_{ik}C_{jk}\langle \phi_j | \hat{F}_{A,x} | \phi_j \rangle = \\ 2\sum_{i=1}^{n} P_{ii}F_{ii} + 4\sum_{i>j}^{n} P_{ij}F_{ij} \end{aligned} \tag{7}$$

where F_{ij} is the element of force matrix.

$$F_{ij} = \langle \phi_i | \hat{F}_{A,x} | \phi_j \rangle \tag{8}$$

On the basis of the work of Bader[12,13] and the LCAO-MO theory, the electronic force exerting on nucleus A can be partitioned into three parts: atomic, screening, and overlap forces.

Atomic Force. The atomic force is the force exerted on nucleus A by the electron density centered on A. If this density is undeformed, then there will be no net force acting upon the nucleus A due to a center of symmetry in this case. However, any polarization of the electron density distribution can give rise to a force on nucleus A in the same direction as that of the polarization.

Therefore the atomic force acted on nucleus A due to the electronic density on nucleus A of the kth molecular orbital can be written as

$$f_{A,A}^{(k)} = 2\sum_{r,s}^{r,s\in A} C_{rk}C_{sk}F_{rs} \tag{9}$$

The total atomic force is summed with all MOs as

$$f_{A,A}^{(p)} = 2\sum_{k=1}^{m}\sum_{r,s}^{r,s\in A} C_{rk}C_{sk}F_{rs} \tag{10}$$

Screening Force. The screening force is the force of nucleus B from nucleus A by electron density described by basis functions centered on nucleus B. It is a measure of the electronic shielding of nucleus B upon nucleus A by electrons of nucleus B.

The screening force acted on nucleus A due to the electronic density on nucleus B (B ≠ A) of the kth molecular orbital is given by

$$f_{B,B}^{(k)} = 2\sum_{r,s}^{r,s\in B} C_{rk}C_{sk}F_{rs} \tag{11}$$

The total screening force is summed with all MOs as

$$f_{B,B}^{(s)} = 2\sum_{k=1}^{m}\sum_{r,s}^{r,s\in B} C_{rk}C_{sk}F_{rs} \tag{12}$$

Overlap Force. The overlap force is the force exerted on nucleus A due to the density which results from the overlap of basis functions on two different nuclear centres. Such overlap results in the transfer of charge density to the region between the two nuclei A and B. The overlap force is a quantitative measure of the effectiveness of this transferred density in binding the two nuclei together.

The overlap force acted on nucleus A due to the electronic density on nuclei A and B (B ≠ A) of the kth molecular orbital is given by

$$f_{A,B}^{(k)} = 4\sum_{r}^{r\in A}\sum_{s}^{s\in B} C_{rk}C_{sk}F_{rs} \tag{13}$$

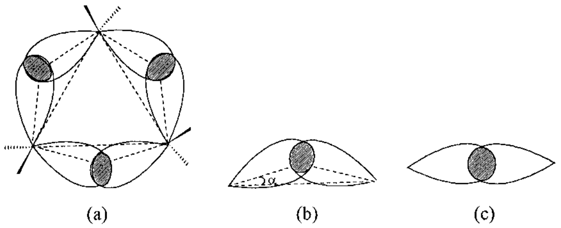

Figure 1. (a) The bent bond model of cyclopropane, (b) overlap force angle α, and (c) a normal σ bond.

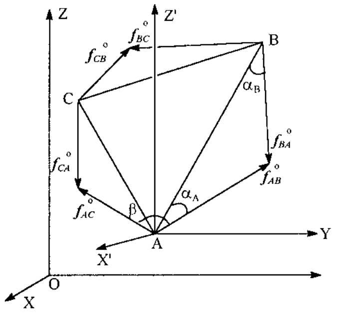

Figure 2. The Cartesian coordinate used for calculating overlap force angles.

The total overlap force is summed with all MOs as

$$f^{(o)}_{A,B} = 4\sum_{k=1}^{m}\sum_{r}^{r\in A}\sum_{s}^{s\in B} C_{rk}C_{sk}F_{rs} \tag{14}$$

The conceptual advantage of interpreting a chemical bond through the consideration of the electrostatic forces exerted on the nuclei lies in the fact that these forces are directly determined by the one-electron density, a measurable quantity, playing the central role in this approach. This density exists in a real space, and thus its pictures may be used to gain a physical insight into the forces acting on the nuclei. With this aspect in mind, we will reproduce the characterization of bent bonds, and strain and bonding behavior of strained organic molecules by virtue of the overlap force in the following section.

(2) Characterization of Bent Bonds and Strain and Bonding Behavior. Due to the geometrical constrains in strained molecules, the overlap of atomic orbitals between two bonded atoms is not exactly pointed toward the interatomic vector, but it departs from this vector and forms an angle with it (Figure 1). This gives rise to the introduction of the concept of bent bond as discussed previously. Because the overlap force acting on nuclei mainly contributes to chemical binding, the direction and bonding extent of bent bonds in a molecule can be determined by the sign and the magnitude of the overlap force.

Figure 2 displays two bent bonds AB and AC in a molecule. Moving the Cartesian coordinate to atom A, the new coordinate of nucleus A will be (0,0,0) and that of B will be ($x_B - x_A$, $y_B - y_A$, $z_B - z_A$). Here (x_A, y_A, z_A) and (x_B, y_B, z_B) are the old coordinates of nuclei A and B. f°_{AB} and f°_{BA} are the overlap forces exerted on nuclei A and B, respectively, and result from the overlap density shared by A and B. Their Cartesian components are (f°_{ABx}, f°_{ABy}, f°_{ABz}) and (f°_{BAx}, f°_{BAy}, f°_{BAz}), respectively.

The overlap force angle α_{AB} (henceforth α_{AB} or α_{BA} will be abbrieviated to α_A or α_B) of bond AB pointing to B can be calculated as the angle formed between coordinate vector **AB** and force vector f°_{AB} (see Figure 2).

$$\alpha_A = \cos^{-1}\frac{\mathrm{AB}\cdot\hat{\mathrm{f}}^\circ_{\mathrm{AB}}}{|\mathrm{AB}||\mathrm{f}^\circ_{\mathrm{AB}}|} = \cos^{-1}\frac{\mathrm{f}^\circ_{\mathrm{ABx}}(\mathrm{x_B}-\mathrm{x_A}) + \mathrm{f}^\circ_{\mathrm{ABy}}(\mathrm{y_B}-\mathrm{y_A}) + \mathrm{f}^\circ_{\mathrm{ABz}}(\mathrm{z_B}-\mathrm{z_A})}{\mathrm{f}^\circ_{\mathrm{AB}}\sqrt{(\mathrm{x_B}-\mathrm{x_A})^2 + (\mathrm{y_B}-\mathrm{y_A})^2 + (\mathrm{z_B}-\mathrm{z_A})^2}} \tag{15}$$

Similarly, the overlap force angle α_{BA} of bond BA pointing A will be (Figure 2)

$$\alpha_B = \cos^{-1}\frac{\mathrm{BA}\cdot\hat{f}^\circ_{BA}}{|\mathrm{BA}||\hat{f}^\circ_{BA}|} = \cos^{-1}\frac{f^\circ_{BAx}(x_A - x_B) + f^\circ_{BAy}(y_A - y_B) + f^\circ_{BAz}(z_A - z_B)}{f^\circ_{BA}\sqrt{(x_B - x_A)^2 + (y_B - y_A)^2 + (z_B - z_A)^2}} \tag{16}$$

It is convenient to define the equivalent point charges[12] q°_A and q°_B of overlap forces f°_{AB} and f°_{BA} as follows (Figure 3)

$$q^\circ_A = \frac{f^\circ_{AB}r^2_{\mathrm{A}}}{Z_A} \tag{17}$$

$$q^\circ_B = \frac{f^\circ_{BA}r^2_{B}}{Z_B} \tag{18}$$

where Z_A and Z_B are the total populations of atoms A and B.

The strain force f can be defined as the projection of overlap forces f°_{AB} and f°_{BA} in the perpendicular direction of interatomic vector **AB** as shown in Figure 3.

$$f = f^\circ_{AB}\sin\alpha_A + f^\circ_{BA}\sin\alpha_B \tag{19}$$

The binding force F is defined as the projection of overlap forces f°_{AB} and f°_{BA} in the direction of interatomic vector **AB** as shown in Figure 3.

$$F = f^\circ_{AB}\cos\alpha_A + f^\circ_{BA}\cos\alpha_B \tag{20}$$

The tension energy ϵ is defined as the work done by the charge equivalents q°_A and q°_B as they are displaced a distance d to the point O shown in Figure 3.

$$\epsilon = \int_0^d f\,\mathrm{d}s = \int_0^d\left[\frac{Z_{\mathrm{A}}q^\circ_A}{s^2 + R^2_A}\frac{s}{\sqrt{s^2 + R^2_A}} + \frac{Z_Bq^\circ_B}{s^2 + R^2_B}\frac{s}{\sqrt{s^2 + R^2_B}}\right]\mathrm{d}s = q^\circ_AZ_A\left(\frac{1}{R_A} - \frac{1}{\sqrt{R^2_A + d^2}}\right) + q^\circ_BZ_B\left(\frac{1}{R_B} - \frac{1}{\sqrt{R^2_B + d^2}}\right) \tag{21}$$

where $d = R_A tg\alpha_A$ or

$$d = R_B tg\alpha_B \tag{22}$$

$$R_A = \frac{R}{\sin(\alpha_A + \alpha_B)}\sin\alpha_B\cos\alpha_A \tag{23}$$

$$R_B = \frac{R}{\sin(\alpha_A + \alpha_B)}\sin\alpha_A\cos\alpha_B \tag{24}$$

The tension energy ϵ (defined here) should not be confused with strain energy which can be obtained on the basis of additivity relationship[10] and experimental heat of formation.

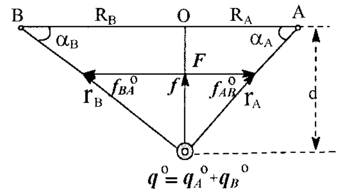

Figure 3. Schematics of the equivalent point charge and bent bonds in a strained organic molecule.

Because the orbital overlap of bent bond AB is not pointed toward the interatomic vector but formed an angle α_A or α_B with this vector, it is easy to obtain the overlap force length r of bent bond AB, the sum of the distances between charge equivalents and the two bonded nuclei shown in Figure 3.

$$r = r_A + r_B = \frac{R_A}{\cos\alpha_A} + \frac{R_B}{\cos\alpha_B} = \frac{\sin\alpha_A + \sin\alpha_B}{\sin(\alpha_A + \alpha_B)}R \quad (25)$$

where R is the interatomic distance.

Another important quantity is the bond force angle, the angle subtended at a nucleus by the overlap force vectors to two bonded atoms, or the sum of the two corresponding overlap force angles and bond angle. That is, the angle is formed by two bent bonds AB and AC which can be determined by the force vectors f^o_{AB} and f^o_{BA} as shown in Figure 2.

$$\beta = \cos^{-1}\frac{\hat{f}^o_{AB}\hat{f}^o_{AC}}{|\hat{f}^o_{AB}||\hat{f}^o_{AC}|} = \cos^{-1}\frac{f^o_{ABx}f^o_{ACx} + f^o_{ABy}f^o_{ACy} + f^o_{ABz}f^o_{ACz}}{f^o_{AB}f^o_{AC}} \quad (26)$$

From the above definitions it is convenient to characterize strain and bonding behavior of bent bonds in any arbitrary strained organic molecules through the *force concept*. The equivalent point charge q^o describes the extent of orbital overlap and the accumulation of charge outside the strained rings. The overlap force angles α_A, α_B and strain force f are the measurements of bond strain. Binding force F and the overlap force length r can be used to estimate the extent of binding. Tension energy ϵ may be used to measure the unstability of a certain bent bond in strained organic molecules. The bond force angle β (angle between two bent bonds or two overlap forces) can be used to describe the torsion degree of a certain bent bond.

It should be noted that in the present definitions, the overlap force angle, α_A or α_B, is based upon Mulliken partitioning of the density, *i.e.*, the overlap force. The other related quantities, such as point charge, strain force, binding force, tension energy, the bond force angle, and the bond force length also come from the overlap force concept. While within the topological theory,[2,8] the related quantities, such as bond path angle and bond path length are determined from the expectation value of a quantum mechanical observable, the total electron density.

3. Results and Discussion

Calculation Results and Basis Set Effects. The geometries of 23 typical organic molecules (Scheme 1) including propane **1**, cycloalkanes **2**−**5**, bicycloalkanes **6**−**12**, small ring propellanes **13**−**16**, spiropentane **17**, and polyhedranes **18**−**22** are optimized by employing Gaussian 92 software[14] with basis set 6-31G* constrained with highest symmetry. The dodecahedrane **23** was only calculated with single-point SCF (CC = 1.54 Å) and the same basis set. Using the wave functions obtained by Gaussian 92, the electrostatic forces acting on each nucleus are computed by Program ABHF.[15] This software can analyze the Hellmann−Feynman force and decompose the electronic force into three parts: atomic, screening, and overlap forces. Then the strain characteristics are computed by eqs 15−25 and listed in Table 3.

SCHEME 1: Structures of the Title Molecules

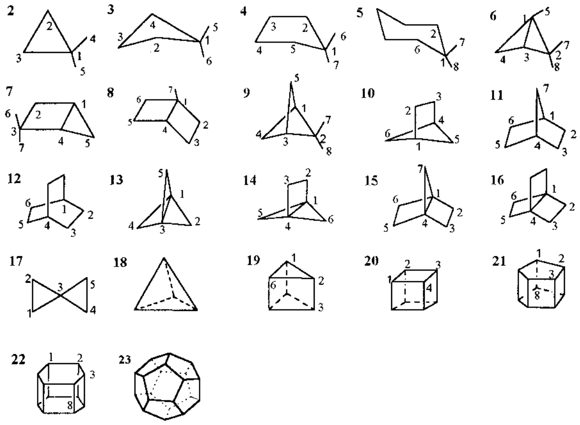

TABLE 1: Effect of Basis Set Selectivity on Strain Characteristics of Cyclopropane

characteristics	STO-3G	3-21G	4-31G	6-31G	6-31G*	6-31G**
overlap force angle α	23.07	38.34	36. 74	37.60	29.50	29.44
strain force f (au)	1.3554	2.5713	2.5286	2.6173	2.0698	2.0592
binding force F (au)	3.1826	3.2515	3.3880	3.3983	3.6580	3.6487
point charge q^o (au)	1.3328	2.0909	2.0764	2.1552	1.7469	1.7662
tension energy ϵ (au)	0.4623	2.0556	1.8495	2.0086	1.0179	1.0092
net force (au)						
C	0.1880	0.4410	0.5165	0.2698	0.1269	0.1314
H	0.0508	0.0845	0.1277	0.0662	0.0472	0.0138
relative error						
C (%)	2.6	6.1	7.2	3.8	1.8	1.8
H (%)	2.3	3.8	5.8	3.0	2.1	0.6

Although many past studies have shown that the magnitude of calculated electrostatic forces is very sensitive to the accuracy of the approximate wave functions used,[16−18] it is believed that the quantitative consequence will be improved with increasing accuracy of the wave function used. Actually, as shown in Table 1, the calculated net force acting on carbon and hydrogen in cyclopropane does show the dependence of basis set. The net forces acting on atoms and their relative errors with 6-31G* or 6-31G** are clearly better than those with STO-3G, 3-21G, 4-31G, and 6-31G. It is noted that the 6-31G** basis set which adds p functions to hydrogen atoms only have a little improvement in the net force acting on hydrogen atoms and in the relative errors but have no significant improvement in the other strain characteristics as shown in Table 1. Taking this into account, we selected the 6-31G* basis set throughout the study both for optimization and for strain characteristics calculations. It is also noted that the net forces acting on carbon and hydrogen and their relative error in cyclopropane, bicyclobutane, [1.1.1]-propellane, and cubane are very small as some of the typically strained organic molecules shown in Table 2. The small net force and small relative error (about 2.0% or less) both indicate that the wave function with 6-31G* is close to the Hartree−Fock limit. This enables us to be sure that the 6-31G* wave function is reliable for computing Hellman−Feynman force. As a consequence, the calculated results could also be reliable for interpretation of chemical binding in molecules.

Geometries and Strain Behavior of Strained Organic Molecules. It can be seen from Table 3 that the C−C bonds in cyclic, bicyclic, propellanes, and polyhedral hydrocarbons

TABLE 2: Electronic Force, Nuclear Force of Repulsion, and Relative Errors[a] of Net Force Acted on Carbon or Hydrogen Nucleus for Some Hydrocarbons

	2		**6**		**13**		**20**	
atom	C	H	C_1	H_5	C	H	C	H
electronic force (au)	7.0588	2.1496	9.3606	2.3633	10.9802	2.5661	12.7941	2.8488
nuclear force of repulsion (au)	7.1857	2.1968	9.5263	2.4146	11.1265	2.6163	12.8828	2.9014
net force (au)	0.1269	0.0472	0.1660	0.0513	0.1463	0.0502	0.0887	0.0526
relative error (%)	1.8	2.1	1.7	2.1	1.3	1.9	0.7	1.8

[a] Relative error (%) = (nuclear force of repulsion−electronic force)/(nuclear force of repulsion (100%)).

TABLE 3: Strain and Bonding Characteristics of Strained Organic Molecules

		bond length		overlap force angle		strain force[a]	binding force	point charge	tension energy
molecule	bond	R (Å)	*r* (Å)	α_A (deg)	α_B (deg)	*f* (au)	*F* (au)	$q°$ (au)	ϵ (au)
C_3H_8, **1**	C−C	1.5284	1.5287	0.79	1.66	0.0894	4.1677	1.1899	0.0019
C_3H_6, **2**	C−C	1.4974	1.7205	29.50	29.50	2.0698	3.6580	1.7469	1.0179
C_4H_8, **3**	C−C	1.5453	1.5724	10.66	10.66	0.7826	4.1588	1.4767	0.1103
C_5H_{10}, **4**	1−2	1.5306	1.5322	2.65	2.65	0.1971	4.2587	1.4142	0.0066
	2−3	1.5355	1.5363	2.32	1.42	0.1381	4.2219	1.3267	0.0039
	3−4	1.5495	1.5500	1.07	1.64	0.0989	4.0873	1.3251	0.0019
C_6H_{12}, **5**	C−C	1.5320	1.5322	0.99	0.99	0.0724	4.2124	1.3990	0.0009
C_4H_6, **6**	1−3	1.4666	1.7869	34.84	34.84	2.5204	3.6210	2.0328	1.6268
	1−2	1.4882	1.7353	33.81	28.31	2.1637	3.5885	1.7930	1.2105
C_5H_8, **7**	1−4	1.5130	1.7324	29.15	29.15	2.1321	3.8224	1.8933	1.0392
	1−2	1.5297	1.5556	11.72	9.33	0.7809	4.2133	1.4611	0.1116
	2−3	1.5564	1.5829	10.50	10.50	0.7499	4.0456	1.4569	0.1048
	1−5	1.4932	1.7286	31.57	28.98	2.1299	3.6459	1.7941	1.1037
C_6H_{10}, **8**	1−4	1.5586	1.5995	12.99	12.99	1.0115	4.3850	1.6633	0.1786
	1−2	1.5450	1.5737	11.87	10.09	0.8066	4.1575	1.4884	0.1200
	2−3	1.5525	1.5772	10.14	10.14	0.7338	4.1019	1.4632	0.0986
C_5H_8, **9**	C−C	1.5457	1.6208	17.63	17.41	1.3004	4.1193	1.6230	0.3218
C_6H_{10}, **10**	1−2	1.5365	1.5376	3.57	1.29	0.1843	4.3574	1.1484	0.0094
	2−3	1.5587	1.5634	4.44	4.44	0.3101	3.9897	1.3827	0.0178
	1−5	1.5466	1.5927	14.54	13.13	1.0226	4.1507	1.5449	0.1941
C_7H_{12}, **11**	1−2	1.5404	1.5413	3.18	1.12	0.1618	4.3065	1.1237	0.0075
	2−3	1.5574	1.5595	3.02	3.02	0.2114	4.0014	1.3766	0.0082
	1−7	1.5370	1.5457	6.36	5.82	0.4559	4.2724	1.4633	0.0358
C_8H_{14}, **12**	1−2	1.5356	1.5358	0.41	1.63	0.0761	4.2973	0.9355	0.0020
	2−3	1.5525	1.5527	0.95	0.95	0.0661	3.9836	1.3576	0.0008
C_5H_6, **13**	1−3	1.5438	1.5438	0.00	0.00	0.00	2.6301	0.9352	0.0000
	1−2	1.5025	1.6761	32.19	21.44	1.8303	3.6013	1.6056	0.9520
C_6H_8, **14**	1−4	1.5960	1.7189	21.79	21.79	1.2716	3.1801	1.5010	0.4282
	1−2	1.5458	1.5708	13.16	7.97	0.7520	4.0490	1.3828	0.1252
	2−3	1.5400	1.5680	10.84	10.84	0.7987	4.1707	1.4690	0.1143
	1−6	1.4917	1.7006	35.98	22.79	2.0113	3.5282	1.6646	1.2973
C_7H_{10}, **15**	1−4	1.5263	1.6091	18.47	18.47	1.6717	5.0050	2.0233	0.4357
	1−2	1.5373	1.6009	20.59	12.72	1.1668	3.9140	1.4383	0.3253
	2−3	1.5638	1.5864	9.69	9.69	0.7054	4.1325	1.4891	0.0909
	1−7	1.4842	1.8069	41.13	29.29	2.4207	3.3847	1.9738	2.0110
C_8H_{12}, **16**	1−4	1.5114	1.5114	0.00	0.00	0.0000	5.9216	2.0069	0.0000
	1−2	1.5481	1.6170	20.44	13.78	1.2053	3.9198	1.5007	0.3317
	2−3	1.5686	1.5885	9.09	9.09	0.6604	4.1282	1.4883	0.0798
C_5H_8, **17**	1−2	1.5171	1.7291	28.67	28.67	1.9722	3.6064	1.7221	0.9386
	2−3	1.4746	1.7072	29.30	31.24	2.1705	3.7187	1.8182	1.1032
C_4H_4, **18**	C−C	1.4634	1.8509	37.80	37.80	2.6827	3.4589	2.1541	2.0326
C_6H_6, **19**	1−2	1.5070	1.7106	28.24	28.24	1.9882	3.7018	1.7721	0.9176
	2−3	1.5489	1.5746	10.37	10.37	0.7691	4.2027	1.5267	0.1056
C_8H_8, **20**	C−C	1.5590	1.6164	15.31	15.31	1.1397	4.1624	1.6284	0.2426
$C_{10}H_{10}$, **21**	1−2	1.5515	1.5974	13.76	13.76	0.9959	4.0681	1.5436	0.1867
	1−8	1.5579	1.5902	11.57	11.57	0.9220	4.5047	1.6795	0.1432
$C_{12}H_{12}$, **22**	1−2	1.5513	1.6056	14.94	14.94	1.0601	3.9719	1.5314	0.2183
	2−8	1.5536	1.5862	11.65	11.65	0.9477	4.5979	1.7067	0.1479
$C_{20}H_{20}$, **23**	C−C	1.5400	1.5412	2.25	2.25	0.1701	4.3204	1.4859	0.0049

[a] Unit of force in table is atomic unit (au). 1 au of force = 1 hartree/1a_0 = (27.212)(1.602 × 10^{-12} erg)/0.5291 67 × 10^{-8} cm = 8.238 67 × 10^{-3} dyn = e^2/a_0^2.

are strained somewhat, though C−C bonds of acyclic propane **1** is strainless according to the calculated overlap force angle α, strain force *f*, and tension energy ϵ. These results are generally consistent with the common chemical intuition about strain concept. The overlap force angle of cyclopropane is calculated to be 29.50°, close to that of 24° determined by X-ray diffraction[6] for the isoelectronic analogs of cyclopropane. The calculated overlap force angle is also in good agreement with that of 27.5° obtained from *ab initio* localized molecular orbitals (LMO).[19] The calculated overlap force angle of cyclobutane is 10.66°, which is much less than that of cyclopropane and corresponds to much smaller angle strain than that in cyclopropane. Although there is no available experimental data for comparison, the value agree well with the bent angle of 10.70° calculated from the *ab initio* LMO.[19] Interestingly, the overlap force angles of bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane are also in good agreement with those determined by atomic orbital hybrid of LMO.[19] In the case of cyclopentane, there is only small distortions (2.65° or 2.32°) for the C−C bonds. The very small distortion (less than 1°) of C−C bonds in cyclohexane is consistent with the well-known fact that the cyclohexane is essentially strainless. For the bicycloparaffins, it is interesting to note that the fusing of two rings to a common bridgehead bond requires more angle strain. The common bridgehead bond C_1-C_3 in cyclobutane (**6**) gives a overlap force angle of 34.84°, which is larger than the ordinary C−C bent bond in cyclopropane. The strain force f and tension energy ϵ also show the same tendency. The overlap force angle α, strain force f and tension energy ϵ of the common C_1-C_4 bond in bicyclo[2.2.0]-hexane, **8**, is also larger than that of corresponding cyclobutane ring ($\alpha = 10.66°$, $f = 0.7826$ au, $\epsilon = 0.1103$). However, the overlap force angle, strain force, and tension energy of the common C_1-C_4 bond in cyclopentane, **7** seems to be close to those of cyclopropane. In the case of bicyclopapaffins **9**−**12**, because each C−C bond can be regarded as a common bridgehead bond for two rings, the overlap force angle and strain of each C−C bonds are slightly larger than those of corresponding small ring cycloparaffins, such as 17.63° or 17.41° and 1.3004 au for C−C bonds in molecule **9** *vs* 10.66° and 0.7826 au for molecule **3** and 14.54° or 13.13° and 1.0226 au for C_1-C_5 of **10** *vs* 10.66° and 0.7826 au for **3** (suppose that the C_1-C_5 in **10** belongs to the smaller ring).

The most strained bond, on the other hand, is the C−C bond of tetrahedrane, **18**. The overlap force angle of C−C bond in **18** is calculated to be 37.80°, which is apparently larger than that of cyclopropane (29.50°) and even greater than the fused bond of bicyclobutane. This can be readily understood by its geometrical constrains in stereo bonding. The other polyhedral hydrocarbons **20**−**23** have slightly larger distorted C−C bond compared to those of corresponding cycloparaffins except that the prismane, **19**, and dodecahedrane, **23**, seem to have similar bent bonds compared to those of corresponding cyclic ring.

In the case of small propellanes **13**−**16**, it is seen that the strain force of C_1-C_2 bond in the so-called most strained [1.1.1]-propellane[20,21] is in fact not very high. Although the overlap force angle 32.19° from bridgehead carbon to the vertex is slightly larger than that of cyclopropane, the overlap force angle 21.44° from the vertex carbon atom to the bridgehead is even smaller by 8° than that of cyclopropane. This leads to the smaller strain force (1.8303 au) and tension energy (0.9520 au) than those of cyclopropane. For the [2.1.1] and [2.2.1]-propellane, the overlap force angle α, strain force f, and tension energy ϵ of triangle ring is apparently larger than those of cyclopropane. On the other hand, the overlap force angle, strain force, and tension energy in [2.2.2]propellane are much smaller than those of cyclopropane. Because of the D_{3h} symmetry, the central bonds in [1.1.1]- and [2.2.2]propellanes are not strained. However, the central bonds in [2.1.1]- and [2.2.1]propellanes are much strained. The large distortions of central C−C bonds and more strained triangle ring in [2.1.1]- and [2.2.1]propellanes make it unstable. The [1.1.1]- and [2.2.2]propellanes are relatively stable due to their small bond strain and unstrained central bonds. As a matter of fact, [1.1.1]propellane has a half-life of 5 min at 114 °C. The [2.1.1]- and [2.2.1]propellanes have not been separated, although they can be identified by IR spectra[21−23] on a low-temperature matrix, while [2.2.2]propellane is reported to have a half-life of 1 h at 20 °C.[24] It is obvious that these relative stabilities of small propellanes are qualitatively consistent with the relative magnitude of strain characters as discussed above.

While the present defined strain parameters can be used to evaluate the bond and angle strain of a certain bent bond, they can also be used to qualitatively account for the molecular strain as a whole. The extent of bond or angle strain are characterized by overlap force angle, strain force, tension energy, bond force angle, or its departure from tetrahedral angle 109.5° (see the detailed discussions in the last section of this part). Generally, the large bond or angle strain corresponds to large strain energies. The cyclopropane and cyclobutane have relative large strain force and tension energy compared to cyclopentane and cyclohexane, consistent with the strain energy (27.5, 26.5 Kcal/mol *vs* 6.2, 0.0 Kcal/mol). The bicyclic hydrocarbons have large strain force and tension energy compared to the corresponding cyclic hydrocarbons, also consistent with the strain energies.[2] The strain energy of cyclopropane (27.5 Kcal/mol) is nearly same as that for cyclobutane (26.5 Kcal/mol) in spite of its overlap force angle being smaller by 20°. This similarity in strain energies can be explained, at least in part, by the much greater relaxation of angle strain between the bonds in cyclopropane than between those in cyclobutane as indicated by the increments $\Delta\alpha$ and $\Delta\beta$ shown in Table 4 or by the lack of 1−3 nonbonded repulsions in cyclopropane. This interpretation is also consistent with that of topological theory given by Wiberg *et al.*[2] In the case of [*n*]prismanes, Disch[33] have computed strain energies of 148.7, 165.0, 140.1, and 177.7 Kcal/mol for $n = 3$, 4, 5, and 6, respectively. These large strain energies correspond to the large total strain forces $\sum_m f_i$ (14.24, 13.68, 14.57, and 18.41 au) or tension energies $\sum_m \epsilon_i$ (5.82, 2.91, 2.58, and 3.507 au). It is of interest to note that the averaged strain energies (SE/m, m is the total number of C−C bent bonds in molecules) for each C−C bent bond are 16.52, 13.75, 9.34, and 9.87 Kcal/mol, respectively, which parallel the averaged strain forces ($\sum_m f_i/m$, $m = 9$, 12, 15, and 18) of 1.58, 1.14, 0.9713, and 1.0226 au and the averaged tension energies ($\sum_m \epsilon_i/m$) of 0.6469, 0.2426, and 0.1722, 0.1948 au for the [*n*] prismanes ($n = 3$, 4, 5, and 6). The strain energy of dodecahedrane[34] is computed to be 65.4 Kcal/mol. For each C−C bond in dodecahedrane, the strain energy is 2.2 Kcal/mol, slightly larger than that of cyclopentane-(1.2 Kcal/mol) because each C−C bond in dodecahedrane is fused by two pentarings and require more angle strain. This result is in accordance with their averaged strain forces (0.1701 and 0.1539 au for dodecahedrane and cyclopentane) and our previous *ab initio* calculations.[35]

In addition, the bent bond and strain characteristics may be regarded as indications of reactivity for the strained rings. Because the overlapping charge is much more shifted from the interatomic vector than is that of cyclobutane, the resultant large overlap force angle, great strain force, and the tension energy of C−C bonds in cyclopropane enable cyclopropane to be easily attacked by electrophile and lead to addition reaction of ring opening, which are not observed at all in the case of cyclobutane or any cycloparaffin that does not contain a cyclopropane ring. The much shifted overlapping charge outside rings and the great bend of three-membered rings are fully consistent with the calculated negative electrostatic potentials in cyclopropane,[25] which are regarded as the reactive sites. This helps us to explain some of the chemical properties of cyclopropane, such as its somewhat olefin-like behavior(for instance, it undergoes certain addition reactions). The conclusions about π-like character, the reactivity of three-membered rings, and the stability of small propellanes are also in agreement with those concluded by Wiberg *et al.* in terms of topological theory.[2]

Bonding Behavior of Strained Organic Molecules. Intuitively, the overlap force due to the overlap density results from two bonded atoms is effective to evaluate the binding extent of

TABLE 4: Bond Angles θ, Bond Force Angles β, and Their Difference from the Tetrahedral Angles $\Delta\theta$ and $\Delta\beta$ (deg, $\Delta\theta = 109.5° - \theta$, $\Delta\beta = 109.5° - \beta$)

				departure	
molecule	angle	θ (deg)	β (deg)	$\Delta\theta$ (deg)	$\Delta\beta$ (deg)
1	C−C−C	112.8	109.5	−3.3	0.0
	C−C−H	109.4	109.6	0.1	−0.1
	H−C−H	106.3	108.9	3.2	0.6
2	2−1−3	60.0	119.0	49.5	−9.5
	3−1−4	118.1	105.9	−8.6	3.6
	4−1−5	114.0	114.7	−4.5	−5.2
3	2−1−4	88.5	109.4	21.0	0.1
	4−1−5	117.7	110.3	−8.2	−0.8
	5−1−6	108.5	109.1	1.0	0.4
4	2−1−5	103.3	107.6	6.2	1.9
	1−5−4	103.3	107.6	6.2	1.9
	3−4−5	105.3	107.6	4.2	1.9
	6−1−5	113.4	110.7	−3.9	−1.2
	6−1−7	107.4	108.8	2.1	0.7
5	2−1−6	111.5	109.5	−2.0	0.0
	1−2−3	111.5	109.5	−2.0	0.0
	2−1−8	110.1	110.2	−0.6	−0.7
	6−1−7	109.2	109.4	0.3	0.1
6	2−1−3	60.5	113.4	49.0	−3.9
	1−2−3	59.0	115.2	50.5	−5.7
	3−1−5	131.0	97.0	−21.5	12.5
	2−1−5	130.3	114.6	−20.8	−5.1
	1−2−7	116.8	108.1	−7.3	1.4
	7−2−8	113.9	114.9	−4.4	−5.4
7	2−3−4	89.2	108.9	20.3	0.6
	3−4−1	90.8	104.5	18.7	5.0
	1−4−5	59.6	117.4	49.9	−7.9
	1−5−4	60.9	118.8	48.6	−9.2
	2−3−6	114.6	110.0	−5.1	−0.5
	2−3−8	114.6	108.6	−5.1	0.9
8	1−4−3	89.9	108.6	19.6	0.9
	2−3−4	90.1	110.1	19.4	−0.6
	3−4−5	115.1	109.4	−5.6	0.1
	6−1−7	116.7	109.2	−7.2	0.3
	4−1−7	123.2	111.7	−13.7	−2.2
9	1−2−3	74.5	109.3	35.0	0.2
	2−3−4	87.2	109.3	22.3	0.2
	1−2−7	116.8	109.0	−7.3	0.5
	7−2−8	110.9	111.5	−1.4	−2.0
molecule	angle	bond θ (deg)	angle β (deg)	$\Delta\theta$ (deg)	$\Delta\beta$ (deg)
10	1−5−4	82.6	108.5	26.9	1.0
	6−1−5	86.0	110.9	23.5	−1.4
	3−4−5	101.9	107.4	7.6	2.1
	1−2−3	99.0	104.8	10.5	4.7
11	1−7−4	94.4	106.0	15.1	3.5
	2−1−7	101.5	107.7	8.0	1.8
	2−1−6	108.6	109.3	0.9	0.2
	4−5−6	103.1	106.9	6.4	2.6
12	1−2−3	109.7	109.0	−0.2	0.5
	2−1−6	109.2	108.8	0.3	0.7
13	2−1−3	59.1	91.3	50.4	18.2
	1−2−3	61.8	104.7	47.7	4.8
	2−3−4	96.0	120.0	13.5	−10.5
14	1−5−4	64.7	110.1	44.8	−0.6
	4−1−5	57.7	104.8	51.8	4.7
	2−1−6	97.4	112.7	12.1	−3.2
	5−1−6	112.1	121.9	−2.6	−12.4
	1−2−3	91.0	109.8	18.5	−0.3
	2−1−4	89.0	80.3	20.5	29.2
15	1−7−4	61.9	120.5	47.6	−11.0
	1−4−7	59.1	118.7	50.4	−9.2
	3−4−7	112.8	105.8	−3.3	3.7
	4−1−2	90.7	103.1	18.8	6.4
	1−2−3	89.3	111.1	20.2	−1.6
16	3−4−5	120.0	107.4	−10.5	2.1
	4−1−2	91.1	111.5	18.4	−2.0
	1−2−3	88.9	111.8	20.6	−2.3
17	1−3−2	59.0	119.0	50.5	−9.5
	1−2−3	61.9	120.5	47.6	−11.0
	1−3−4	137.3	104.2	−27.8	5.3
18	C−C−C	60.0	111.9	49.5	−2.4
19	1−2−6	60.0	112.5	49.5	−3.0
	1−2−3	90.0	103.6	19.5	5.9
20	C−C−C	90.0	109.0	19.5	0.5
21	1−2−3	108.0	107.5	1.5	2.0
	2−1−8	90.0	109.8	19.5	−0.3
22	1−2−3	120.0	109.1	−10.5	0.4
	1−2−8	90.0	110.7	19.5	−1.2
23	C−C−C	108.0	110.2	1.5	−0.7

a chemical bond. The resultant binding force, defined as the projection of overlap forces acting on the two bonded atoms, should also provide a good measure of bond strength. This definition yields binding forces of 3.6580, 4.1677, 5.1408, 5.9612, and 6.8200 au for the typical strained, strainless, conjugated, double, and triple bonds in cyclopropane, propane, benzene, ethylene, and acetylene, respectively. This trend in bond strength suggests that binding force could be reliable for evaluating the binding degree of a chemical bond. As shown in Table 3, the binding forces in triangle rings are clearly smaller than those of tetraangle rings. It shows the order of bond strength in these molecules. The result is in accordance with the fact that the bond strength of cycloproapane is weaker than that of cyclobutane. The penta- and hexa-angle ring seem to have similar bond strength to those of ordinary bond in propane. The overlap force lengths, defined as the sum of distances between the charge equivalents and two binding nuclei, of triangle rings range from 1.70 to 1.85 Å, which are larger by 0.2 ∼ 0.3 Å than those of tetra- or pentarings. The lengthened bonds correspond to smaller bond strength, while the interatomic distances (bond length) are very short. Actually the C−C bond lengths in all triangle rings are nearly 1.50 Å, which are quite less than those in other rings. The shortened bond lengths and lengthened overlap force length can be account for by the geometrical constraints in stereobonding for highly strained molecules. In fact, the molecules have to choose a compromise in space in order to get proper degree of orbital overlap. Thus the only way is to shorten the interatomic distances.

The unusual propellanes with "inverted" tetrahedral geometries such as [1.1.1]propellane, **13** have drawn much attention from theoreticians and experimentalists due to their distinctive central bonds. Whether the bridgehead atoms are bonded or not has been controversial for a long time. The deformation density analysis evidenced that there is no accumulation of charge between the bridgehead atoms, and thus the two bridgehead atoms are not bonded. However, there seems to have sufficient evidences that the bond should be bonded, such as the normal C_1-C_3 distance (1.54 Å calculated with 6-31G*) in [1.1.1]propellane and the clear shortening by 0.33 Å of the C_1-C_3 bond distance in [1.1.1]bicyclopentane, a compound in which no formal bridgehead−bridgehead bond (C_1-C_3 distance: 1.87Å) exists. Wiberg[26] estimated that 65 Kcal/mol of energy is required to rupture the bridgehead bond in [1.1.1]-propellane to obtain the corresponding biradical. These observations imply that the bridgehead carbons should be "bonded". In the present work our calculated binding forces of C−C central bonds for [1.1.1]-, [2.1.1]-, [2.2.1]-, and [2.2.2]propellane are 2.6301, 3.1801, 5.0050, and 5.9216 au, respectively. This suggests that the bridgehead carbons in [1.1.1]- and [2.1.1]-propellane are weakly bonded because the binding forces are smaller than that of ordinary strained bond, *e.g.*, in cyclopropane. The conclusion is consistent with Wiberg's that the bridgehead carbons are bonded[2] in small propellanes in terms of their *bond critical points.*[8,27,28] It is interesting to note that the binding force (5.9216 au) of the central bond in [2.2.2]propellane is even greater than that of normal C−C bond in propane. This case is similar to its large bond order as Bader proposed.[8]

Bond Force Angle β (Interforce Angle), Its Departure ($\Delta\beta$) from Tetrahedral Geometrical Angle 109.5° and the Relation with Molecular Strain. The bond force angle β is defined as the interforce angle between two overlap forces. This quantity can be readily computed by eq 26 and is listed in Table 4. For comparison, the bond angles are also listed in Table 4. In order to evaluate the degrees of relaxation of strained bonds in molecules, the departures $\Delta\theta$, $\Delta\beta$ of bond angles θ, and bond force angles β from the tetrahedral angle 109.5° are calculated and shown in Table 4. It is very interesting to note that, although the bond angles θ largely range from 60° to 132° due to the geometrical constrains imposed by the nuclear framework, the bond force angles β in molecules still prefer the tetrahedral angle 109.5° as shown in Table 4. However, the bond force angles of triangle rings seem to prefer the angle 120° over the angle 109.5°. The HCC, HCH, and CCC bond force angles in triangle rings also have a tendency toward the angle 120° rather than the angle 109.5°. It can be inferred from the large $\Delta\theta$ and small $\Delta\beta$ that the molecular strain of highly strained organic molecules can be relieved or relaxed. For the less strained or strainless molecules, the bond force angles defined as the interforce are only slightly departed from the standard tetrahedral angle 109.5°. On the other hand, the bond force angles of highly strained molecules are largely departed from the angle 109.5°. It can be seen from Table 4 that, in the case of [1.1.0]-bicyclobutane, the large $\Delta\beta$ corresponds to its large strain energy(69 Kcal/mol). The large departure of bond force angles from tetrahedral angle 109.5° in small propellanes such as [1.1.1]-, [2.1.1]-, [2.2.1]-, and [2.2.2]propellane also correspond to their large strain energies of 104, 107, 105, and 95 Kcal/mol, respectively, as given by Bader.[8] These large $\Delta\beta$ and strain energies in small propellanes may give rise to their unstabilities as discussed above.

The nearly 120° HCH or HCC bond force angles in triangle rings can be understood by the increase of s character of the associated C−H bonds. This case is consistent with the large ^{13}C−H coupling constant, such as 161 Hz for cyclopropane, 205 Hz for the bridgehead carbon-hydrogen bond of bicyclobutane. The increased s character of C−H bond in triangle rings is also consistent with the high reactivity of triangle rings as discussed above. In fact, the compounds containing three-membered rings have some olefin-like properties in reactions, *e.g.*, electrophilic addition leading to ring opening, etc. The ^{13}C−H coupling constant of tetrahedrane was predicted by us[29] to be 246 Hz by virtue of the bond force angles. This value seems to correspond much higher s character of C−H bond for tetrahedrane. In addition, the increments $\Delta\beta$ can be used to accurately predict the ^{13}C−H coupling constant of polycyclic and polyhedral hydrocarbons as indicated by our previous *ab initio* calculations.[29]

In the case of tetrahedrane, *ab initio* studies[30] predicted that it is likely to be identified by vibrational spectroscopy in a low-temperature matrix even if it is not isolable. Although it has a large molecular strain as shown by the overlap force angle, strain force, and tension energy, as well as strain energy(141 Kcal/mol),[8] its very small $\Delta\beta$ increment seems to indicate that the large strain can be much relieved or relaxed. In view of the medium magnitude of binding force (3.4589 au) and the small $\Delta\beta$ (−2.4°), tetrahedrane could be experimentally detected some day. In fact, the tetramethyltetrahedrane and tetra-*tert*-butyltetrahedrane have been synthesized,[31,32] though they have large molecular strains according to our *ab initio* calculations. Similar to tetrahedrane, their large molecular strain can also be relaxed and thereby lead to small $\Delta\beta$s, so both of them are stable.[31,32] As shown in Table 4, cubane molecule with a small $\Delta\beta$ is another example with the same propeties even if it has large strain energy (159 Kcal/mol).[8]

4. Concluding Remarks

In the present work we have proposed a way of characterizing the molecular strain and bonding characteristics of strained organic molecules in terms of equivalent point charge, overlap force angles, strain force, binding force, and tension energy. The equivalent point charge $q°$ can properly describe the degree of orbital overlap and the charge accumulation outside the rings. The overlap force angles α_A, α_B, and strain force f are important in quantifying the concept of bond strain in molecules. Binding force F and the overlap force length r could be used to estimate the extent of bonding. Tension energy ϵ may be a measure of the unstability of a certain bent bond in strained organic molecules. The bond force angle β and its departure from tetrahedral geometrical angle 109.5° ($\Delta\beta$) can be used to describe the torsion degree of a certain bent bond. On the basis of these chemically meaningful definitions, the overlap force angle of cyclopropane is calculated to be 29.5°, consistent with the experiment and other theoretical studies. Strain characteristics calculations show that α, f, ϵ, and β can be used to account for the relative stabilities of small propellanes. The binding force suggests the existence of central bonds in small propellanes. The bond force angles in most strained organic molecules seem to prefer the tetrahedral angle 109.5°, while the bond force angle in triangle rings have a preference for the 120° over the 109.5° angle, though the bond angles (geometrical angles) can largely range from 60° to 132°. The high reactivity of triangle ring is attributed to the largely shifting of overlapping charge. The existence of tetrahedrane can be predicted by the relative large magnitude of binding force and the small $\Delta\beta$. The departure of bond force angle from tetrahedral angle ($\Delta\beta$) provides a measure of the degree of relaxation of the charge density from the geometrical constraints imposed by the nuclear framework and may be used as a way of assessing the molecular strain and stability for strained organic molecules. In summary, the theoretical approach in terms of the *force* concept proposed here enables us to systematically investigate the molecular strain, reactivity, and stability for any strained organic molecules.

Acknowledgment. The authors thank the support of this project of the State Science and Technology Commission, Natural Science Foundation of China, and Science and Technology Commission of Gansu Province of China.

References and Notes

(1) Baeyer A. *Chem. Ber*. **1885**, *18*, 2269. See Also, for example, see: Huisgen, R. *Angew. Chem., Int. Ed. Engl*. **1986**, *25*, 297.

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

(3) (a) Cremer, D.; Kraka, E. *J. Am. Chem. Soc*. **1985**, *107*, 3800. (b) Cremer, D.; Gauss, J. *J. Am. Chem. Soc*. **1986**, *108*, 7467.

(4) (a) Coulson; C. A.; Moffitt, W. E. *Philos. Mag*. **1949**, *40*, 1. (b) Coulson, C. A.; Googwin, T. H. *J. Chem. Soc*. **1963**, 2851, 3161.

(5) Walsh, A. D. *Trans. Faraday Soc*. **1949**, *45*, 179.

(6) (a) Fritchie, C. J., Jr. *Acta Crystallogr*. **1966**, *20*, 27. (b) Hartman, A.; Hirshfeld, F. L. *Acta Crystallogr*. **1966**, *20*, 80. (c) Ito,T.; Sakurai, T. *Acta Crystallogr., Sect. B* **1973**, *29*, 1594.

(7) Stevens, R. M.; Switkes, E.; Laws, E. A.; Lipscomb, W. N. *J. Am. Chem. Soc*. **1971**, *93*, 2603.

(8) (a) Bader, R. W. F.; Nguyen-Dang, T. T. *Adv. Quantum Chem*. **1981,** *14*, 63. (b) Bader, R. W. F.; Tang, T. H.; Tal, Y.; Bieglerkonig, *J. Am. Chem. Soc*. **1982** *104*, 940, 946.

(9) Politzer, P. *Chem. Phys. Lett*. **1983**, *102*, 74.

(10) Schleyer, P. V. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377.

(11) Hellmann, H. *EinfÅhrung in Die Quantenchemie*; Franz Deuticke and Co.: Leipzig, 1937. Feynman, R. P. *Phys. Rev.* **1939**, *56*, 340.

(12) Bader, R. W. I. In *The Force Concept in Chemistry*; Deb, B. M., Ed.; Van Nostrand Reinhold Co.: New York, 1981; Chapter 2.

(13) Bader, R. W. F.; Henneker W. H., *J. Am. Chem. Soc.* **1965**, *87*, 3063.

(14) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W. Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92/DFT*, Revision F.2; Gaussian, Inc.: Pittsburgh, PA, 1993.

(15) Du, Q.-S.; Peng, Z.-R. Lanzhou Daxue Xuebao, Ziran Kexueban **1983**, *19*, 112.

(16) Goodisman, J. *J. Chem. Phys*. **1966**, *45*, 4689.

(17) Bader, R. W. F.; Jones, G. A. *J. Am. Chem. Soc.* **1966**, *88*, 280.

(18) Salem, L.; Wilson, E. B., Jr. *J. Chem. Phys*. **1962**, *36*, 3421.

(19) Schaefer, H. F., III *Applications of Electronic Structure Theory*; Plenum: New York, 1977; p 242.

(20) Steve, S. *Chem. Eng. News***1982**, (Oct 25), p 25.

(21) Wiberg, K. B. *J. Am. Chem. Soc*. **1982**, *104*, 5239.

(22) Michl, J.; Radziszewski, G. J.; Downing, J. W. *Pure Appl. Chem*. **1983,** *55*, 315.

(23) Wiberg, K. B.; Burgmaier, G. J.; Shen, K.; La Placa, S. J.; Hamilton, W. C.; Newton, M. D. *J. Am. Chem. Soc*. **1972**, *94*, 7402.

(24) Eaton, P. E.; Temme, G. H., III *J. Am. Chem. Soc.* **1973**, *95*, 7508.

(25) Politzer P.; Domelsmith, L. N.; Sjoberg, P. *Chem. Phys. Lett*. **1982,** *92*, 366.

(26) Wiberg, K. B. *J. Am. Chem. Soc.* **1983**, *105*, 1227.

(27) Runtz, G; Bader, R. W. F.; Messer, R. R. *Can. J. Chem.* **1955**, *55*, 3040.

(28) Bader, R. W. F.; Chandra, A. K. *Can. J. Chem*. **1968**, *46*, 953.

(29) Zhao, C.-Y.; Xiao, T.; Xu, X.-F.; You, X.-Z. Gaodeng Xuexiao Huaxue Xuebao **1996**, *17*, 769.

(30) Schulman, J. M; Venanzi, T. J. *J. Am. Chem. Soc*. **1974**, *96*, 4739.

(31) Zefirov, N. S.; Kirin, V. N.; Yureva, N. M; Kozmin, A. S.; Kulikov, N. S.; Luzikov, Y. N. *Tetrahedron Lett*. **1979**, *21*, 1925.

(32) Maier, G.; Pfriem, S.; Schafer, U; Matusch, R. *Angew. Chem., Int. Ed. Engl*. **1978**, *17*, 520.

(33) Disch, R. L.; Schulman, J. M. *J. Am. Chem. Soc.* **1988**, *110*, 2102.

(34) Beckhaus, H.-D.; Ruchardt, C.; Lagerwall, D. R.; Paquette, L. A.; Prinzbach, H. *J. Am. Chem. Soc.* **1994**, *116*, 11775.

(35) Zhao, C. Y.; Wang, Y. C.; Qiu, W. Y.; Wei, T. S. *Chin. Sci. Bull*. **1992**, *37*, 1529.