The Corinthian

Volume 6 Article 4

2004

Comparing Models for Measuring Ring Strain of Common Cycloalkanes

Brad A. Hobbs
Georgia College

Recommended Citation

Hobbs, Brad A. (2004) "Comparing Models for Measuring Ring Strain of Common Cycloalkanes," *The Corinthian*: Vol. 6 , Article 4.
Available at: https://kb.gcsu.edu/thecorinthian/vol6/iss1/4

Comparing Models for Measuring Ring Strain of Common Cycloalkanes

Brad A. Hobbs
Chemistry Major

Dr. Kenneth C. McGill
Faculty Sponsor

Introduction

The number of carbon atoms bonded in the ring of a cycloalkane has a large effect on its energy. A molecule's energy has a vast impact on its stability. Determining the most stable form of a molecule is a useful technique in the world of chemistry. One of the major factors that influence the energy (stability) of cycloalkanes is the molecule's ring strain. Ring strain is normally viewed as being directly proportional to the instability of a molecule. It is defined as a type of potential energy within the cyclic molecule, and is determined by the level of "strain" between the bonds of cycloalkanes. For example, propane has the highest ring strain of all cycloalkanes. Each of propane's carbon atoms is sp3-hybridized. The normal bond angle of sp3-hybridized carbons (tetrahedral arrangement) is 109.5°; however, in cyclopropane, the bond angles are approximately 60°. This large deviation from the normal bond angle causes cyclopropane to exhibit a high level of angle stain, which is the source of its ring strain.

Theoretical calculations of ring strain are difficult to acquire. In this project, the vibrational spectra of certain unbranched cycloalkanes were calculated using HyperChemTM. The vibrations of the carbon-carbon bonds that contribute to the molecule's rigid, ringed structure were analyzed with HyperChemTM. The frequencies of each vibration of interest were then used to measure the respective ring strains of the cycloalkanes. This computational method of determining ring strain was compared to the more common method of normalizing the molecule's energy by dividing the total energy of the molecule by the number of carbon atoms composing the molecule.

Theory

Two methods of measuring the ring strain of selected cycloalkanes were employed in this project. The theory behind each method is explained below.

Vibrational Frequency Method: As mentioned above, theoretical calculations of ring strain are difficult to perform. Nevertheless, this project employs the correlation of specific vibrational frequencies of cycloalkanes to their respective ring strains. The vibrational frequencies of the cycloalkanes were assumed to be directly proportional to the energy of the molecule. Therefore, ring strain approximations can be made by comparing vibrational frequencies. The first E and A irreducible representation frequencies were determined for each applicable cycloalkane (cycloalkanes of $n = 5$ and $n > 6$ showed no E symmetry). E and A irreducible representations were chosen because of the apparent vibrations represented by these symmetries. The E and A vibrations showed a simultaneous oscillation of every bond angle of the cycloalkanes and represented strain energy. Therefore, these frequencies were of interest. The first E and A irreducible representations of each molecule were chosen to ensure valid data comparison between each molecule.

Normalizing Energy by Dividing by Number of Carbons: Another more common method of determining a cycloalkane's ring strain was performed as a comparison to the first vibrational method. In this method, the total energy of each cycloalkane was normalized by dividing each molecule's total energy by the number of carbon atoms of the respective molecule. The total energy of each cycloalkane gets larger as the number of carbons increases. However, this increase in energy is not necessarily the result of higher ring strain. In order to key in on the actual strain energy of each carbon-carbon bond, which indeed causes the ring strain of each cycloalkane, the normalization was utilized.

Experimental

- The following cycloalkanes were modeled in HyperChemTM:
    - Cyclopropane
    - Cyclobutane
    - Cyclopentane
    - Cyclohexane
    - Cycloheptane
    - Cyclooctane
    - Cyclononane
    - Cyclodecane

- Each molecule was built with sp3 hybridized carbon atoms with average internuclear distances.

- First, the geometry-optimized energy of each molecule was calculated using ZINDO/1.

- Next, a molecular vibrational spectrum for each molecule was generated by diagonalizing the force matrix.

- Finally, the frequencies of the first E irreducible representation and the first A irreducible representation of each molecule were determined from the vibrational spectra and recorded.

- The mode number and exact symmetry of each vibration were recorded.

- The normalization energies were calculated by dividing the total energy of each cycloalkane by the number of carbon atoms.

Data

Molecule	# Carbons	Mode (E)	Symmetry (E)	Frequency (E)	Mode (A)	Symmetry (A)	Frequency (A)	Total Energy	E / # carbons
Cyclopropane	3	1	1 E'	911.18	3	1A1'	976.15	-2364.8	-788.26
Cyclobutane	4	5	1 EU	1016.23	2	1A1G	794.01	-3223.9	-805.98
Cyclopentane	5	E symmetry does not exist for cyclopentane			1	1A	630.99	-4078.9	-815.77
Cyclohexane	6	2	1 EG	558.10	1	1A1G	517.23	-4910.3	-818.39
Cycloheptane	7	E symmetry does not exist for cycloheptane			1	1A	-423.38	5722.8	817.55
Cyclooctane	8	E symmetry does not exist for cyclooctane			1	1A	364.20	-6538.4	-817.30
Cyclononane	9	E symmetry does not exist for cyclononane			1	1A	291.15	-7357.0	-817.45
Cyclodecane	10	E symmetry does not exist for cyclodecane			3	2AG	305.06	-8179.0	-817.90

Table 1.
Vibrational frequency and irreducible representation data collected in HyperChemTM.

Data (con't)

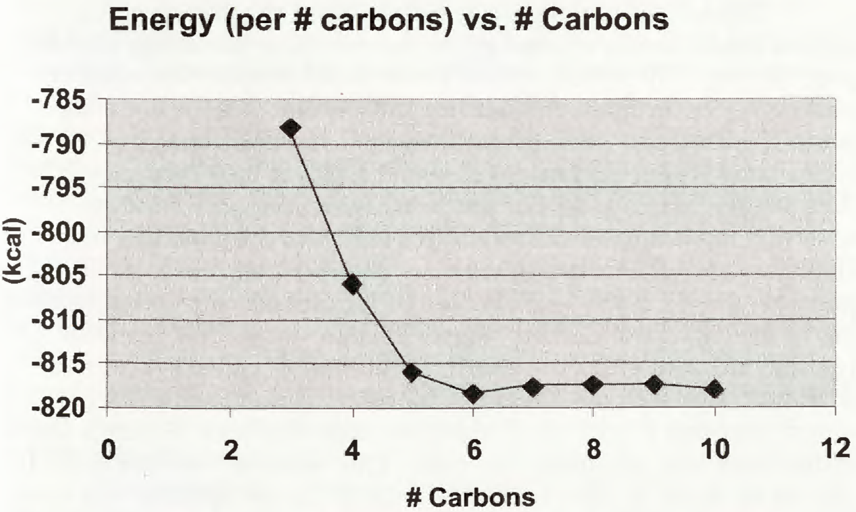

Figure 1. *Energy vs. Number of Carbons.* This figure shows cyclohexane as having the lowest energy of all the other cycloalkanes because of the absence of ring strain. This phenomenon matches the widely-accepted view of scientists.

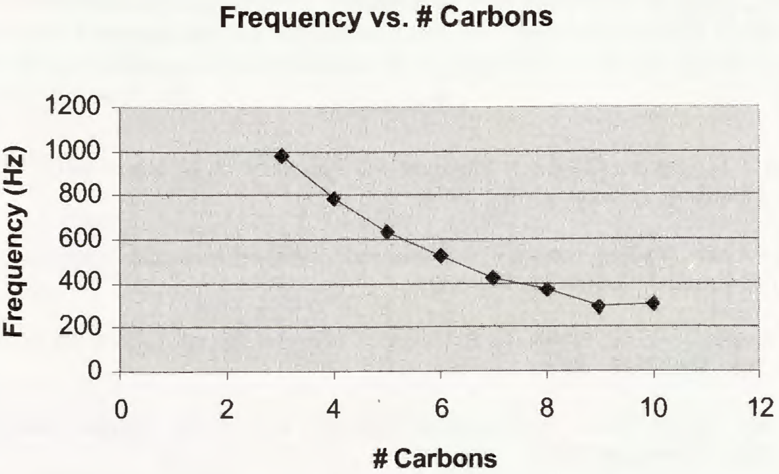

Figure 2. *Frequency vs. Number of Carbons.* This figure shows that cyclopropane (3 carbons) clearly has the highest frequency (energy) of all the cycloalkanes. However, according to this figure, cyclohexane does not exhibit the lowest frequency (energy).

Results and Conclusion

In conclusion, this project has confirmed that the energy of cycloalkanes is directly affected by the number of carbon atoms that compose the ring. The stability of a molecule is directly proportional to the total energy of the molecule, and ring strain is one of the major components of cycloalkanes' total potential energy. The strain energy of cycloalkanes is directly linked to the bond angles of each cyclic molecule. Ring strain of cycloalkanes can also be measured computationally by observing representative vibrational frequencies of the molecules by employing chemical modeling software. However, this method did not prove as effective as the normalization of the cycloalkanes' energy by dividing by the number of carbons. Figure 2 indeed shows that frequency (energy) increases with a decrease in the number of carbons of a ringed structure. However, this figure does not show cyclohexane as having the lowest frequency (energy) as is highly accepted in science. Figure 2 shows cyclononane with the lowest frequency. This deviation from the expected may be the result of higher molecular mass of the cycloalkanes with more carbons than cyclohexane. The higher masses may alter the vibrational frequencies of these molecules and thereby distort the effectiveness of directly correlating vibrational frequency with ring strain. The normalization of energy (ring strain) can be found by dividing the total energy by the number of carbons of each cycloalkane proved to be the most effective method in this project.

References

Ege, S. N. Organic Chemistry Structure and Reactivity. D. C. Heath and Company: Lexington, MA, 1994.

HyperChem Student, version 7; software and lessons for molecular modeling; Hypercube: Gainesville, FL, 2003.

Solomons, T. W. G., Fryhle, C. B. Organic Chemistry 7th ed. John Wiley & Sons, Inc.: New York, 2000.

Dr. Ken McGill, Chair, Department of Chemistry and Physics, Georgia College & State University, 2004.

Campring Models for Measuring Ring Strain of Common Cycloalkanes

Abstract

The number of carbon atoms bonded in the ring of a cycloalkane has a large effect on its energy. A molecule's energy has a vast impact on its stability. Determining the most stable form of a molecule is a useful technique in the world of chemistry. One of the major factors that influence the energy (stability) of cycloalkanes is the molecule's ring strain. Ring strain is normally viewed as being directly proportional to the instability of a molecule. Ring strain is actually a type of potential energy within the cyclic molecule. Ring strain is determined by the level of "strain" between the bonds of cycloalkanes. For example, propane has the highest ring strain of all cycloalkanes. Each of propane's carbon atoms is sp3-hybridized. The normal bond angle of sp3-hybridized carbons (tetrahedral arrangement) is 109.5°; however, in cyclopropane, the bond angles are approximately 60°. This large deviation from the normal bond angle causes cyclopropane to exhibit a high level of angle stain, which is the source of its ring strain.

Theoretical calculations of ring strain are difficult to acquire. In this project, the vibrational spectra of certain unbranched cycloalkanes will be calculated using HyperChemTM. The vibrations of the carbon-carbon bonds that contribute to the molecule's rigid, ringed structure will be analyzed with HyperChemTM. The frequencies of each vibration of interest will then be used to measure the respective ring strains of the cycloalkanes. This computational method of determining ring strain will be compared to the more common method of normalizing the molecule's energy by dividing the total energy of the molecule by the number of carbon atoms composing the molecule.