

Predicting Trends in Ring Strain of Cycloalkanes

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Description: In this experiment we will estimate the amount of ring strain in cycloalkanes, and use our estimates to order the molecules from cyclopropane to cyclooctane from most to least strained.

Suggested level: Beginning graduate/advanced undergraduate.

Learning objectives: Learn how to build and manipulate molecules; how to optimize molecular geometry; how to compute energy differences from total energies. Review basic concepts of structure of organic molecules containing sp^3 -hybridized carbon atoms.

I. BACKGROUND

Ring strain arises in small ring structures because the bond angles must deviate from their ideal (tetrahedral) values. In smaller rings there is also an eclipsing effect of the hydrogens as there is not enough flexibility for the atoms to move out of each others way. This results in an increased van der Waals repulsion.

Cyclic alkanes can be thought of as rings of CH_2 groups. If there was no ring strain, then we would be able to estimate the energy of the C_nH_{2n} cyclic alkane as simply n times the energy of a CH_2 group in an infinite straight-chain alkane. Deviations from this estimate are a measure of how much strain there is in the ring. Thus we can write:

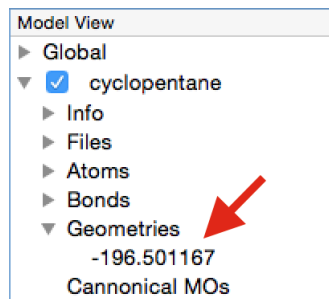
$$E_{RS}[n] = E[C_nH_{2n}] - nE[CH_2] \quad (1)$$

where $E_{RS}[n]$ is our ring strain energy, $E[C_nH_{2n}]$ is the energy of the cyclic alkane and $E[CH_2]$ is the energy of a CH_2 group in an infinite straight chain alkane.

II. METHOD

In this first section we will determine a value for $E[CH_2]$.

1. Draw the propane molecule and clean-up your structure by optimizing it using the built-in UFF force field. Symmetrize your structure and make a note of the point group reported.
2. Calculate the B3LYP/6-31G energy by going to the Calculate ► QChem Setup menu option to open the QUI. Use the default settings for all options except the **Method**, which you should set to **B3LYP**. Click Submit to start the calculation.
3. When the calculation has finished, copy the results from the server and make a note of the total energy. You can find this under the Geometries item in the Model View.



Note that the energy will be given in Hartrees.

Repeat steps 1–3 for butane, pentane, hexane, heptane, and octane. Create a new molecule for each system by going to the File ► New Molecule menu option. Save the results from each calculation in a separate directory in case you need to re-open the files. It is recommended that you submit your calculations one at a time to avoid overloading the server.

We can now extrapolate our alkane energies to the infinite chain limit. Scale your total energies by dividing them by the number of carbon atoms, n , to get the energy per carbon. Plot these scaled energies against n using either Excel or Google Docs. You should see that they lie on a hyperbola:

$$E(n) = a + \frac{b}{n} \quad (2)$$

To determine the unknown parameters a and b , replot the scaled energies against $1/n$. You should see a straight line with the intercept and slope corresponding to a and b , respectively. Use your fitted parameters to determine the energy of a CH_2 moiety in the infinite chain limit.

Now repeat steps 1–3 for the cyclic alkanes with 3-8 carbon atoms. While you are waiting for each calculation to finish, you should determine the average C-C-C bond angle in the system.

III. EXERCISES

Your report should include a table of all your computed energies (always specify the units; use hartrees for total energies and kcal/mol or kJ/mol for energy differences), average bond angles and point groups, along with answers to the following questions:

1. What values of the a and b parameters did you obtain when fitting your linear alkane energies?
2. What energy did you obtain for a single CH_2 group and how did you obtain this?
3. Use Eq. 1 to calculate the strain energy in each ring system, and list the cycloalkanes in order of decreasing ring strain.
4. Using only bond angles, devise another measure of strain in the ring and use this to list the cycloalkanes in order of decreasing ring strain. Do you see the same order as before?

5. Why do cyclobutane and cyclopentane not form D_{4h} and D_{5h} structures, respectively?

Bonus point: Dispersion is poorly described by standard functionals such as B3LYP. To improve its description, '-D' correction can be used. Repeat the calculations using B3LYP-D (set **Method** to B3LYP-D). What is the impact of better treatment of dispersion on the computed ring strain energies?