

Learning from Molecular Models II - Alkanes and Cycloalkanes

Textbook Reference - Hart, Chap 2.8-2.10

Molecular models can be very helpful for the 3-D visualization of organic molecules. The models can be manipulated (for example, bonds can be rotated) in order to mimic the types of dynamic processes the actual molecules undergo.

The C-C single bonds that are present in almost all organic molecules, rapidly rotate at room temperature. Thus, organic molecules can exist as a variety of different structures that come about by varying degrees of bond rotation. These structures are easily interconverted by single bond rotation(s) and are, therefore in equilibrium with each other and are referred to as "**conformations**". The equilibrium constant will always favor the most stable conformation available to a molecule, so this conformation can be thought of as the predominant form of the molecule.

In this exercise you will use molecular models to discover and learn about some of the most important concepts that allow us to predict the most stable conformation of a simple alkane. You will also look at some ring structures (cycloalkanes especially cyclohexane) and learn how to predict the predominant conformation.

Pre-lab Assignment

Use the formula $180^\circ - 360^\circ/n$ to determine the interior angles of the regular polygons from $n = 3$ to 8 and make a table which shows drawings of each of these with the interior angles labeled.

Some Important Definitions

Strain - Any interaction in a structure that causes it to have a higher potential energy is called strain. The difference in potential energy between any particular conformation and the lowest energy conformation of the same molecule is a measure of the amount of strain that conformation possesses.

Torsional Strain is the strain associated with an eclipsed single bond. With a molecular model in hand you can check for torsional strain by sighting directly down each C-C bond in the molecule to see if any of them are eclipsed or partially eclipsed.

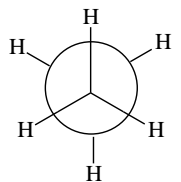
Steric Strain comes about when two atoms are too close to each other. If the distance between the atoms is less than the sum of the Van der Waal's radii of the atoms then there is steric strain. With your molecular models you can check for steric strain by testing whether there are any pairs of hydrogen atoms (attached to non-adjacent carbons) that are "bumping" into each other.

Angle Strain is present in cyclic molecules where the bond angles are forced to be significantly different from the ideal angles predicted by VSEPR theory. The strain results from a combination of electron pair repulsion (bonding electron pairs too close) and poor orbital overlap resulting in weak, bent bonds. Our model kits use balls atoms with predefined "ideal" bond angles. Therefore, when a molecular structure requires non-ideal bond angles the bonds are forced to bend. Inspect your models for the presence of bent bonds as an indication of angle strain.

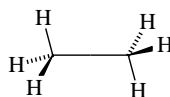
PROCEDURES – The numbered questions in *italics* that appear throughout this worksheet, should be answered on a separate sheet of paper. Attempt to be neat and precise with your drawings and write complete answers to word questions.

Part I. Non-cyclic Alkanes

Staggered Ethane. Construct a model of ethane, $\text{CH}_3\text{-CH}_3$. Look straight down the C-C bond and rotate it until the C-H bonds in front exactly bisect the H-C-H angles of the back carbon. You now have a model of the staggered conformation of ethane. This structure can be represented on paper in a number of ways, including wedge-dash formulas and Newman projections (see next page).



Newman projection



Wedge/Dash formula

The Newman projection sights straight down the bond with the bonds off the front carbon represented by the three lines that meet in the middle of the circle. The bond off of the back carbon are represented by the lines that end at the edge of the circle.

1. *Draw your own Newman projection and wedge/dash structures of staggered ethane.*

The angles between groups around the outside of a Newman projection describe stages of rotation of the bond being depicted and are termed “dihedral” or “torsion” angles.

2. *What are the torsion angles between Hs in staggered ethane? (Define the 3 torsion angles between a single H on one end of the bond with all three of the Hs on the other end)*

Eclipsed Ethane. Rotate the C-C bond $1/6^{\text{th}}$ of a turn (60°) so that all of the C-H bonds are lined up. You now have a model of the eclipsed conformation of ethane.

3. *Draw Newman projection and wedge/dash depictions of eclipsed ethane.*

4. *What are the torsion angles between Hs in eclipsed ethane?*

Eclipsed vs Staggered Ethane.

It has been shown experimentally that eclipsed ethane has potential energy (P.E.) approximately 3 kcal/mol higher than that of staggered ethane. Hence the eclipsed conformation possesses 3 kcal/mol of strain and the staggered conformation is “strain free”.

5. *In which of conformation do the sigma electrons of the C-H bonds on one carbon come closer to the sigma electrons of the C-H bonds of the other carbon?*

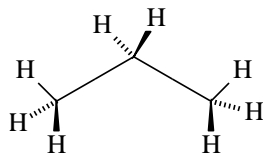
6. *Could this explain the difference in energy between the eclipsed or the staggered? Explain*

7. *What happens to the P.E. as the bond rotates gradually from staggered to eclipsed and then back to staggered?*

8. *Sketch a graph of relative potential energy versus the torsion angle). Start with the eclipsed*

conformation (torsion angle = 0°) and go through one full rotation (360°). Indicate on the graph where each conformation would be found.

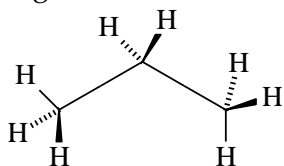
Staggered Propane. Remove a hydrogen from the ethane model and add a CH_3 group in its place. You now have a model of propane. Rotate each of the C-C bonds so that both of these bonds are staggered. A wedge/dash formula of the model should look like the figure below.



Staggered propane

9. Draw a Newman projection that represents staggered propane. Represent the extra methyl group simply by " CH_3 ". (Note - the Newman projection should look the same regardless of which C-C bond you sight down.)

Eclipsed Propane. Rotate one of the C-C bonds in this model so that it is now eclipsed. It should look like the figure below.



Eclipsed propane

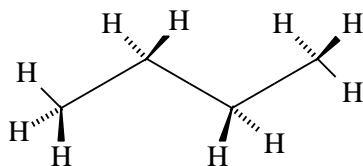
10. Draw a Newman projection that shows the conformation around the eclipsed bond.

11. Sketch a graph of energy versus torsion angle for one of the C-C bonds in propane. (Assume the other C-C bond stays staggered.)

12. Which propane conformation is strained and by about how much? (Assume the strain is from the same factor that causes strain in eclipsed ethane)

Conformations of Butane

Make a model of butane. Rotate each of the C-C bonds so that they are all staggered and the two end CH_3 groups are opposite each other. A wedge/dash formula of the model should look like the figure below. This model represents the "**anti**" conformation of butane. We will also refer to it as conformation **A**.



13. Draw a Newman projection that shows the conformation of the bond between the center two carbons (use " CH_3 " to represent each of the end carbons).

14. Now rotate the center C-C bond 60° to form conformation **B**. Draw a Newman projection of this conformation.
15. Rotate the center bond another 60° to give conformation **C** and again draw a Newman projection. This model represents the **gauche conformation** of butane.
16. Rotate the center bond another 60° to give conformation **D** and again draw a Newman projection.
17. Rotate the center bond another 60° and again draw the Newman Projection. Is this a new conformation of butane or is it the same as one of those already examined?
18. Rotate the center bond another 60° and draw it. Is this a new conformation of butane or is it the same as one of those already examined?
19. Rotate the center bond another 60° and what do you have?
20. Label your Newman projections for conformations A – D with the value of the torsion angle between the methyl groups.

Note that both conformations B and D are eclipsed and therefore both have the same amount (approx. 3 kcal/mol) of the type of strain encountered previously in the eclipsed conformations of propane and ethane. This strain associated with eclipsed bonds in molecules is commonly referred to as "**torsional strain**".

Conformations C (gauche) and D, on the other hand, also contain a different kind of strain involving hydrogen atoms on nonadjacent carbons being too close to each other and causing repulsion increasing the potential energy. This type of strain is referred to as "**steric strain**".

21. If the steric strain present in gauche butane is about 1 kcal/mol, how much steric strain must be present in conformation D and what can you say about the overall strain of D as compared to the other conformations?
22. Sketch a graph of energy versus torsion angle for the central C-C bond in butane.

Part II Cycloalkanes

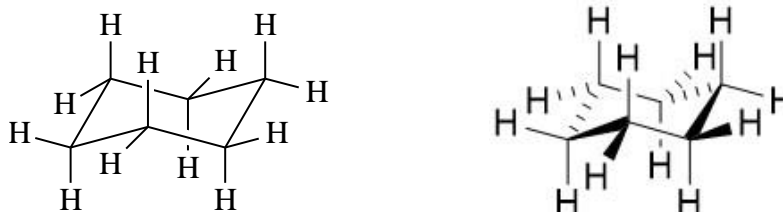
Conformations of Cyclohexane

The Chair

Construct a model of cyclohexane by joining six carbons in a ring and then adding two hydrogens to each carbon. First force the six carbons all lie in one plane.

23. What types of strain would be present in this hypothetical planar form of cyclohexane? Draw a structural diagram and label it to show the types of strain present.

By rotating some of the bonds you should be able to make your cyclohexane model look like the drawings below. The model should sit firmly on the desktop with three hydrogens serving as legs. This is a model of the **chair conformation** of cyclohexane.



Although the chair conformation is three dimensional and contains six tetrahedral carbons we generally draw it without the need for wedged/dashed bonds using perspective as in the figure at top left. However, when we look at such a drawing we need to picture it in 3-D as shown in the figure at right. The carbons at far left and far right are pictured as being in the plane of the paper and thus the Hs attached to them are also in the plane of the paper. Notice also that the six bonds pointing straight up or down do not point toward the viewer or away and so are not wedged or dashed.

24. Draw the chair conformation as shown above left. (The instructor can give you some tips about how to quickly draw an acceptable chair conformation but please realize that this is an essential skill in this course which will most likely require lots of practice.)

25. Look for strain in the chair conformation using the definitions on page 1. What types of strain if any does cyclohexane possess? Explain.

Note that the cyclohexane chair is not flat, in other words it is “puckered”. Also note that puckering of a ring will always reduce the bond angles around the carbons. In this case they decrease from 120° in the hypothetical flat form to almost exactly 109.5° in the chair.

The cyclohexane chair is highly symmetrical with all six carbons each playing exactly the same role. It is important to recognize this symmetry when looking at perspective drawings of the cyclohexane chair, which can disguise the fact that all six carbons are exactly equivalent in terms of their chemical environments and their relationships to other carbons in the ring.

Axial positions. Note that in the chair three of the carbons are puckered upwards above the plane of the other three carbons. Also notice that each of the three “up carbons” has a hydrogen bonded to it pointing straight up. Similarly, the “down carbons” have attached hydrogens pointing straight down. These six hydrogens are said to be in **axial** positions.

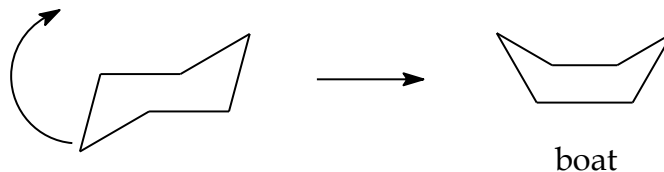
26. If you numbered the six carbons of the ring, which carbons would have axial hydrogens that are on the same side of the ring?

Equatorial positions. The other six hydrogens radiate outward along the perimeter of the ring. These hydrogens are in **equatorial** positions. It is very important to realize that the equatorial positions point in the opposite direction from the axial group on the same carbon. In other words, if the axial position is **up** then the equatorial is angled **downwards** and visa versa.

27. Once again, draw the chair conformation of cyclohexane and this time label all of the hydrogens as equatorial (eq) or axial (ax).

The Boat

By grasping one of the carbons with an axial hydrogen pointing down and forcing it to point up (bond rotations are required), you should be able to get your model to look like a boat. (See figure below.) This conformation of cyclohexane is referred to as the **boat**.

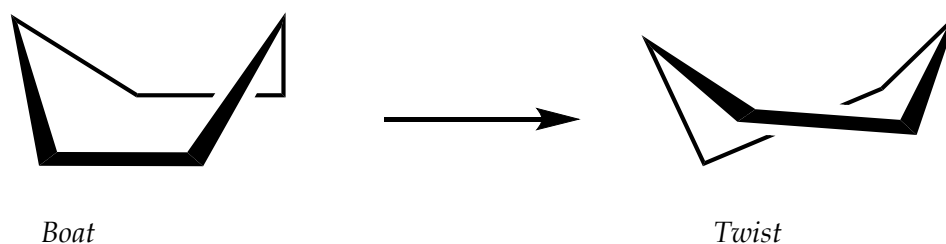


28. Look for strain in the boat conformation using the methods outlined previously. Draw the boat and depict and label all strain interactions that are present.

Other conformations of cyclohexane include the **half chair** and the **twist** conformations:

The Twist

The **twist** (also called the "twist boat") can be arrived at by starting with the boat, grasping the carbons that would represent the bow and stern of the boat, and pulling them slightly away from each other and in opposite directions with respect to the plane of symmetry which they lie in. (See figure below).



29. Check for strain in the twist conformation using the same process as before. Compared to the boat, does the twist have more or less strain?

30. Which conformation of cyclohexane is the predominant form of the molecule?

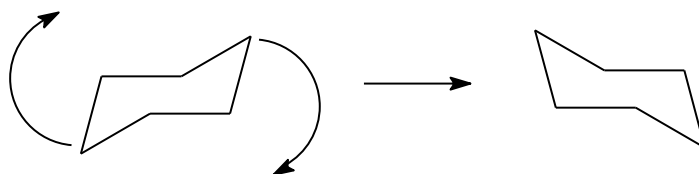
Conformations of Monosubstituted Cyclohexanes

For the remainder of the lab consider chair conformations only.

Remove an equatorial hydrogen from the cyclohexane model and add a CH_3 group in its place to form methylcyclohexane

31. Neatly draw the structure represented by the model.

Now grasp and invert any carbon (C-1) to form a boat conformation. Then take C-4 and invert it to remake a chair conformation. This process inverts the chair conformation and is called **chair flipping** (See figure below).



32. Draw this other chair conformation of methylcyclohexane.

33. Generalize as to what chair flipping does to substituents in terms of their equatorial/axial status.

See <http://course1.winona.edu/tnalli/s21/lab.html> for an animation of this process.

Notice that chair flipping is accomplished easily by single bond rotations and so happens very rapidly at room temperature (like any conformational interconversion).

34. Observe both chair conformations of methylcyclohexane looking for strain. Label any strain you find on your drawings of these conformations above.

35. Which chair conformation of methylcyclohexane has more strain and what type of strain does it have?

36. Which methylcyclohexane conformation is the predominant form of the molecule?

Part 3. Conformers of *tert*-Butylcyclohexane

tert-Butylcyclohexane with equatorial t-Bu

Replace the methyl group of your previous model with a *tert*-butyl group. Make sure the t-Bu group is an equatorial position.

37. Draw this conformation and assess the strain present in it.

tert-Butylcyclohexane with axial t-Bu

Flip the chair on the previous model and you end up with this molecule.

38. Draw this conformation and assess the strain present in it. Which conformation of *tert*-butylcyclohexane is more stable?

39. Compared to the energy difference between the two methylcyclohexane chairs, the energy difference between *tert*-butylcyclohexane chairs is quite large. Why is this? (Why does *tert*-butyl cause more strain?)

Part 4. Conformations of some other Cycloalkanes

Make a model of cyclopropane.

40. Are there multiple conformations of the cyclopropane ring possible like there are with cyclohexane?

41. Is cyclopropane strained? If so, which type(s) of strain is(are) present? (Revisit the definitions of the different types of strain on page 1 of this document.)

42. Illustrate your answer to #41 by drawing the molecule, labeling the bond angles, and labeling the strain interactions.

43. Cyclopropane undergoes quite a few reactions that other alkanes do not. For example, it reacts with

HBr to form 1-bromopropane whereas other alkanes do not react with HBr. Explain why.

Make a model of cyclopentane.

44. Draw it in its most stable conformation and label it to show the strain interactions that are present.

45. Which cycloalkane is more stable, cyclopentane or cyclohexane?

Make a model of cyclooctane.

46. At least 8 different somewhat stable conformations of this molecule can exist. Draw at least two of the conformations you find. Can you find a conformation of this ring that is strain-free? Identify the types of strain present in the conformations you draw.