Lab Workshop 1: Alkane and cycloalkane conformations

Each student work group choose a Leader (reads activity out loud, poses questions to group), Facilitator (makes sure everyone is participating equally, directs the conversation), Recorder (takes notes on discussion, learned concepts and any conclusions), and Presenter (announces conclusions or presents activity to class).

A. Conformers of Alkanes

**Alkane** = Molecule consisting entirely of carbon and hydrogen atoms connected by single bonds.

**Sigma bond** (σ) = Single bond. A bond formed when electrons occupy the bonding σ orbital formed by the end-on overlap of orbitals on adjacent atoms. Free rotation occurs around single bonds at room temperature.

**Pi bonds** (π) = Double bond. A bond formed from the overlap of parallel p-orbitals electrons on adjacent atoms. Free rotation doesn’t occur around double or triple bonds at room temperature.

Alkanes contain only sigma bonds, a double bond of an alkene contains a sigma and pi bond, and an alkyne triple bond contains a sigma and 2 pi bonds.

**Conformations** = Temporary molecular shapes that result from rotations of groups around σ or single bonds. Conformers can be interconverted without breaking bonds via rotations around a single bond.

**Conformational Analysis** = Energy changes that a molecule undergoes as a group of atoms is rotated about a single bond.

**Torsional Barrier** = Energy barrier to rotation of groups joined by a single bond caused by the repulsion between aligned electron pairs in adjacent bonds (in the eclipsed conformer).

**Model 1: Ethane and Butane:** Build a model of ethane, CH₃CH₃ and butane, CH₃CH₂CH₂CH₃.

![Ball and Stick Representation](image)

![Newman Projection- looking down the C-C bond](image)

Critical Thinking Question (CTQ):

1. With your models, rotate the atoms around each carbon-carbon bond (do this for both ethane and butane). Each time you move atoms by rotating a single bond you are changing the conformation of the molecule. Molecules are constantly changing their conformation at room temperature due to the free rotation around single bonds.

2. If all the atoms line up along a bond, this is called the **eclipsed conformation** (see above) which is a high energy conformation due to **torsional strain** between adjacent bonds (and **steric strain** if an atom or group of atoms are present on that bond). If all the atoms on one carbon bisect the atoms on the other, this is called the **staggered conformation** which is a low energy conformation.
   a. Explain the names staggered and eclipsed.
   b. Construct an explanation for why the staggered conformation is more favorable (low energy) than the eclipsed conformation.

3. **Newman projections:**
   - Newman projections are representations of molecule by viewing directly down a bond axis to the next atom (usually carbon atoms).
   - The front carbon and its other bonds are represented as
   - The back carbon and its bonds are represented as
Newman projections are often used to conduct a conformation analysis on a molecule and to determine the relative energies associated with each conformation.

4. Draw all staggered and eclipsed conformation of butane looking down the C2-C3 bond by putting in the atoms on the Newman projections below and then rotating 60 degrees between conformations.

5. Label each staggered (S) and eclipsed (E) conformation above

6. Which of the 3 staggered conformations (excluding $360^\circ$) do you think is/are the lowest energy and why?

7. In the staggered conformation, if a group on the front carbon is opposite ($180^\circ$) from a group on the back carbon, the groups are said to be anti from each other. Label the anti conformers.

8. In the staggered conformation, if a group on the front carbon is adjacent to a group on the back carbon, the groups are said to be gauche to each other. Label the gauche conformers.

9. Among the staggered conformations, which do you think is the highest energy? Label and explain why.

10. Which eclipsed conformations do you think are the lowest energy? Why? Label as lowest.

11. If you were to plot the potential energy as you rotated around a single bond, the result would appear sinusoidal. Staggered conformations are always valleys in the curve (lower energy) and eclipsed conformations are always peaks in the curve (higher energy). Why do you think this is so?

12. For ethane all the valleys (staggered conformations) are at the same potential energy and all the peaks (eclipsed conformation) are at the same potential energy. Why?

13. This is not true for butane when it is rotated around the C2-C3 bond. Why? Draw the potential energy curve for butane being rotated around the bond joining the C2-C3.

B. Isomers of Cycloalkanes

Rings prevent complete rotation around a single bond, thus leading to different constitutional isomers or stereoisomers. (This is similar to the alkene behavior.)

**Constitutional Isomer** = same molecular formula, but different connectivity of atoms.

**Stereoisomers** = same molecular formula and same connectivity of atoms, but different arrangement of atoms in space (cannot be interconverted via single bond rotations).
Ring structures have a higher relative energy than their linear chain analogs. This is due to **ring strain** in the compounds. Cycloalkanes do not all have the same relative stability. Heat of combustion experiments illustrate that cyclohexane is the most stable cycloalkane (see below). **Ring Strain** is the higher potential energy of the cyclic form of a molecule compared to its acyclic form and is made up of **angle strain** and **torsional strain**.

**Angle Strain** = deviations in ideal bond angles in small ring systems caused by the inefficient overlap of sp³ orbitals resulting in weaker bonds with greater potential energy.

**Torsional Strain** = the repulsion between aligned electron pairs in adjacent bonds that cannot be relieved due to restricted conformational mobility.

**Table 1: Heats of Combustion and Ring Strain of Cycloalkanes**

<table>
<thead>
<tr>
<th>Cycloalkane</th>
<th>n (# of CH₂ units)</th>
<th>Heat of Combustion (kJ/mol)</th>
<th>Heat of Combustion per CH₂ group (kJ/mol)</th>
<th>Ring Strain (kJ/mol) [change in heat of combustion per CH₂ group vs. cyclohexane times number of CH₂ units]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclopropane</td>
<td>3</td>
<td>2091</td>
<td>697.0</td>
<td>115</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>4</td>
<td>2744</td>
<td>686.0</td>
<td>109</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>5</td>
<td>3320</td>
<td>664.0</td>
<td>27</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6</td>
<td>3952</td>
<td>658.7</td>
<td>0</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>7</td>
<td>4637</td>
<td>662.4</td>
<td>27</td>
</tr>
<tr>
<td>Cyclooctane</td>
<td>8</td>
<td>5310</td>
<td>663.8</td>
<td>42</td>
</tr>
<tr>
<td>Cyclononane</td>
<td>9</td>
<td>5981</td>
<td>664.6</td>
<td>54</td>
</tr>
<tr>
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<td>10</td>
<td>6636</td>
<td>663.6</td>
<td>50</td>
</tr>
<tr>
<td>Cyclopentadecane</td>
<td>15</td>
<td>9885</td>
<td>659.0</td>
<td>6</td>
</tr>
</tbody>
</table>

**Critical Thinking Question (CTQ):**

1. Based on the shape of the molecule, what bond angles would you expect between the carbon atoms in cyclopropane? What is the ideal bond angle for an sp³ hybridized carbon atom?

2. Based on the shape of the molecule, what bond angles would you expect between the carbon atoms in cyclobutane? Based on an sp³ hybridized carbon atom, what is the ideal bond angle?

3. Build two models of 1,2-dimethylcyclopentane. The two methyl groups can be on the same face or opposite faces of the ring. No matter how the molecule is twisted, they cannot be superimposed on each other. These compounds are **stereoisomers** of each other.

4. When two groups are present, the prefix **cis** (same face) or **trans** (opposite face) can be used in IUPAC nomenclature to specify which stereoisomer is being considered. For drawings, a solid wedged line indicates the bond to a carbon is coming out of the page and a dashed wedged line indicates the bond going into the page.

5. Write the IUPAC name of the compounds below, including **cis** or **trans** where appropriate.

![Chemical structures](image-url)

6. For two of the compounds above, **cis** or **trans** is not needed. Circle those compounds and state why.

7. Draw the wedge/dashed bond line representation of **trans**-1,3 diethylcyclohexane.
Model 2. Cyclohexane Chair Conformation

Another helpful way to draw a non-planar example of cyclohexane is to draw its most stable (lowest energy) conformation called a chair conformation.

8. Build two models of cyclohexane.

9. The chair conformation is the most stable conformation of cyclohexane because all of the bond angles around the carbon atoms are at 109.5° and all carbon atoms are in the more stable staggered conformation. Cyclohexane is the only cyclic structure that allows all the bond angles around each carbon to be 109.5°, thus is the only ring that adopts a true chair conformation. Form the chair conformation with both of your cyclohexane models. Look down each carbon carbon bond and verify that all carbons are in a staggered conformation.

10. Because of this conformation, there are two types of positions a group can occupy when it is attached to a cyclohexane chair, either axial (A) or equatorial (E).

11. Axial hydrogens alternate straight up and straight down as we proceed around the ring (Figure III above). Identify the axial hydrogens on your model of cyclohexane.

12. Equatorial hydrogens also alternate up and down, but at an angle around the equator of the ring (Figure II above). Identify the equatorial hydrogens on your model of cyclohexane.

13. Groups or atoms in axial positions experience 1,3-diaxial interactions (additional strain that increases the energy of that conformation) due to the axial bonds on the 1 and 3 carbons lining up with each other (torsional strain) and steric strain, if one or both of the axial groups are larger than a hydrogen atom. Below is a Newman projection of methylcyclohexane looking down the 1-2 and 5-4 carbon bonds. Circle the structure with the lowest 1,3-diaxial interactions (lowest energy conformation of the two molecules).

14. Add a methyl group to one of the carbons of your model of cyclohexane. Is the methyl group currently in the axial or equatorial position?

15. Arrange the chair in your hands so that the carbon bearing the methyl group is in one hand and the 4th carbon on the ring is in the other. Flip the chair by pushing down on the up end carbon and up on the down end carbon. The methyl group should be in the axial position, if it was in the equatorial position and vice versa. (note: when a chair flips, all axial groups become equatorial and all equatorial groups become axial).
16. Which of the two chairs above do you think is the most stable (lowest energy) and why? Once you are sure, circle the more stable chair conformation. (*It is important to note that at room temperature, molecules continually flip between chair conformations and their intermediate conformations, but spend the majority of their time in the more stable conformations.*)

17. Make a model of *trans*-1,2-dimethylcyclohexane and *cis*-1,2-dimethylcyclohexane. Draw their chair conformations below including the chair flip for each.

18. Circle the most stable chair conformation(s) of *trans*-1,2-dimethylcyclohexane above. Why is it most stable?

19. Circle the most stable chair conformation(s) of *cis*-1,2-dimethylcyclohexane above. Why is it most stable?

20. Is *trans*-1,2-dimethylcyclohexane or *cis*-1,2-dimethylcyclohexane lower energy? Why?

21. Make a model of *trans*-1,3-dimethylcyclohexane and *cis*-1,3-dimethylcyclohexane. Draw their chair conformations below including the chair flip for each. Repeat questions 15-16 on this model.

22. Make a model of *trans*-1,4-dimethylcyclohexane and *cis*-1,4-dimethylcyclohexane. Draw their chair conformations below including the chair flip for each. Repeat questions 15-16 on this model.

**Assignment** Finish this packet if you did not do so in lab, and see the lab syllabus for additional information about this week’s assignment.