

Experiment 10

Modeling Chirality and Cycloalkanes

Reading: Organic Chemistry by Marc Loudon, 6th ed., pp. 237-241 (6.3); pp. 273-291 (7.2-7.4); pp. 293-301 (7.6).

There is no prelab, lab report or quiz for this experiment. Instead, bring your modelling kit to lab and work through these exercises during class. There are several parts labeled “Practice Exercise” that will be helpful to do, but the only part you need to turn in is the worksheet at the end of each modeling exercise. These are due before you leave lab today.

Modeling Chirality

Some molecules are identical to their mirror images, and some are not. Some examples are shown in Figure 10-1. The pair of molecules on the left are identical mirror images of each other. The pair of molecules on the right are non-identical (noncongruent) mirror images of each other. This makes them enantiomers of each other. Every molecule that has an enantiomer is **chiral** (from the Greek word for hand), because it has a “handedness” or “chirality” to it.

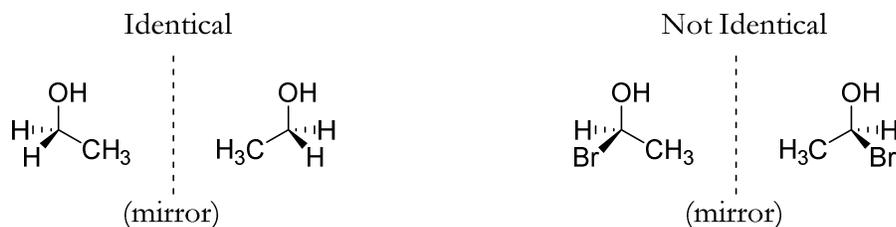


Figure 10-1: An example of one molecule that reflects into its mirror image, and another that does not.

Practice Exercise: Build the four structures shown above. Rotate the first pair of molecules to show that they can overlap with each other, and rotate the second pair to show that they cannot.

The easiest way to check whether a molecule is chiral is to look for an **internal mirror plane of symmetry** – a place where you can cut the molecule in half so that each half reflects perfectly into the other. If it exists, then the molecule is not chiral (in other words, it is achiral). Some examples are shown in Figure 10-2.

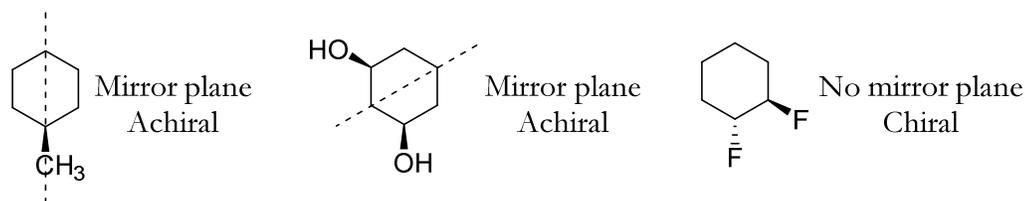


Figure 10-2: Two molecules with internal mirror planes, and one without. The last molecule has no mirror plane because there is no way to cut it in half such that each half reflects perfectly into the other.

Practice Exercise: Build the three structures shown above. Look for the internal plane of symmetry in the first two molecules, and check that there is no plane for the third.

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The part of a molecule that gives it chirality is often, but not always, an **asymmetric carbon**. This is a carbon with four different groups attached to it. Asymmetric carbons are one example of a **stereocenter** – a part of the molecule where swapping any two groups converts the molecule to a different molecule.

Stereochemical designation (*R,S* and *E,Z*)

Since each stereocenter can have two different possible three-dimensional structures, we need a system to describe the configuration at each stereocenter. The Cahn-Ingold-Prelog (CIP) system is used to do this. In this system, groups are assigned priorities based on atomic number as described in your text book. The relationship of the groups to each other can then be examined and the stereocenter can be unambiguously assigned a descriptor. For tetrahedral stereocenters (e.g., asymmetric carbons) the descriptor is either *R* or *S*, while for planar stereocenters (e.g., alkenes), it is *E* or *Z*.

To determine if a tetrahedral stereocenter is *R* or *S*, we first assign a CIP priority to each group bonded to the stereocenter. The highest priority group is 1, the lowest is 4. The groups are then oriented such that group 4 points away from the observer. Groups 1, 2, and 3 will then be oriented towards the observer. We then trace an arc from group 1 to group 2, then to group 3. This arc will be either clockwise, or counter clockwise. If it's clockwise, the stereocenter is designated as *R*; if it's counterclockwise, it is *S*. This is shown in Figure 10-3.



Figure 10-3: Determining *R* and *S* at tetrahedral stereocenters.

To determine if a planar stereocenter (such as an alkene) is *E* or *Z*, we first assign a CIP priority to the two groups bonded to each carbon of the alkene. So, each carbon will have a group labeled as 1 (higher priority) and 2 (lower priority). If the two groups labeled as 1 are on the same side of the molecule, the molecule is designated as *Z* (also called *cis*, if each carbon of the alkene has one H and one non-H). If they are on the opposite sides, it is designated as *E* (also called *trans*, if each carbon of the alkene has one H and one non-H).

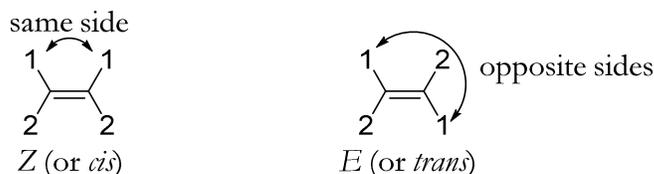


Figure 10-4: Determining *E* and *Z* and planar stereocenters.

2-Chlorobutane

2-Chlorobutane is one of the simplest chiral molecules, yet it can be depicted in many different ways. This exercise is intended to stress this point and illustrate that simple reorientation of a molecule and bond rotations provide structures which can look different on paper. It also illustrates the point that interchanging the two groups on a stereocenter provides the opposite configuration of the stereocenter.

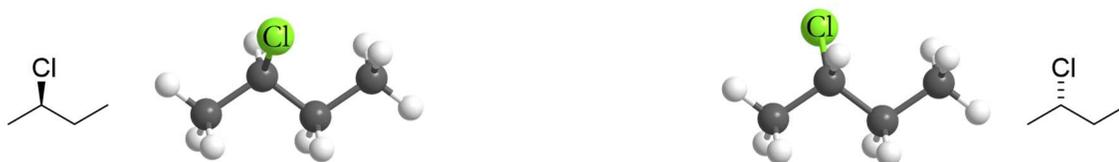


Figure 10-5: Enantiomers of 2-chlorobutane

Practice Exercise: Shown in Figure 10-5 are the two enantiomers of 2-chlorobutane. Make models of the two molecules and then attempt to superimpose them (you won't be able to.) Now, assign a CIP priority to the four different groups (Cl=1, Et=2, Me=3, H=4) bonded to the stereocenter and orient your models such that the lowest priority group (H) is pointing away from you. Determine whether each molecule is *R* or *S*. Note that the hydrogen and chlorine have been exchanged, which means that one molecule must be *R* and one must be *S*. The worksheet at the end of this exercise has several similar problems, so you may want to keep your models of 2-chlorobutane intact and solve these problems, then come back to this point.

Visualizing σ -bond rotations

Students often find visualization of rotations about C-C bonds difficult without the aid of models, but there is an informal yet systematic way of doing this that can help. Consider compound **A** shown in Figure 10-6. It is drawn in a zig-zag conformation so that the line of carbons is parallel to the bottom of the paper. Notice that there are two orientations of the carbons: the substituents on some carbons (C2 and C4) point towards the top of the page, while the substituents for other carbons (C3) point towards the bottom. Neither C1 nor C5 is an asymmetric carbon so the direction of their substituents are less important. Note that the chlorine atom on C2 and the methyl group on C3 are both attached with bold bonds, indicating that they are coming out of the plane of the paper.

Now, consider Compound **B** shown Figure 10-6. It is the same structure as Compound **A**, but it has been flipped over so it is upside-down. Note that every carbon atom that was pointing up is now down, and vice-versa. Note also that, since the molecule has been rotated by 180° , every group that was bold is now dashed.

Practice Exercise: Prepare a model of compound **A** in Figure 10-6, and flip it such that it adopts the orientation of compound **B**. Examine the position of the substituents.

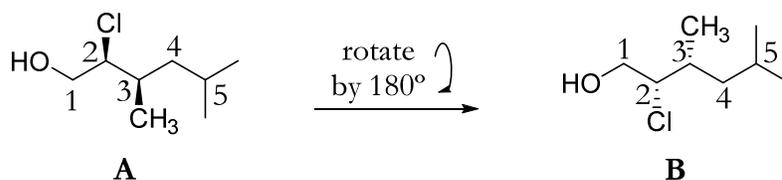


Figure 10-6: Identical molecules drawn in different orientations.

The difference between these two renditions of the same molecule is fundamentally related to the "zig-zag" orientation of the carbons in each drawing; in **A**, carbon 2 "zigs" while in **B** carbon 2 "zags". In other words, in compound **A**, the arc formed from following C1 to C2 to C3 runs clockwise while the same arc in compound **B** runs counterclockwise (see the arrows in the drawings in Figure 10-7). Similarly, the arc traced from C2 to C3 to C4 in compound **A** is counterclockwise while in **B** it is clockwise. In general, if we have a substituent on a molecule which is bold when tracing an arc clockwise, it will be

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dashed if it is rendered in such a way as to trace a counterclockwise arc. Similarly, if we have a substituent on a molecule which is dashed when tracing an arc clockwise, it will be bold if it is rendered in such a way as to trace a counter-clockwise arc.

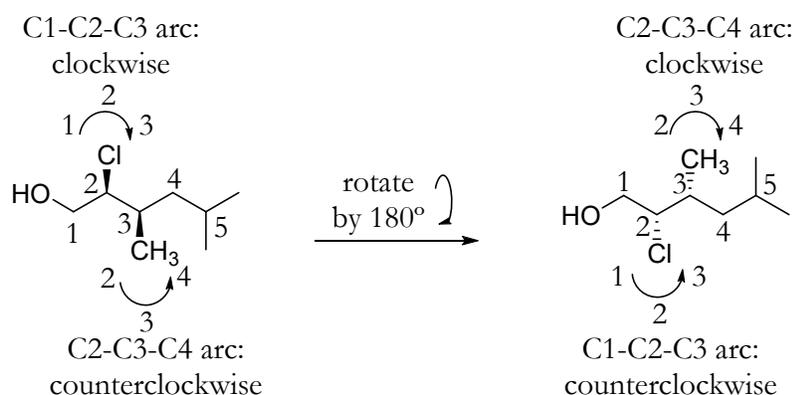


Figure 10-7: By flipping the molecule, you change the direction of the C1-C2-C3 arc from clockwise to counterclockwise, and vice versa for the C2-C3-C4 arc.

Rotating about C-C bonds can have the effect of switching the arc from clockwise to counterclockwise. This is illustrated in Figure 10-8. Compound **C** is drawn in the zig-zag conformation, whereas in compound **D** the bond between C2 and C3 has been rotated by 180°, while in compound **E** the bond between C5 and C6 has been rotated by 180°. All three are the same isomer; it's just that they have been drawn differently with C-C bonds rotated in different orientations. In compound **C**, the arcs traced upon going from C1-C2-C3 and C5-C6-C7 are both clockwise. In compound **D** the arc traced upon going from C1-C2-C3 is now counter clockwise, and as a consequence, the OH at C2 is now drawn dashed. Similarly, in compound **E** the arc traced upon going from C5-C6-C7 is now counter clockwise, and as a consequence, the chlorine at C6 is now drawn bold.

Practice Exercise: Prepare models of the compounds in Figure 10-8 and rotate the bonds to get the molecules into the conformations depicted. Convince yourself that these are all the same compound.

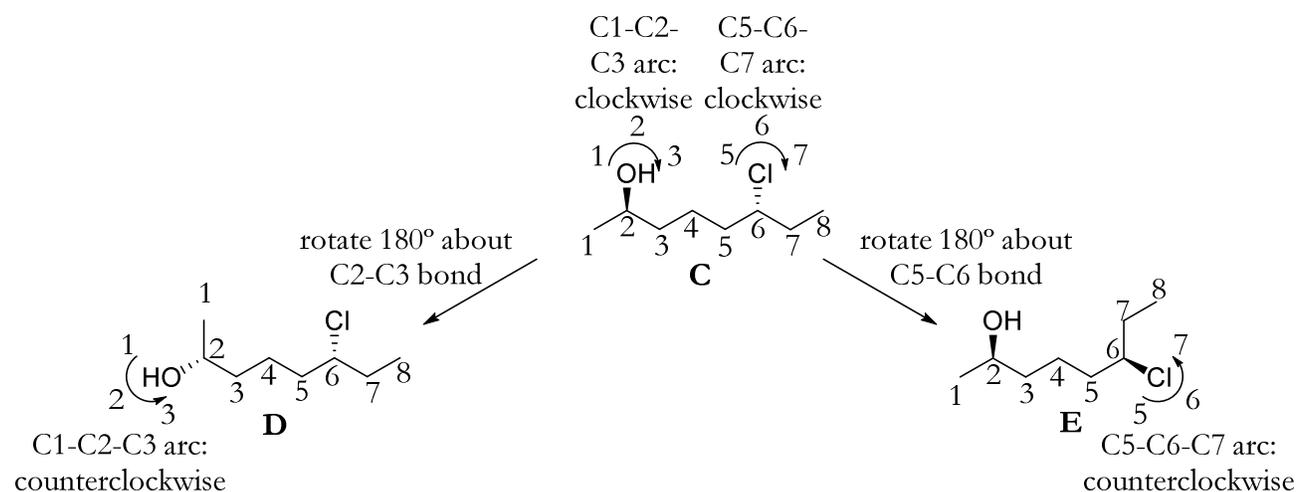


Figure 10-8: Identical molecules drawn in different orientations.

Enantiomers, diastereomers, and meso compounds

We've already seen that enantiomers are molecules that are noncongruent mirror images of each other. The simplest way to draw the enantiomer of a chiral molecule is to invert the stereochemistry at each tetrahedral stereocenter as shown in Figure 10-9, replacing bold bonds with dashed bonds and vice versa. (There is no way to draw the enantiomer of an achiral molecule – why not?)

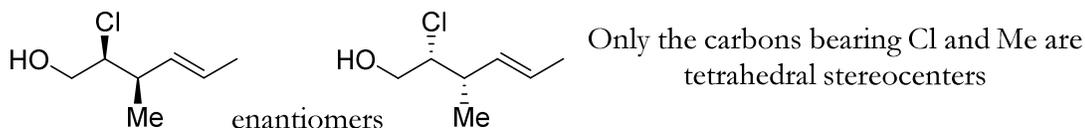


Figure 10-9: Inverting the stereochemistry at each stereocenter gives the enantiomer.

Practice Exercise: Build the molecule shown above and verify that you can convert it to its mirror image by inverting the two tetrahedral stereocenters.

What if we invert some of the stereocenters but not all? In this case, we generate structures with the same connectivity which are noncongruent non-mirror images. These are called **diastereomers** - several examples are shown in Figure 10-10. Note that changing the alkene from *E* to *Z* also creates a diastereomer, since there is no way to reflect this alkene onto its previous configuration.



These compounds are diastereomers of each other, and of the two compounds in the previous figure.

Figure 10-10: Inverting the stereochemistry at some stereocenters but not all gives a diastereomer.

In some cases, it is possible for a molecule to have asymmetric carbons but still have an internal plane of mirror symmetry, so that it is achiral. All of the compounds shown in Figure 10-11 have the same connectivity, but two of them are chiral and two are not.

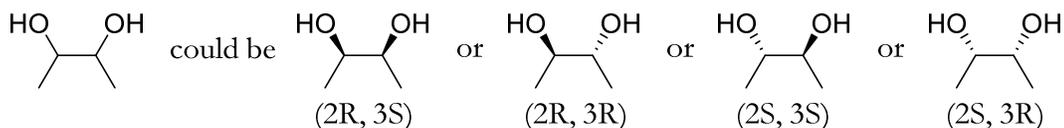


Figure 10-11: Four structures with the same connectivity.

Of these compounds, the $(2R, 3S)$ and the $(2S, 3R)$ have an internal plane of symmetry and should be achiral. In fact, if we flip one of the molecules over, we can see that they're actually both the same molecule, as shown in Figure 10-12.

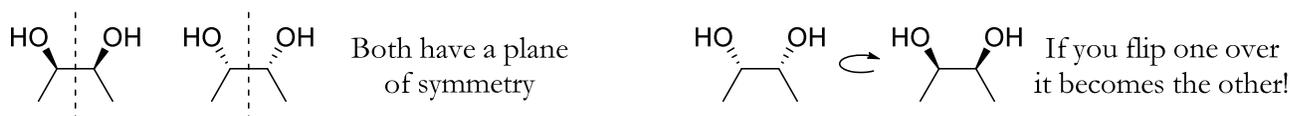


Figure 10-12: Two of the structures are identical and meso.

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These compounds are called **meso compounds**. A more rigorous definition of meso is "an achiral molecule which has a diastereomeric relationship to a chiral molecule." In other words, if an achiral molecule has a stereoisomer which is chiral, then the achiral molecule is also meso. Most achiral molecules do not have chiral diastereomers, but some do.

Chirality without asymmetric carbons

Not all stereocenters are asymmetric carbons or alkenes. In the case of more complex ring structures (especially spirocyclic compounds, as shown in Figure 10-13), it is possible to have stereocenters which are not asymmetric carbons, but which will still produce a different molecule if two groups at that atom are swapped.



Figure 10-13: An example of a spirocyclic compound which is chiral without having any asymmetric carbons. The atoms marked with asterisks are stereocenters.

Practice Exercise: Build the molecules shown above and verify that they are non-superimposable mirror images. Pick one stereocenter on one of the molecules, swap two groups attached to it, and verify that the molecules are now identical. Put the stereocenter back the way it was, and repeat this step for each of the carbons marked with an asterisk.

Conformational chirality

As we saw in the first molecular modeling exercise in this course, there are three staggered conformations for butane: one anti and two gauche conformers. The two gauche conformers for butane are gauche-(+) and gauche(-). These are named after the right-hand rule: in the (+) compound, when sighting along the C2-C3 bond from C2 to C3, one travels in a clockwise direction from C1 to C4. In the (-) compound, when sighting along the C2-C3 bond from C2 to C3, one travels in a counterclockwise direction from C1 to C4. These conformations, shown in Figure 10-14, are chiral conformers: the (+) conformer is the mirror image of the (-) conformer, and these two conformers are not superimposable. If it were possible to isolate either of these forms of the molecule, then butane would exist as a mixture of three different stereoisomers. However, since butane undergoes rapid rotation about the C2-C3 bond, none of the conformers can be isolated at room temperature. Thus, butane is NOT a chiral molecule, even though it has chiral conformers.

Practice Exercise:

- Build a model of anti-butane. In Figure 10-14, draw a Newman projection of your model sighting along the C2-C3 bond with C2 in front and H_d pointing downwards, and label the substituents.
- Convert your model of anti-butane to the gauche-(+)-butane conformation by rotating C2 and its substituents by 120° . Draw a Newman projection of your model sighting along the C2-C3 bond with C2 in front and H_d pointing downwards, and label the substituents.
- Convert your model of gauche-(+)-butane to the gauche(-)-butane C2 and its substituents by another 120° . Draw a Newman projection of your model sighting along the C2-C3 bond with C2 in front and H_d pointing downwards, and label the substituents.

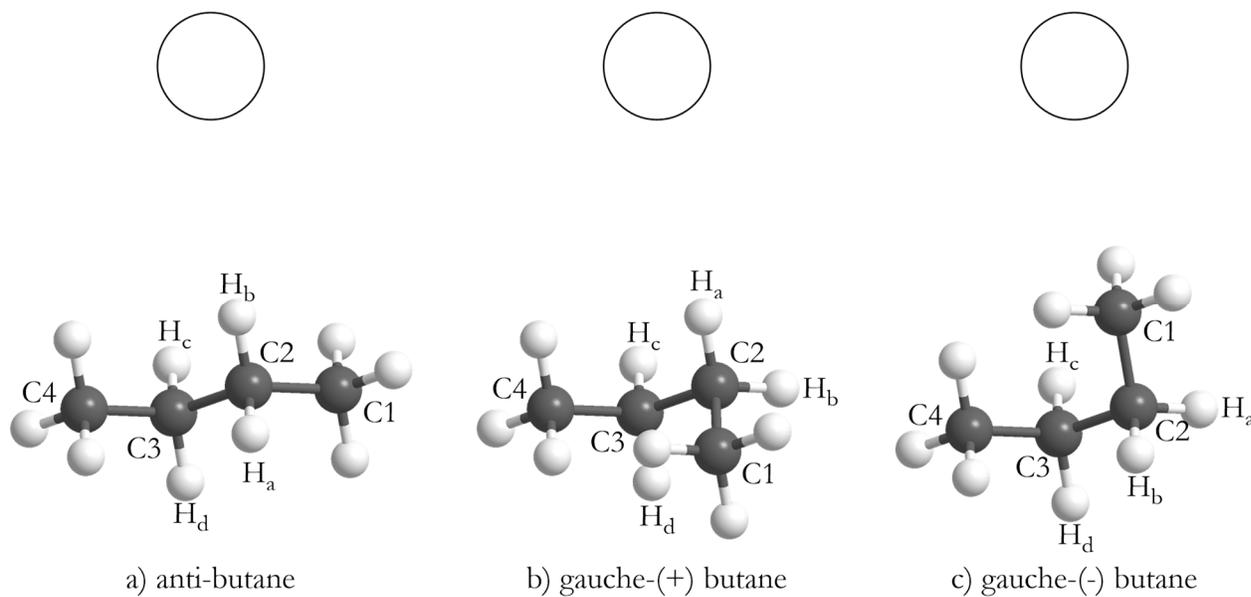


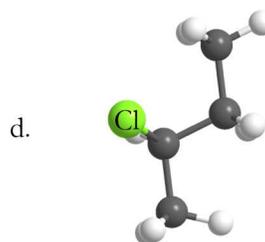
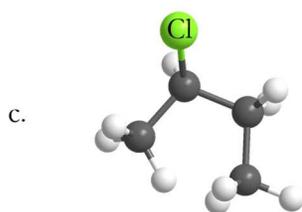
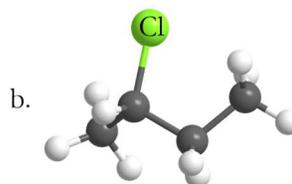
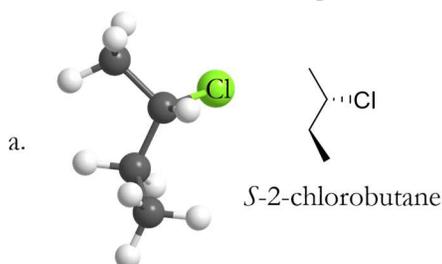
Figure 10-14: Draw the Newman projections as directed in each molecule.

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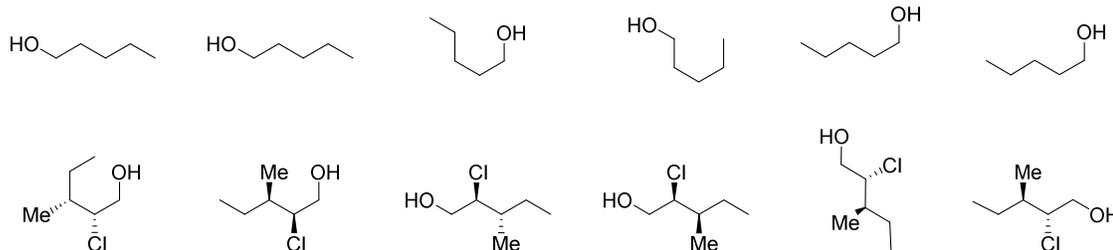
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Chirality Modeling Exercise

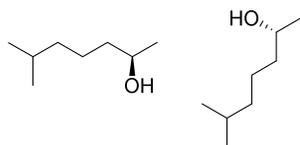
1. Several other conformations and orientations of 2-chlorobutane are shown below. Make a model of each by rotating about the σ -bonds of either the R- or S- model and holding it in the same orientation as in the drawing. Then use your model to help you draw a line-bond structure to the right of each conformation. Indicate if each molecule is the R- or S- enantiomer (the answer to the first one is provided as an example). (3 pts)



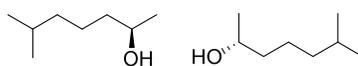
2. Various isomers of 2-chloro-3-methylpentan-1-ol are shown below in different conformations and orientations. Using the template provided on top of each drawing, add the chloro- and methyl-substituents with the correct stereochemistry. Try to do this by seeing if the arc traced by each stereocenter is the same as it is in the compounds shown below the templates. If this is difficult, make models of the starting conformation and orientation, and rotate the model to the same conformation and orientation as the template. (6 pts)



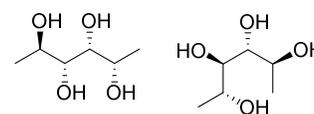
3. Several pairs of compounds are shown below. Are they isomers, or the same compound drawn differently? (3 pts)



isomers or
same compound?



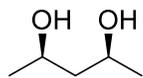
isomers or
same compound?



isomers or
same compound?

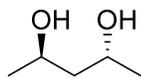
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4. Several compounds are shown below. For each, make two models: one model of the compound as shown, and the other where each tetrahedral stereocenter is inverted. Compare the two models side-by-side to see if the model with the inverted stereocenter(s) is the enantiomer, or if it is identical to the original. Remember, you can rotate around σ -bonds to place the molecule in the conformation with the highest symmetry. Is each compound meso or not? (4 pts)



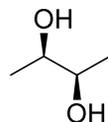
a. Enantiomers or identical?

b. Meso: yes or no?



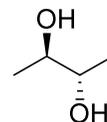
a. Enantiomers or identical?

b. Meso: yes or no?



a. Enantiomers or identical?

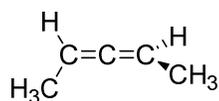
b. Meso: yes or no?



a. Enantiomers or identical?

b. Meso: yes or no?

5. In the molecule shown below, which of the carbons are stereocenters? (4 pts)



Modeling Cyclic Compounds

The principles that govern the conformations of acyclic alkanes also govern cyclic alkanes; there is a preference for staggered conformations over eclipsed ones, and in cases where more than one staggered conformation is possible, anti-conformers are lower in energy than gauche conformers. This is illustrated with the structure of cyclohexane. If we consider the lowest energy conformation of this molecule, we may be tempted to simply draw it flat and leave it at that. However, the dihedral angle of all C-C bonds in the flat structure is 0° , which renders all the C-C bonds eclipsed. As such, we would have 12 eclipsed H – H interactions. Furthermore, the C-C bond angles in this conformation would be 120° , which is larger than the ideal angle of 109.5° . Thus, in addition to the strain of the H – H eclipsing interactions, there is angle strain due to the bending of the C-C bonds away from their ideal angle. All these are relieved when the molecule puckers and adopts what we call the “chair” conformation shown in Figure 10-15.

Practice Exercise: *This can be hard to visualize, so it is useful to make a model of this structure. Some students have a hard time getting their models in the chair conformation, but it's easy if you follow these steps. Start with your model in the planar conformation as shown in Figure 10-15 (the carbons are numbered for reference). Notice how the C-C bond angles are not an ideal 109.5° , then sight down the C-C bonds and notice how they are all eclipsed. Now, move C4 up and C1 down; the molecule will naturally adopt the chair conformation. Sight down each C-C bond and adjust your model such that each bond is perfectly staggered (or as close to it as you can get it). Your model is now in chair cyclohexane conformation. Notice how the bond angles are no longer distorted.*

This simple movement of these two carbons alleviates all the strain in this molecule as it provides a structure wherein every C-C bond is staggered and all the bond angles are 109.5° . This can also be seen in a Newman projection sighting down any of the C-C bonds as shown in Figure 10-15 (note that in the chair conformation, all the C-C bonds are equivalent and it doesn't matter which ones we choose to sight down).

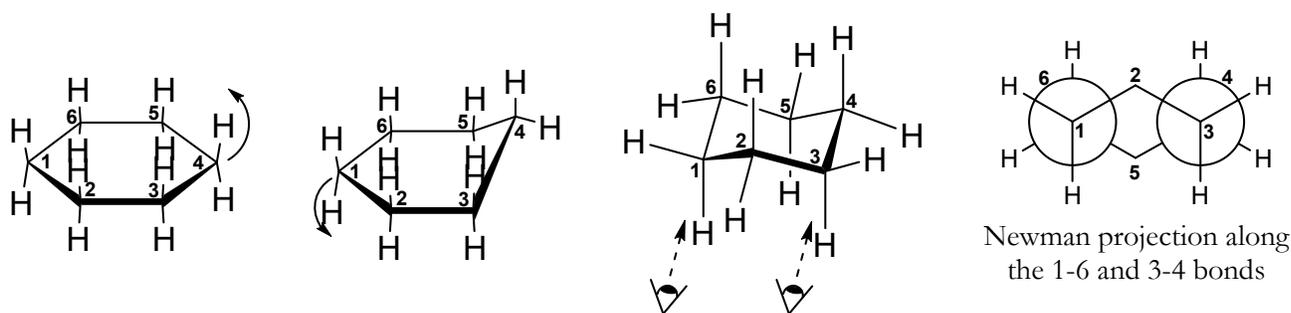


Figure 10-15: How to get a flat cyclohexane model into the “chair” conformation, and how to make a Newman projection of it.

Cyclohexane, boats and twisted boats

In relieving the strain of the planar structure of cyclohexane, why did we pull on carbon down and one carbon up; why not pull them both up? The answer is that if we pull both carbons up, we generate

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what's known as boat cyclohexane, and still have two eclipsed C-C bonds. This is illustrated in Figure 10-16 where we start with planar cyclohexane, and then pull both C1 and C4 up. In this structure, the C2-C3 bond and C6-C5 bond are eclipsed. We can better visualize the eclipsing by drawing a Newman projection looking down one of these bonds as shown in Figure 10-16. In addition, in this structure, two hydrogens, one on C1 labeled H_a and one on C4 labeled H_b , point directly toward each other and bump into each other. This is called a “peri” interaction (it's also called a “flagpole” interaction because the hydrogens are canted towards each other as though they were each on a long flagpole). Also, the sequence of carbons C1-C2-C3-C4 is similar to a syn-butane structure, as is the sequence C4-C5-C6-C1. In fact, just as syn-butane is not an energy minimum structure (recall it is at the top of the energy profile; see Experiment 1 in this lab manual), neither is boat cyclohexane. By twisting just a little, the peri-interaction and the eclipsing interactions are partially, but not completely, relieved. The twist that occurs is one where H_a moves a little bit in one direction and H_b moves a little in the other. This conformation is appropriately called the “twist boat” conformation and is more difficult to visualize and draw than the other conformations, and is best understood with models.

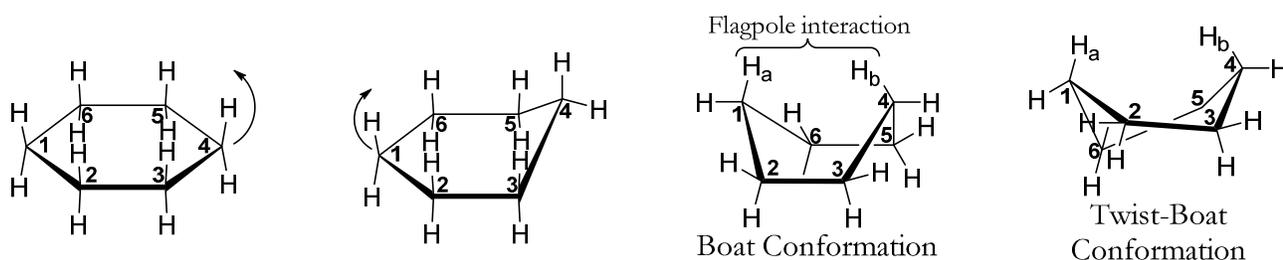


Figure 10-16: How to get a cyclohexane model into the “boat” conformation.

Practice Exercise: Make a model of cyclohexane with all the atoms in the same plane. Now, pull both C1 and C4 down, and adjust the model such that the C2-C3 bond and C6-C5 bond are eclipsed (sight down these bonds in order to visualize this). Observe the flagpole interaction between the hydrogens at C1 and C4. Now, convert your model to a twist boat conformation. Do this by pulling the hydrogens involved in the flagpole interaction (H_a and H_b) slightly in opposite directions. Notice that if you pull them too far apart, you eventually generate a different boat structure, so be careful not to do this.

Chair cyclohexane, axial and equatorial hydrogens

As is the case with all sp^3 hybridized carbons, the carbons of cyclohexane are tetrahedral. A careful examination of these reveals that there are two different types of hydrogens, axial and equatorial (H_{ax} and H_{eq} , Figure 10-17). When drawn in the perspective previously described, the axial hydrogens point up and down, and the equatorial hydrogens point out around the equator of the molecule, hence the name equatorial. This conformation contains a threefold axis of rotation that runs through the center of the molecule, parallel to the axial hydrogens. This means that if we rotate the molecule $1/3$ of a full turn (i.e., $1/3$ of 360° , or 120°) we produce a structure with an orientation that is identical with the starting structure, and therefore indistinguishable in all respects. The axial hydrogens are called axial because they are parallel to this axis.

Practice Exercise: It is important to be able to visualize this structure, so make a model and identify the axial and equatorial hydrogens. Also, label all the axial hydrogens (this will be useful

in the next section): if your model set allows you place an atom of a different color where the hydrogens should be, then you can use this to identify the axial hydrogens. Otherwise, you can label them with a piece of tape.

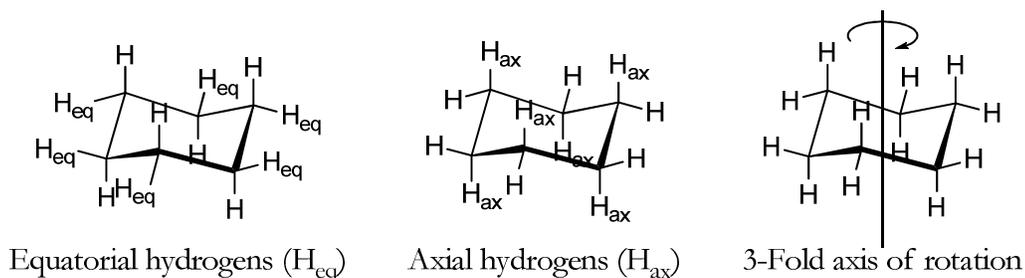


Figure 10-17: Axial and equatorial hydrogens on cyclohexane.

Cyclohexane and chair flips

Cyclohexane is capable of undergoing what's called chair-chair interconversion, or ring flips. This is easy to visualize and illustrate with your models.

Practice Exercise: Orient the chair cyclohexane model with the axial hydrogens labeled (that you prepared in the previous section) as shown in Figure 10-18. Orient your molecule such that the carbon at the far left hand side of the structure points down and the one on the far right hand side points up. Now, pull the carbon at the far left of the structure up such that the molecule is now in the boat conformation. Then, pull the carbon on the far right side of the structure down such that the molecule is converted back to the chair conformation.

If you did the above task exactly as described, you will notice that all the hydrogens that were labeled as axial are now equatorial, and all the equatorial hydrogens are now axial. And it always works regardless of which carbons you use to do the chair flip; it's always the case that all the axial hydrogens end up equatorial and all the equatorial hydrogens end up axial. Repeat this with two different carbons to convince you that this is indeed true. The barrier to this chair flipping is low, and it occurs constantly and rapidly in cyclohexane at room temperature.

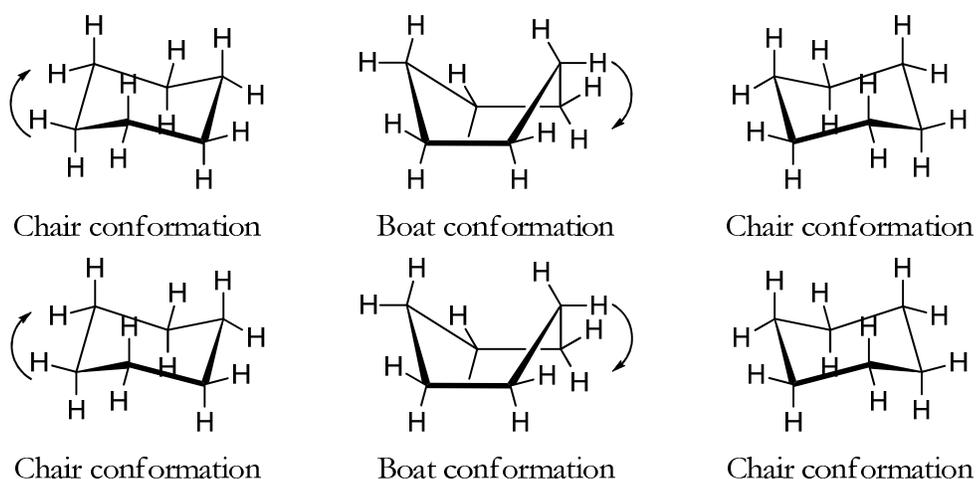


Figure 10-18: Illustrating chair-boat-chair interconversion using models.

Substituted cyclohexanes - gauche butane revisited

If we substitute a cyclohexane with a methyl group, we get methyl cyclohexane. If we draw this molecule flat, we don't really get a sense of how it looks in three dimensions. We know that cyclohexane is not flat; it adopts the chair conformation, and in the chair conformation, there are axial and equatorial bonds. It turns out that a methyl group substituent at the equatorial position is lower in energy than one at the axial position (Figure 10-19). In the equatorial conformer, all the bonds are completely staggered and the methyl group is in an anti-butane conformation. Thus, there are no interactions that raise the energy of the molecule. In the axial conformation, all the bonds are also completely staggered, however, the methyl group is gauche to C2 and C6, and the molecule, therefore, experiences two gauche butane interactions.

Practice Exercise: Make a model of these two conformations. Notice that in the equatorial conformer, the dihedral angle made by C2-C3-C4-Me is 180° , as is the angle made by C6-C5-C4-Me. Now, recall that in anti-butane, the lowest energy conformation of butane, the dihedral angle is also 180° .

Gauche-butane is 0.9 kcal/mol higher in energy than anti-butane, and since there are two gauche-butane-like interactions in the axial conformer, we would predict this molecule to be 1.8 kcal/mol higher in energy than the equatorial conformer. This is, in fact, the case.

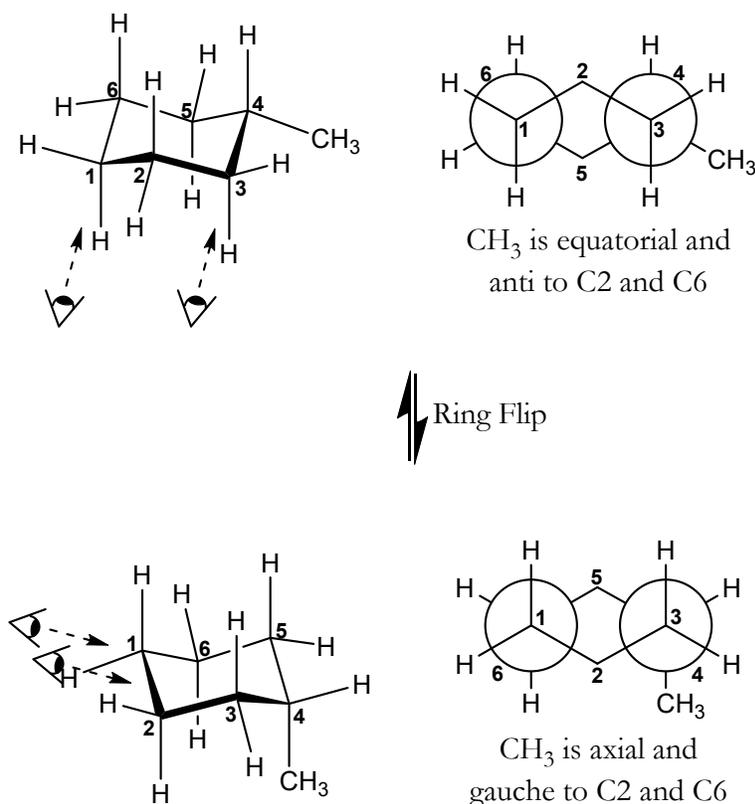


Figure 10-19: Axial and equatorial conformations of methyl cyclohexane.

Drawing cyclohexane with parallel lines

Cyclohexane is composed of a number of parallel bonds, and this is reflected in our drawings. The carbon framework of cyclohexane is shown in Figure 10-20, and for those of us who lack artistic talent, there's a simple method one can use to draw this molecule. Begin by drawing a sideways "V" with lines of approximately equal length as shown in Figure 10-20 (these lines are labeled "a" and "b"). Now, from the ends of this V draw two parallel lines that point slightly down and are just as long as lines a and b (these lines are labeled "c" and "d"). From the end of line d, draw a line parallel to line a (this line is labeled "e"). Again, this line should be the same length as line a. The last line (line "f") now connects line c with line e, and if everything was drawn exactly as described, it should be parallel to line b.

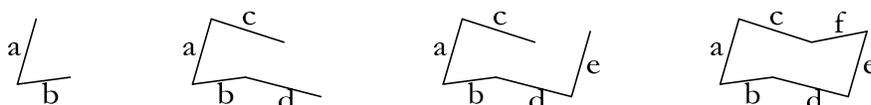


Figure 10-20: How to draw cyclohexane using a series of parallel lines.

With the carbon framework drawn, we can draw the hydrogens. Recall that there are two types of hydrogens on a cyclohexane ring, axial and equatorial. The axial hydrogens are easy to draw, they point up and down on alternating carbons, and are parallel to each other (Figure 10-21). Note that C2 and C3 are in front of C5 and C6, and, therefore, the hydrogen bonded to C2 is in front of the C5-C6 bond. This is indicated by drawing a broken line for the C5-C6 bond where the line representing the axial bond at C2 intersects with it. Similarly, the axial hydrogen at C5 is behind the C2-C3 bond, and it is drawn with a broken line as well.

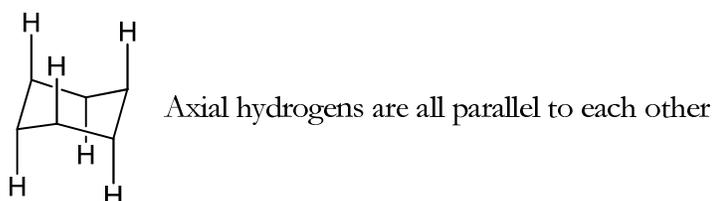


Figure 10-21: Axial hydrogens are all parallel to each other.

The equatorial hydrogens are NOT parallel to each other. Instead, they are each parallel to two of the C-C bonds in the cyclohexane ring, as shown in Figure 10-22. The equatorial hydrogens bonded to C1 and C4 are parallel to the C2-C3 bond and to the C5-C6 bond (structure **A** in Figure 10-22 in which the relevant parallel lines are drawn in bold). Those bonded to C2 and C5 are parallel to the C3-C4 bond and to the C6-C1 bond (structure **B** in Figure 10-22). Finally, those bonded to C3 and C6 are parallel to the C4-C5 bond and to the C1-C2 bond (structure **C** in Figure 10-22).

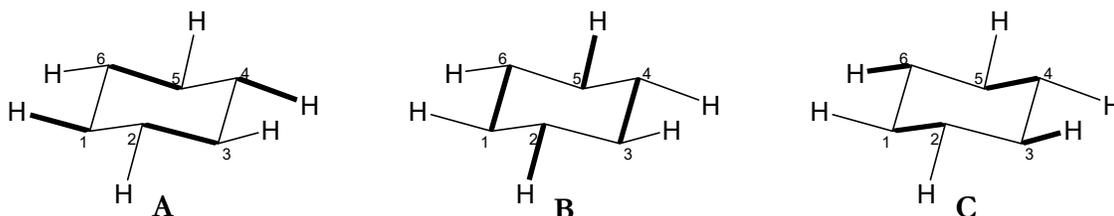


Figure 10-22: Equatorial hydrogens are all parallel to carbon-carbon bonds within the ring.

Bicyclic compounds

Cyclohexane is one example of a monocyclic compound – it contains only a single ring. Many compounds contain two rings, but there are several different ways for these rings to be attached to each other, as shown in Figure 10-23.



Figure 10-23: Examples of types of compounds with two rings.

Fused bicyclic compounds have more than one way for the rings to be joined together. The classic example is decalin, shown in Figure 10-24. Decalin is named for its ten carbon atoms, but it can also be thought of as two cyclohexane rings attached together along a shared carbon-carbon bond. There are two ways for these rings to be connected: if both hydrogens at the joining face point in opposite directions (in other words, if one is shown with a bold bond and one with a dashed bond), then they are *trans* to each other and the compound is *trans*-decalin. If both hydrogens at the shared bond point in the same direction (they are both shown with bold bonds, or both shown with dashed bonds), then they are *cis* and the compound is called *cis*-decalin. This has consequences for the ability of the rings to undergo chair-flip, as shown below.

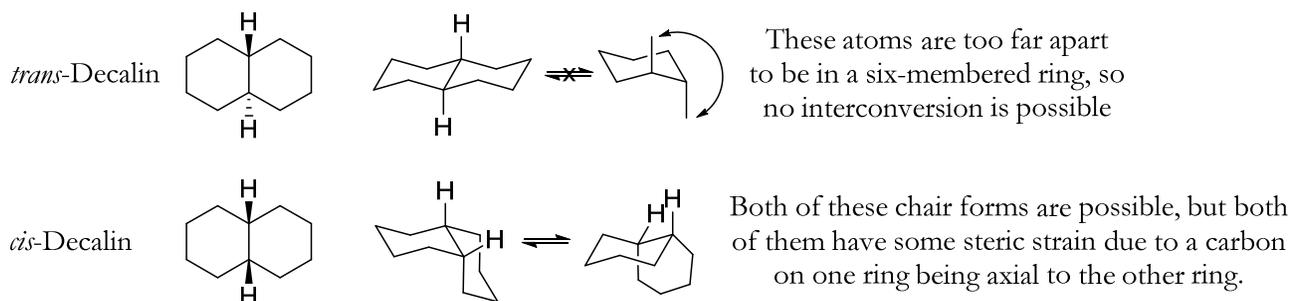
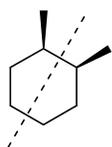


Figure 10-24: *trans*-Decalin is locked into one chair-flip form, but *cis*-decalin can interconvert freely. However, none of *cis*-decalin's forms are as stable, since it always has at least one axial interaction between the two rings.

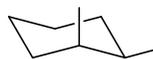
Practice Exercise: Choose a partner. One of you should make a model of *cis*-decalin and the other should make a model of *trans*-decalin. Arrange each of these compounds so they match Figure 10-24, then try to perform chair flips on each of them.

Conformational chirality in cyclic compounds

Conformational chirality in cyclic compounds is similar to that in acyclic compounds: even though the top-down view of the molecule might have a plane of symmetry and thus be achiral, it is still possible for neither of its chair conformations to have a plane of symmetry, making them chiral conformers. An example is shown below in Figure 10-25.



Plane of symmetry in
top-down view:
achiral molecule



Neither chair conformer
has a plane of symmetry:
chiral conformers

Figure 10-25: An achiral cycloalkane with two chiral conformations.

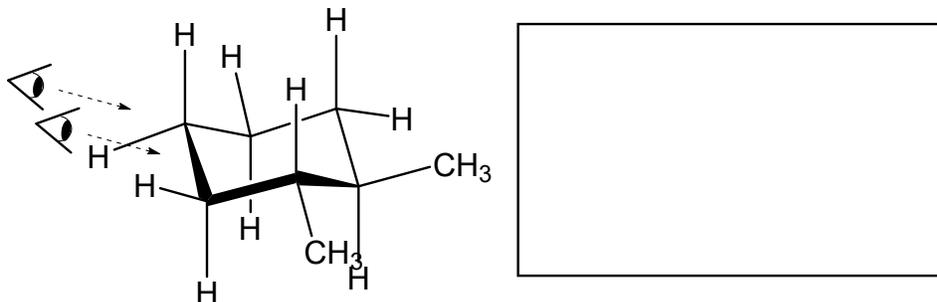
Practice Exercise: Build the molecule shown in Figure 10-25. Verify that it is achiral, but that its two chair conformations are each chiral conformers.

Experiment 10: Modeling Chirality and Cycloalkanes

Name _____

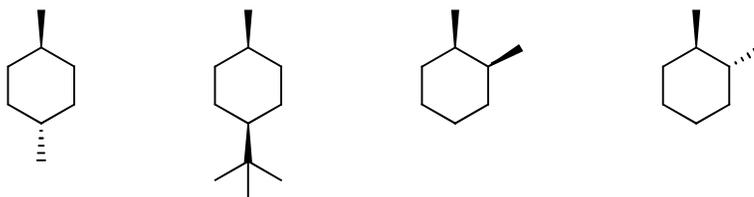
Cycloalkanes Modeling Exercise

1. Draw Newman projection for the molecule below from the perspective indicated. (3 pts)



2. For the Newman projection you drew, indicate if there are any eclipsed bonds, or gauche butane interactions. (3 pts)

3. Draw the lowest energy conformations of the molecules shown below and identify all the gauche-butane interactions in these molecules. (8 pts)



Experiment 10: Modeling Chirality and Cycloalkanes

4. Some cyclohexane derivatives are shown below; make a model of each compound. Is each compound chiral? If not, show the internal plane(s) of symmetry. Draw both the chair conformations for each molecule. Is each chair a chiral conformer? If not, show the internal plane(s) of symmetry in each chair. (6 pts)

