Mag Biochemistry Name ______________________________ # _____

Isomerism in Alkanes, Cycloalkanes, Haloalkanes, and Alkenes using Molecular Models

Background

In uncharged, stable molecules a carbon atom almost always forms four bonds, nitrogen forms three, oxygen two, hydrogen one, and the halogens all one. Within these limitations, an atom may bond to many other atoms, using many possible combinations of single, double, and triple bonds. Because of the many different bonding possibilities, it is often possible to arrange a particular set of atoms in more than one way to form molecules with different structures that represent different compounds. **Different molecules with the same number of atoms of each element (the same molecular formula) are known as <u>isomers</u>.** For example, ethyl alcohol and dimethyl ether both have the same molecular formula, C_2H_6O, yet they have very different properties. One of the main purposes of this experiment is to acquaint you with the phenomenon of isomerism and help you to develop the ability to determine when two molecules are the same and when they are different.

Isomerism can be categorized based on the exact difference in molecular structure between the pair of isomers being examined. There are two broad categories of isomerism: **constitutional isomerism** and **stereoisomerism**:

> **Constitutional isomers have their atoms connected in different ways.** Constitutional isomerism includes such types as ***positional isomerism*** (for example, 2-methylpentane and 3-methylpentane both of which are C_6H_{14}), and ***functional group isomerism*** (for example, ethyl alcohol and dimethyl ether, both of which are C_2H_6O).
>
> **Stereoisomers have their atoms connected in the same way.** However, the three-dimensional arrangement of the atoms (i.e., the shape) is different. The category of stereoisomers includes ***cis-trans isomerism*** (*cis*-2-butene vs. *trans*-2-butene, both of which are C_4H_8), and ***optical isomerism*** [(+)-lactic acid vs. (-)-lactic acid, both of which are $C_3H_6O_3$].

Determining whether two molecules represent the same or different compounds, seems at first glance to be a rather easy problem and it would indeed be easy if we could actually see molecules. We would simply ask, "For every atom in the first molecule, is there a corresponding atom of the same element in the same position in the second molecule?" If this were true, the two molecules would be said to be ***<u>superimposable</u>*** (and therefore identical) and would be shown to be molecules of the same compound. If two molecules cannot be superimposed without breaking bonds, they are different compounds. If two molecules are superimposable but we must rotate around single bonds in order to superimpose them, they are ***conformations***, really just different forms of the same compound.

Most of the problem in determining whether two molecules are the same or not arises because we have to visualize them from simple drawings. Because the same molecule can be drawn in many ways, we need to be able to tell **whether or not two drawings that look different actually represent different molecules.** A good way to determine whether two drawings represent the same or different molecules is to make models of the two molecules and see if they are superimposable. If the models are superimposable, then the drawings they represent must be the same molecule.

PRE-LABORATORY QUESTIONS

Isomerism in Alkanes, Haloalkanes, and Alkenes using Molecular Models

1. **Draw structural formulas of (a) *n*-hexane (b) cyclohexane (c) cyclohexene (one double bond).**

2. **Which if any of the above are isomers of each other? Explain your answer fully.**

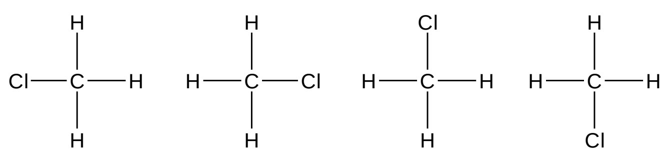
Procedures and Questions: Part 1

As you work through this lab make sketches of the models you build and answer the questions as observations (using complete sentences) in your lab notebook.

I. **Positional Isomerism of Haloalkanes**.

A. **Methanes**.

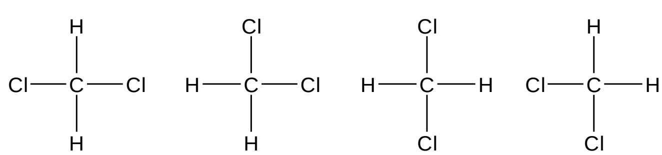
1. Make a model for each of the following structures:



Are all four of the above superimposable on each other?

Do the four formulas represent different molecules?

2. Now make a **model** for each of the following structural formulas.



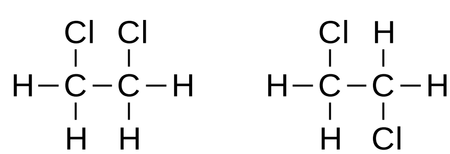
Are all four of the models superimposable on each other?

Do the four formulas represent different molecules?

Chloroform is $CHCl_3$. How many different molecules are possible for $CHCl_3$?

B. **Ethanes**.

1. Prepare **models** of each of the molecules shown below.

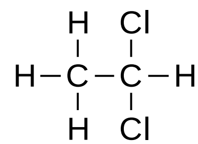


Are the two models superimposable? <u>Remember that rotation of the C-C bond easily occurs</u>.

Are the two molecules isomers or the same compound?

What is the IUPAC name of this compound? (A chlorine atom is named as a "chloro" substituent.)

2. Now rearrange one of the models to form the molecule shown at right.



Is the new model superimposable on the one you did nothing to?

What is the name of the compound represented by the new model?

You now have models of two molecules that are isomers of each other: they are different compounds (with different names) that have the same molecular formula ($C_2H_4Cl_2$). Furthermore, because the only difference in their structures is the position of a substituent (the chlorine) these isomers are considered to be ***positional isomers*** of each other.

Post-lab assignment: Using a chemical handbook or internet reference source to **<u>fill out the following table</u>** illustrating the different physical properties of these two compounds.

Compound Name	literature boiling point (°C)	literature melting point (°C)

Reference used ____

C. **<u>Propanes</u>**.

1. Prepare a model of propane, C_3H_8.

Can the three carbons and eight hydrogens of propane be arranged to form more than one different molecular structure that are not merely different conformations of the same compound?

2. Now replace any one hydrogen attached to an end carbon on the molecule with a chlorine atom.

Draw the structural formula for the molecule and label it with its proper name.

3. Prepare another propane molecule. Replace any one H attached to the middle C with a chlorine atom.
Draw the structural formula for this new molecule and label it with its proper name.

Are the two chloropropane molecules that you prepared (in parts C.2. and C.3.) superimposable?

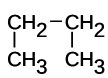
____

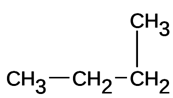
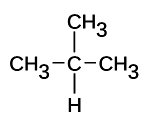
Are they isomers? _________ If so, what type of isomerism do they exhibit? ________________

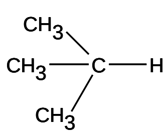
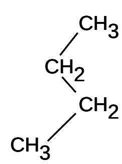
D. **<u>Butanes</u>**.

1. Replace the chlorine atoms in your two chloropropane molecules with methyl (CH_3) groups.
Draw structural formulas for the two positional isomers of butane you have just prepared and give IUPAC names for them.

Note that one of the isomers has a carbon chain while that branches in the middle. The unbranched isomer is commonly called *n*-butane while the branched molecule is called isobutane.
For each of the structures below, indicate whether it is n-butane, isobutane, or neither.

 ________ $CH_3CH_2CH_2CH_3$ ________

 ________  ________

 ________  ________

What is the molecular formula for n-pentane? ______________
<u>Build</u> n-pentane and its 2 isomers. <u>Draw</u> structures for n-pentane & its two isomers. Note that one of the isomers contains a quaternary (4°) carbon atom. 1) <u>Name</u> all three isomers (IUPAC) below each structure; 2) Beneath the IUPAC name, <u>write the</u> <u>condensed formulas</u> (no "lines").

What is the molecular formula for n-hexane? ______________
<u>Build</u> n-hexane and its isomers. Draw structures for n-hexane & its isomers. 1) <u>Name</u> all isomers (IUPAC) below each structure; 2) Beneath the IUPAC name, <u>write the condensed formulas</u> (no "lines"). You may use the <u>back of this page</u>, if an additional blank page was not attached to this handout.

Isomers Lab- PART 2: **Name ______________________________ # ______**

II. ***Cis-Trans* Isomerism** is a type of stereoisomerism in which atoms are connected in the same way. However, the three-dimensional arrangement of the atoms (i.e., the shape) is different. One category of stereoisomerism is cis-trans isomerism and the other is optical isomerism. The latter will briefly be introduced here (Part 3) and covered in much more depth in Unit 4. Refer to the Isomers "flow chart" given in class for an overview of the isomer categories.

A. **Alkanes**: There is no cis-trans isomerism in staggered ("linear") alkanes because there is free rotation around single bonds. However, **Cycloalkanes**: do display cis-trans isomerism (see the last section of Isomers Lab- Part 2).

B. **Alkenes**: While these display cis-trans isomerism, they will be covered more extensively in Unit 3 and only introduced in this lab. Alkenes have one or more double bonds. Below are a few examples and questions:

1**-Ethene**.

Prepare one model of ethane and another of ethene, C_2H_4. *-ene means double bond. Draw both, below.

Is ethene an isomer of ethane? ________________. Can you rotate the carbon-carbon double bond? _______

2-**Propene**.

Now substitute a methyl group for one of the hydrogen atoms in the ethene model. Build a second ethene model and substitute a methyl group for a different H atom.
Are the two models superimposable?

Does it matter which hydrogen in ethene you replace with the methyl group? (Is there any way to make a propene model that is not superimposable on the first one?)

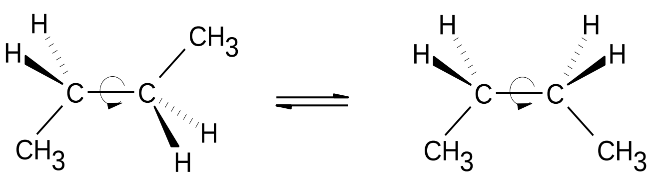
*What is the C-C-C bond angle in propene, approximately? (*protractors are available)*

Draw a chemical structure for propene that realistically shows the C-C-C bond angle.

3-**Butenes**.

There are four butene isomers, C_4H_8. You can come up with a model of each by in turn replacing different hydrogens on propene with a methyl group. Prepare models of all four isomers of butene. Make sure none of them are superimposable on each other and that you have all four before going on.
Draw the structures of the four different butene isomers (show C-C bond angles realistically please).

Notice that there are two isomers that have a double bond between the second and third carbon atoms of a chain. The compound with both methyl groups on the same side of the double bond is *cis*-2-butene (*cis* = on this side), and the one with the methyl groups on opposite sides of the double bond is *trans*-2-butene (*trans* = across). These are different compounds because ***rotation around carbon-carbon double bonds is difficult and does not ordinarily occur***, a fact accurately depicted by your models. Isomers of this type are called **cis/trans isomers**. (Remember, though that the structures shown below, which would be alkanes analogous to *cis*- and *trans*-2-butene, ***are <u>NOT</u> isomers*** but are the ***same molecule in different conformations*** due to the fact that ***rotation <u>CAN</u> occur around carbon-carbon <u>single bonds</u>***.)



C. Cycloalkanes

1. **<u>Cyclopropane</u>**. Make a ring of three carbon atoms using single bonds. Fill in the remaining positions with hydrogen. This molecule is cyclopropane.

    What are the C-C bond angles in cyclopropane?

    What is the preferred bond angle for these carbon atoms as predicted by VSEPR theory?

    Is cyclopropane a stable molecule?

2. **<u>Cyclobutane</u>**. Make a ring of four carbon atoms using single bonds. Fill in the remaining positions with hydrogen.
    What are the C-C bond angles in cyclobutane?

    What is the preferred bond angle for these carbon atoms as predicted by VSEPR theory?

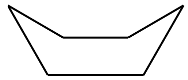
    Is cyclobutane a stable molecule?

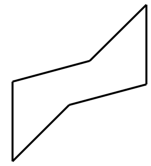
3. **<u>Cyclopentane</u>**. Make a ring of five carbon atoms using single bonds. Fill in the remaining positions with hydrogen.
    What are the C-C bond angles in cyclopentane?

    What is the preferred bond angle for these carbon atoms as predicted by VSEPR theory?

    Is cyclopentane a stable molecule?

4. **<u>Cyclohexane</u>**. Build a ring of six carbon atoms using single bonds. <u>Fill in the remaining positions with hydrogen</u> (VERY IMPORTANT TO DO THIS!). This molecule is cyclohexane.
Cyclohexane can exist in the two non-planar forms shown below. First, **<u>build the chair form</u>** (p.335)





boat form chair form

Place your model on the table/counter (3 H's should be touching the table). Using a protractor, determine the C-C bond angles in cyclohexane: ___________.
What is the preferred bond angle for these carbon atoms as predicted by VSEPR theory?

Does the chair form of cyclohexane appear to be a stable molecule?

While the model is still on the table, continue to refer to p. 335 and compare the **axial bonds** and **equatorial bonds**.
Which type of bonds are in the vertical positions & parallel to the central axis (meaning, either up or down)? See Fig 11.8a in text

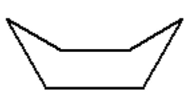
Which type of bonds are (approximately) perpendicular to the central axis?

While still in the chair position, arbitrarily assign the C in the "foot-rest" position as C #1 and the C in the "head-rest" position as C #4.
How do axial bonds alternate as you proceed from C1-C6? *be specific as to which ones are up or down

How do equatorial bonds alternate as you proceed from C1 to C6? (which ones are "up" or "down")

Using the below diagram (and your model, observing from a "side" view: see Fig 11-8b) ***label the carbons*** (C1→C6). ***Draw the C-H bonds.*** *Use a PENCIL & protractor (or ruler) to make your lines as close to scale as possible. ***Circle the axial bonds and put squares around equatorial.***

Change your model to the boat position (rotate/flip C1 upward). *Refer to diagram on previous page of this handout.*
Do the positions of the H atoms change in the boat position? __________
Label the H's below *(draw to scale with ruler or protractor)*



Note the positions of the "upper" H atoms on C1 and C4 in the boat position.
Are the "upper" H's on C1 and C4 closer or further apart in the boat (compared to the chair)?

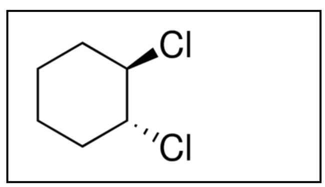
Which confirmation appears more stable (boat or chair)? <u>Justify your response (or no credit).</u>

What is the relationship between the chair and the boat form of cyclohexane? *(circle answer)*
A. structural (constitutional) isomers *B. different conformations of the same molecule*

5. **Cis-trans (stereo)isomerism in Cycloalkanes:**
A. Using the cyclohexane <u>chair</u> model, remove the axial H atom from the same C-1 atom (that was "assigned" before) and replace it with chlorine (or any halogen). Do the same with the axial H atom from C-2. ***Draw the molecule below***. Use straight lines and approximate angles as closely as possible.

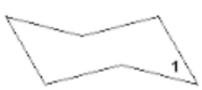
This is one example of the trans geometric stereoisomer. IUPAC name: trans-1, 2-dichlorocyclohexane

This is likely how you'll see it on a test:

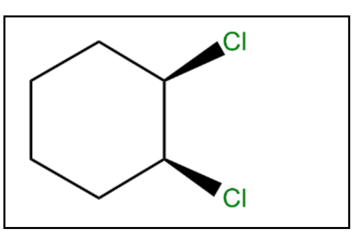


The bold wedge line means the C2 is coming toward you (when viewing from above) and the dashed line means C1 is going away from you. The molecule would also be trans if the chlorines were placed on the equatorial H's from both C1 and C2 (C1 points up and C2 points down).

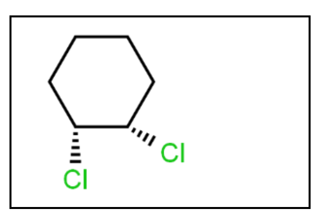
So…how do you get cis using these same two carbons? If the chlorine had been placed in the equatorial position for C1 (it points "up") and the (upward) axial position for C2, that's one way to get the cis conformation. Another would be to put a Chlorine on the C1 axial bond (going downward) and the equatorial C2 (it points "down). Draw either of the cis positions below: (straight lines,approximate angles)



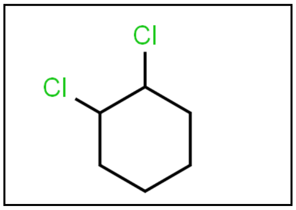
On your test, you will likely see the cis position drawn this way:



Or this way:



If it’s drawn this way, don’t worry about the cis or trans designation in your answer:



Why is there is no cis-trans designation on “straight chain” alkanes?

FYI: Substituents are more stable in the equatorial position than the axial position in the cyclic formation.
Speculate as to WHY that is the case:

Part 3 of the lab will be done in class tomorrow.

Isomers Lab- PART 3: **Name _________________________ # ______**

<u>Enantiomers</u>- <u>an Introduction</u>

Refer to the handout regarding types of isomers. Thus far, this lab has addressed both constitutional isomers and geometric stereoisomers.

In your own words, distinguish between the two.

We will briefly introduce a 2nd type of stereoisomer called an **<u>enantiomer</u>**. This will be covered in more detail in a later unit. Before the definition is given, let's see if you can come up with your own definition after following the below procedure:

1. **Build 2 models of chlorofluoromethane.**
   A. For the first model, position the chlorine so it is coming toward you, the fluorine going away from you and each of the H's are directly lying in the plane of an imaginary piece of paper (one H is up and the other to the right). *<u>Do not deconstruct the first model</u>*.
   B. For the second model, have the fluorine coming toward you, the chlorine away from you and each of the H's directly in the plane (one H is up and the other to the left). ***Place both of the models side by side and sketch them below in a 3-D manner***. Use a wedge for atom(s) coming toward you and a dashed line for atom(s) going away from you. Simply draw "regular" lines for any atoms that are directly in the plane.

   Model 1: Model 2:

2. ***Are the 2 molecules superimposable (meaning, can you place one on top of the other so that they are <u>identical</u>)?*** Try turning and inverting the structures several times before giving your final answer (but do NOT remove one atom and switch positions with another one!).

3. Imagine placing a mirror between the 2 models. ***Are the two molecules mirror images of each other?*** _________. ***Can you turn either of them around, in any either direction, to become mirror images?***

4. Return the 2 models to their **<u>original positions</u>** that you drew for #1
   A. Model # 1 has Cl forward and F back, with both H's in the plane (one H is up and the other is to the right).
   B. Model # 2 has F forward and Cl back, with both H's in the plane (one H is up and the other is to the left).
   C. For Model #1 (Cl is forward), <u>remove the **UPPER** H</u> on model #1 and replace it with another halogen from your kit, such as bromine.
   D. For Model #2 (F is forward), <u>remove the **LEFT** H</u> on model #2 and replace it with the same kind of halogen (SAME COLOR) that was used for #1. If there are no more halogens (with only

one hole) in your kit, find any other atoms of the **<u>same color</u>** and use them as the replacements…just pretend they each have only one hole). Presuming (or pretending) the new atom is bromine, you should now have 2 molecules of bromochlorofluoromethane. **BUT…are they the same (meaning, identical)? Hmm…let's see.**

E. ***Are the 2 molecules superimposable (meaning, can you place one on top of the other so that they are <u>identical</u>)?*** Try turning and inverting the structures several times before giving your final answer (but do NOT remove one atom and switch positions with another one!).

F. ***Are the two molecules mirror images of each other?*** _________. ***Can you turn either of them around, in any either direction, to become mirror images?***

G. ***If the answer to F is yes, draw them below.***

Model 1: Model 2:

H. Congratulations! You have discovered 2 enantiomers.
Based on what you have observed, <u>define enantiomer</u>:

I. Think back on chlorofluoromethane (#1 from the last page). ***How many DIFFERENT kinds of atoms did each carbon have bonded to it?***

J. ***How many different kinds of atoms did C have bonded to it in bromochlorofluoromethane?***

K. The C in the latter model is called a <u>chiral carbon</u>. ***Based on what you've learned, define it.***

L. Check your book & see if you are correct (no penalty if you aren't)***. Book definition?***

<u>Part 4</u>: Using your book (and online resources), answer the following questions on Alkanes (yes, this is on your test!):

1. ***What is petroleum?***

2. ***How is petroleum fractioned and what main fractions is it separated into?***

3. ***Which burns better, straight chain alkanes or branched alkanes?***

4. ***Explain: Octane rating***

5***. Explain: Catalytic cracking***