

## EXPERIMENT 5

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

#### Relevant Textbook Reading

Smith, chap 12.1-12.5, 13.1-13.3, 14.9b

#### 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 isomers.** 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 structural drawings represent the same or different compounds is not always straightforward. It would be much easier if we could actually see the 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 **superimposable** 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.

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PRE-LABORATORY QUESTIONS

Names \_\_\_\_\_ Section \_\_\_\_\_ Date \_\_\_\_\_

1. Draw structural formulas of (a) *n*-hexane (b) 1-hexene (c) cyclohexane (d) cyclohexene.

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

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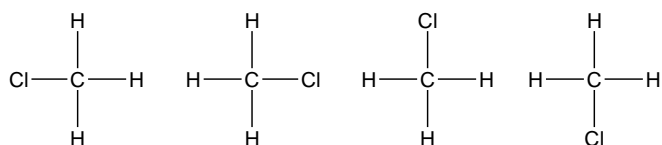
Name \_\_\_\_\_ Section \_\_\_\_\_ Date \_\_\_\_\_

**Constitutional Isomerism**

**Positional Isomerism of Haloalkanes.** The models you will prepare in this section require four different items from the kit: tetrahedral carbons, hydrogens, chlorines, and sticks for single bonds.

A. **Methanes.**

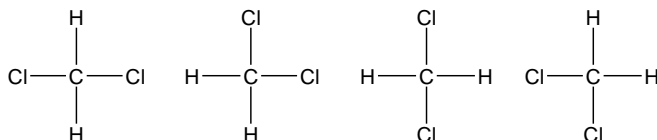
Make a model for each of the following structures:



Are all four of the above superimposable on each other? \_\_\_\_\_

Do the four formulas represent different molecules? \_\_\_\_\_

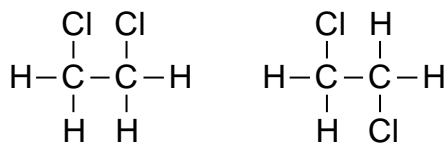
Now make a model for each of the following structural formulas:



Are all four of the models superimposable on each other? \_\_\_\_\_

Do the four formulas represent different molecules? \_\_\_\_\_

Chloroform is  $\text{CHCl}_3$ . How many different molecules are possible for  $\text{CHCl}_3$ ? \_\_\_\_\_

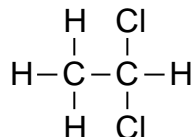
B. **Ethanes.** Prepare models of each of the molecules shown below..

Are the two models superimposable? Remember that rotation of the C-C bond easily occurs. \_\_\_\_\_

Are the two molecules isomers or the same compound? \_\_\_\_\_

What is the IUPAC name of this compound? \_\_\_\_\_

Now rearrange one of the models to form the molecule shown below.



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 ( $\text{C}_2\text{H}_4\text{Cl}_2$ ). 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 fill out the following table illustrating the different physical properties of these two compounds.

Compound Name	literature boiling point ( $^{\circ}\text{C}$ )	literature melting point ( $^{\circ}\text{C}$ )

Reference used \_\_\_\_\_

- C. **Propanes.** Prepare a model of propane,  $\text{C}_3\text{H}_8$ . Can the three carbons and eight hydrogens be arranged to form more than one different molecular structure that are not merely different conformations of the same compound?

Now replace any one hydrogen attached to an end carbon on the molecule with a chlorine atom. Draw the structural formula for the molecule in the space below, and label it with its proper name.

Prepare another propane molecule and then replace any one hydrogen attached to the middle carbon with a chlorine atom. Draw its structural formula, and label it with its proper name.

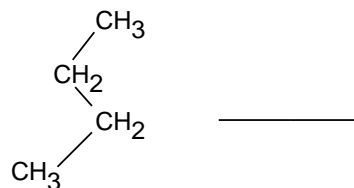
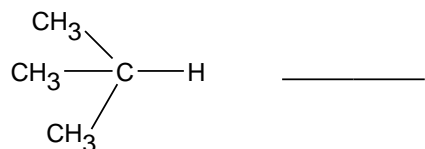
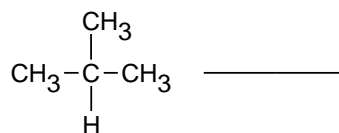
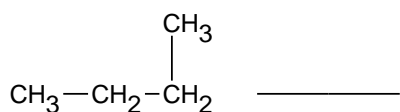
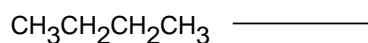
Are the two chloropropane molecules that you have just prepared superimposable? \_\_\_\_\_

Are they isomers? \_\_\_\_\_ If so, what type of isomerism do they exhibit? \_\_\_\_\_

- D. **Butanes.** Replace the chlorine atoms in your two chloropropane molecules with methyl ( $\text{CH}_3$ ) 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 contains an unbranched carbon chain while the other has a branch 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.



Give structures for *n*-pentane, and its two isomers. Note that one of the isomers contains a quaternary ( $4^\circ$ ) carbon atom. Name all three isomers using IUPAC naming rules.

**Cis-Trans Isomerism of Alkenes**

A. **Ethene.** Prepare two models of ethene, C<sub>2</sub>H<sub>4</sub>.

Can you rotate the molecule around the double bond? \_\_\_\_\_

B. **Propene.** Now substitute a methyl group for one of the hydrogen atoms in each of the ethene models to form a model of propene.

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 approximately? \_\_\_\_\_

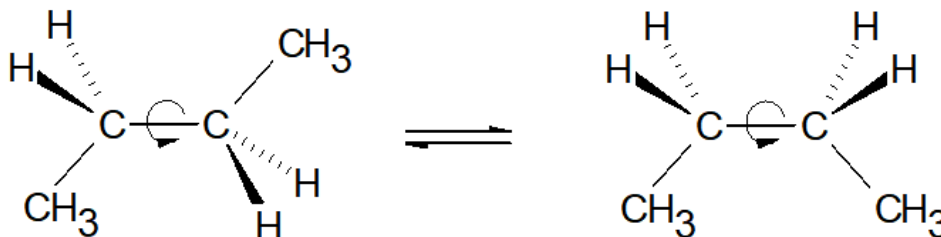
Give a structure for propene that realistically shows the C-C-C bond angle.

C. **Butenes.** There are four butene isomers, C<sub>4</sub>H<sub>8</sub>. You can come up with a model of each by in turn replacing different hydrogens on propene with a methyl group.

Prepare the four isomers of butene, give their structures (show C-C-C bond angles realistically please), and name them by IUPAC rules.

Structure	name
1.	_____
2.	_____
3.	_____
4.	_____

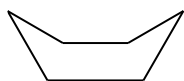
Notice that there are two isomers that have a double bond between the second and third carbon atoms of a chain. The compound with both methyl groups on the same side of the double bond is *cis*-2-butene (*cis* = on this side), and the one with the methyl groups on opposite sides of the double bond is *trans*-2-butene (*trans* = across). These are different compounds due to the fact that **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 not isomers** but are the **same molecule in different conformations** due to the fact that **rotation can occur around carbon-carbon single bonds**.)



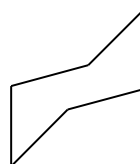
### Cycloalkanes

- (A) **Cyclohexane**. Make a ring of six carbon atoms using single bonds. Fill in the remaining positions with hydrogen. This molecule is cyclohexane.

Cyclohexane can exist in the two non-planar forms shown below.



boat form



chair form

Change your model back and forth between the chair and boat forms. This process occurs very rapidly at room temperature.

What is the relationship between the chair and the boat form of cyclohexane?

- A. stereoisomers B. structural isomers C. different conformations of the same molecule

The chair conformation is much more stable than the boat. Thus, cyclohexane mainly exists in the chair conformation. Answer the following questions by looking at your model of the chair conformation.

What are the bond angles around the carbon atoms? (Hint: The tetrahedral atom pieces that we have been using to represent carbon atoms in this lab have tetrahedral bond angles between the holes. Therefore, if the bonds are not forced to bend when preparing the molecular model, then the bond angles must be tetrahedral 109.5°.)

What is the ideal bond angle for these carbon atoms as predicted by VSEPR theory? \_\_\_\_\_

Is cyclohexane a stable molecule? Explain





- (B) **Cyclopropane**. 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-C bond angles in cyclopropane? \_\_\_\_\_

What is the ideal bond angle for these carbon atoms as predicted by VSEPR theory? \_\_\_\_\_

How stable is cyclopropane as compared to cyclohexane? Explain