Chem 210, Winona State University, Fall 2022

EXPERIMENT 6

Stereoisomerism: Molecular Models and Specific Rotation Measurements

Textbook Reading: Chapter 15

Materials Needed

molecular model kit, polarimeter
(+) and (-) carvone, α-phellandrene, 2-octanol, 4-hydroxy-3-methoxybenzaldehyde

Definitions

A carbon atom that has four different groups bonded to it is called a ***chiral carbon or chirality center****. If an object can be visually divided into halves that are mirror images of each other then the object possesses a* ***plane of symmetry.*** *(Biologists describe such objects as having "bilateral symmetry" see* http://www.shelterpub.com/_symmetry_online/sym1_mirror_symmetry.html *for a nice description.)*
Chiral*. Chiral objects possess a "handedness". In other words, they exist as two different mirror-image forms, a "right-handed" and a "left-handed" form. Any object that is not identical to its mirror image is chiral.*

Achiral. *Achiral objects do not possess a "handedness". They do not exist as two different mirror-image forms. Any object that is identical to its mirror image is achiral.*

Superimposable. *This is the criterion we use to decide if molecules/models are identical to each other. If by turning a model around in space and/or rotating single bonds you can make it into a form that will superimpose atom for atom on a second model then the two models are identical.* ***Superimposable molecules/models are identical.***

Stereoisomers. *Stereoisomers are isomers that have all of the atoms bonded to each other in the same manner (i.e., the same connectivity). The only difference is the 3-D arrangement of the atoms. Examples of stereoisomers are cis/trans isomers, enantiomers, and diastereomers.*

Enantiomers. *The two mirror-image forms of a chiral molecule are called* ***enantiomers****. Enantiomers are isomers that are mirror images of each other. Please note, in order to be isomers the structures must be non-identical. Hence, enantiomers are often defined as non-superimposable mirror images.*

Diastereomers *are stereoisomers that are* ***not*** *mirror images of each other.*

A ***polarimeter*** *is an instrument that for measuring the degree of rotation (α) of plane polarized light.*

Specific Rotation ([α]) *is the degree of rotation of plane-polarized light by a compound (α)* ***per*** *concentration (c) of solution (in g/mL)* ***per*** *length (l) of polarimeter tube:* $[\alpha] = \alpha / (c \times l)$

Part 1 - Molecular Models of Chiral Compounds

Chiral Carbons and Planes of Symmetry.

Make a model in which a tetrahedral carbon atom has four different color balls bonded to it. For purposes of consistency, please use orange, green, red, and white as the four colors.

1. Does the model possess a plane of symmetry?

This model can be used to represent any molecule that contains one chiral carbon. As an example, consider 3-methylhexane.

2. Show the structure of 3-methylhexane and use an asterisk to label the chiral carbon.
3. List the four different groups attached to the chiral carbon in 3-methylhexane.

Note that the model with four different color balls can be used to represent 3-methylhexane by simply stipulating that each ball represents one of the four groups you listed in #3.

4. Does 3-methylhexane possess a plane of symmetry?
5. For further practice in finding chiral carbons, draw structures of each of the following and mark all chiral carbons present with an asterisk: 1-chlorobutane, 2-chlorobutane, 1,2-dichlorobutane, 1,3-dichlorobutane, 1,4-dichlorobutane, and 2,3-dichlorobutane.

Replace the red ball on your model with a second white ball so that now you have a model of a tetrahedral carbon atom with two identical groups attached.

6. Does the model possess a plane of symmetry?

Part 2 - Chirality and Enantiomers

As you have just seen, the presence of one chiral carbon in a molecule means it cannot have a plane of symmetry. Objects that lack a plane of symmetry are usually ***chiral****. (The only exceptions are when they possess other symmetry elements such as a center or axis of symmetry.)* ***This means that they possess a "handedness" and can exist as two different forms, a "right-handed" and a "left-handed" form.***

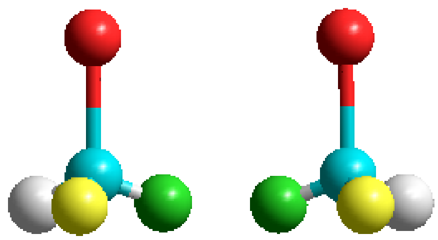
7. Which of the following objects are chiral: a baseball hat, a baseball glove, a baseball bat, a baseball, a baseball pitcher, a baseball diamond? (Ignore the presence of logos or other writing on these objects)
8. Which of the following molecules are chiral: 1-chlorohexane, 2-chlorohexane, 3-chlorohexane, 1-chloropentane, 2-chloropentane, 3-chloropentane?

Go back to your original model (4 different colors) and make a second identical model of it. Make sure the two models are identical by trying to superimpose them; all of the atoms on one should superimpose on atoms of the same color in the other. *Superimposability is a foolproof way to test whether two molecules are identical or not.* ***Superimposable molecules are identical to each other.***

Now switch any two balls on one of the models.

9. Are the models still superimposable?
10. Are they identical?
11. What is the word for non-identical structures that have the same molecular formula?

Place the two models side-by-side on the desktop so that they both have the white ball pointing up. Now rotate them (keeping the white ball up) so that the red ball of each is pointing at the other model. (like in the picture below).



*You should now be able to observe that the models are **mirror images** of each other. At the same time, they are clearly not identical. Hence, the two models represent mirror-image isomers of each other. Mirror-image isomers are called **enantiomers**.*

(When checking for whether models or structures have a mirror image relationship, one is allowed to rotate them around in space, just like when testing for whether they are identical through superimposability. In other words, models are mirror images if they are "mirror-imageable".)

*To resummarize all of your previous work, **all molecules that possess one chiral carbon and, therefore, lack a plane of symmetry are chiral and exist as a pair of enantiomers.***

Again, switch any two balls on one of the models.

12. Are the models still mirror images of each other?
13. Does either possess a plane of symmetry?
14. Are the models superimposable?
15. Do the models represent identical or different structures?
16. Do the models represent enantiomers? Why or why not?

Note that switching any two groups on a chiral carbon creates the enantiomer of the molecule you started with.

Part 3 - Molecules that are not Chiral

Now replace the red ball on each of the models with a second white ball so that each now could be representing a CH_2 group with two different things attached to it.

17. Are the models mirror images of each other?

18. Does either possess a plane of symmetry?
19. Are the models superimposable?
20. Do the models represent identical or different structures?
21. Do the models represent enantiomers? Why or why not?

Now switch any two balls on one of the models.

22. Does that change anything in terms of the answers to questions #17-21?
23. Objects that possess a plane of symmetry are never chiral. Explain why.

When a tetrahedral atom has two identical groups attached there will always be a plane of symmetry cutting between the two identical groups. (The only exception would be if one of the two non-identical groups contained a chiral carbon or was in some other way chiral.) Molecules represented by the models used in this part of the lab are, therefore, not capable of existing as enantiomers and are, thus, not chiral. Such molecules have mirror images that are identical to themselves.

Part 4 - Molecules with Two Chirality Centers

Part 4a - Two Chirality Centers with Same 4 Groups

Remake the first model of the lab (4 different colors around a central carbon atom) and again make a second identical model of it. Make sure the two models are identical by superimposing them. Now remove the red ball from each and connect the two carbons to each other. How many chirality centers does this molecule possess?

24. Does the molecule represented by the model possess a plane of symmetry in any of its conformations?

Construct a new model that is the mirror image of the one previously constructed.

25. Are the two models identical or different?
26. What term should be used to describe the relationship between the two models?
27. Are these molecules chiral or achiral?

Take one of the previous models and interchange any two groups on one of the carbons. Do the same with the other model. Notice that both models now have a conformation that possesses a plane of symmetry.

28. Draw this conformation (use a wedge/dash formula) and indicate the location of the mirror plane.
29. Are the two models identical or different?
30. Are the models mirror images of each other?
31. Do the models represent stereoisomers of each other?
32. Do the models represent enantiomers of each other?
33. Is this molecule chiral or achiral?

The two models just examined represent an example of a meso compound. ***A meso compound is a compound that contains two (or more) chirality centers but is not chiral due to the chirality centers being mirror images of each other.*** *Thus, all meso compounds possess a plane of symmetry and because of this are not chiral. Note well that a meso compound is only possible if the two chirality centers have the same four groups attached.*

34. Which of the following alkanes can exist as a meso compound? (Do not make models, just draw out structures, mark chirality centers with asterisks and use the definition of meso from the previous page.)
    (a) 2,3-dimethylbutane (b) 3,4-dimethylhexane (c) 2,3-dimethylpentane

The four models just looked at prove that a compound with two chirality centers, each with the same groups attached, can exist as three stereoisomers; a pair of enantiomers and a meso compound.

Think about what the relationship is between one of the enantiomers (one of the first two models in this part) and the *meso* form.

35. Are they enantiomers of each other?
36. Are they identical to each other?
37. What is the relationship? (See definitions.)

Part 4b - Two Chirality Centers with Different Groups

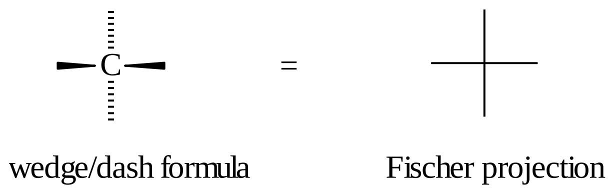
Now replace one of the balls on one of the models with a different color ball. Replace a same color ball on the other model so that you end up with mirror-image structures. Are the two models identical or enantiomers?

38. How many stereoisomers exist for a compound such as this with two chirality centers that do not have the same groups attached? Explain and check your answer with the instructor.

Part 5 - Representing Molecules with Chirality Centers

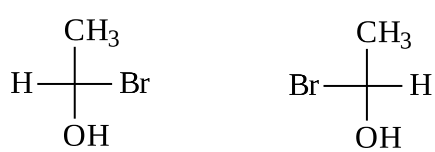
The great German chemist, Emil Fischer, often worked with compounds with multiple chiral carbons. In order to make representing these structures on paper easier, he devised the structural convention known as a Fischer projection.

Go back to a simple model with a central carbon atom and four different colors attached. Hold the model do that the bonds to two of the attached balls are parallel to the floor and pointing straight at you. The other two bonds should be pointing away from you and be perpendicular to the floor. Verify that the molecule in this orientation is represented by wedge/dash representation shown at left below.

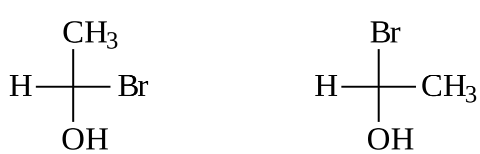


A Fischer projection (or "cross formula") uses a simple cross to represent this orientation of a chirality center. Pay special attention that a molecule drawn with a simple cross as in a Fischer projection always indicates that the horizontal groups are wedged towards you and the vertical groups are dashed away from you.

Make models of each pair of molecules before answering the corresponding question. Hint: Notice that the molecule on the left is drawn exactly the same for all of these so once you have made a model of it you can label it as “Left” and reuse it for each question in turn.



39. Are the structures above enantiomers or identical structures?



40. Are the structures above enantiomers or identical structures?

41. Are the structures above enantiomers or identical structures?

42. Are the structures above enantiomers or identical structures?

Note that all of the above examples involve switching two groups on a Fischer projection.

43. When the only difference between two Fischer projections is that two groups have been switched then the relationship between those two structures is what?

Part 6 - Specific Rotation and Fragrance Assessment of some Natural Products

Samples of (+) and (-) carvone, α-phellandrene, 2-octanol, and 4-hydroxy-3-methoxybenzaldehyde, will be available in the lab. Fan your hand over each open bottle and toward your nose just enough to where you can detect an odor. (Don't overdo it, too much of each chemical can be harmful!) Describe the odors on your observations sheet. (Please try very hard to describe the odor adequately! It is insufficient to merely relate the strength of the odor. You need to try to compare it to things that most people have encountered in everyday life and smell similar.)

We will also use a polarimeter to measure the specific rotation of each sample except for the solid, 4-hydroxy-3-methoxybenzaldehyde, which would not show any rotation anyways (why?). Read Chapter 15.7 in the textbook for some background information on specific rotation. More details on the procedures to be used will be provided in the lab.

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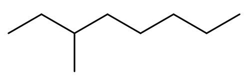
Experiment 6 - Stereoisomerism: Molecular Models and Specific Rotation Measurements

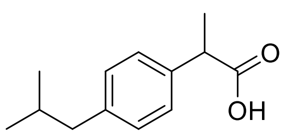
PRE-LABORATORY QUESTIONS

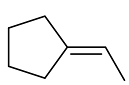
Name ____ Section ____________ Date ____________

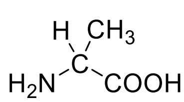
Read Chapter 15.3 in the Smith Textbook before attempting these.

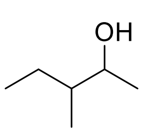
For each molecule, locate the chirality centers that are present and label them with an asterisk. (Note: Not all of these have chirality centers and some have more than one.)











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Experiment 6 - Stereoisomerism: Molecular Models and Specific Rotation Measurements

IN-LAB OBSERVATIONS/DATA

Names ____ Section _______ Date ________

Molecular Models

Answer questions 1-43 on a separate sheet of paper and attach it to your report.

Specific Rotation and Fragrance Assessment of some Natural Products

Note your observations (odor and appearance) on each of the following in the spaces below. Also record your optical rotation data where applicable.

4-hydroxy-3-methoxybenzaldehyde

(+)-carvone

(-)-carvone.

2-octanol

α-phellandrene

Experiment 5 - Stereoisomerism: Molecular Models and Specific Rotation Measurements

REPORT SHEET

Results Table

Compound	Structure	Appearance	Fragrance	Specific Rotation	Chiral? Yes or No
4-hydroxy-3-methoxybenzaldehyde				N/A	
(+)-carvone					
(-)-carvone					
2-octanol					
α-phellandrene					

Show your specific rotation calculations on a separate sheet of paper.

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Questions

1. What is the common name of 4-hydroxy-3-methoxybenzaldehyde? Why is it expected to be optically inactive (i.e., have specific rotation = 0°)?

2. What can you conclude about the 2-octanol we used based on the specific rotation we measured for it?

3. (+) and (-) Carvone have identical physical properties and yet smell different. Why? Explain .