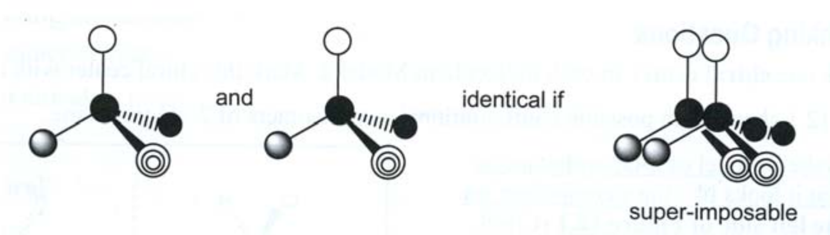
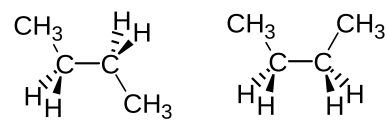
CHM 204—Organic Chemistry
Introduction to Stereochemistry

Recall that two models are <u>identical</u> if they can be superimposed without breaking bonds. Recall that <u>conformations</u> (conformers) are structures that differ only in rotation about a single bond.





conformers

Recognizing Relationships Between Molecules

1. Make two superimposable models of bromochloroiodomethane. Position your models on your desk to prove that they are superimposable.

2. Switch any two atoms on <u>one</u> of your molecules.

3. Which one term below best describes the relationship between the two new models? Explain.

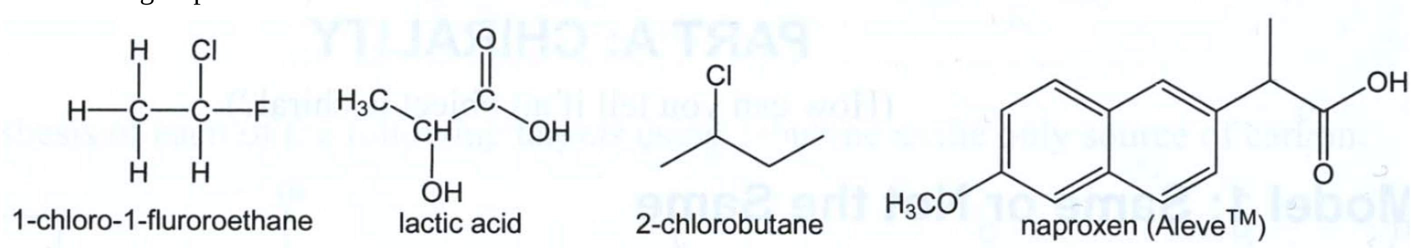
   Identical   Conformers   Stereoisomers   Constitutional isomers

Stereocenters and Chirality

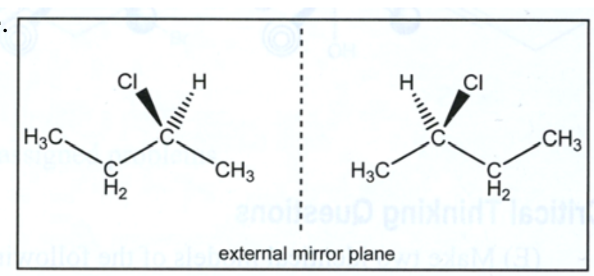
4. If you have a carbon atom attached to four different groups (called a *stereocenter* or a *center of chirality*) there will always be two different 3-D structures in which you can connect the groups. These two arrangements are called *enantiomers*, and they are non-superimposable mirror images of each other.

5. Hold your models from #3 in such a way that you can see they are mirror images of each other.

6. The four molecules below each have one stereocenter. Mark it with a * and circle the four different groups attached to it.



7. The figure here shows the two enantiomers of 2-chlorobutane. Build a model of the left structure.



8. Can you make your model look like the right structure without breaking bonds?

9. Identify the stereocenter in your model, and switch any two groups attached to it. Now does your new structure superimpose with the right or the left structure?

10. Structures that are not identical with their mirror images are called *chiral*. Is your model of 2-chlorobutane chiral?

Mirror (Symmetry) Planes

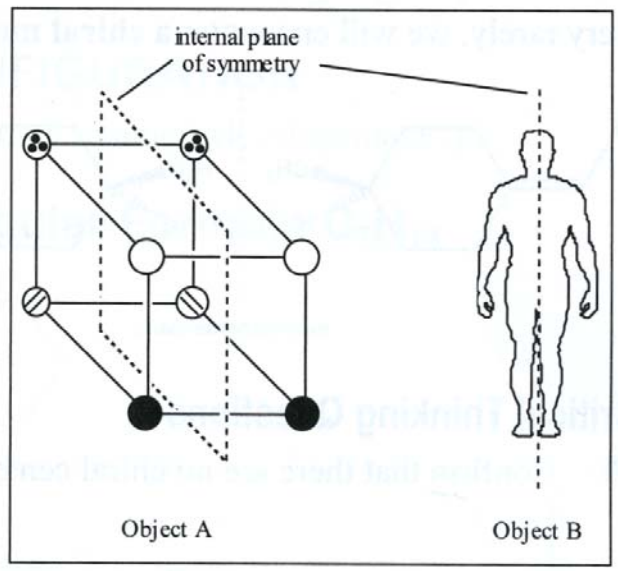
11. It is always true that an object or molecule with an internal mirror plane (plane of symmetry) is not chiral (*achiral*) and is identical to its mirror image. An object with no internal mirror plane is chiral, as described above.

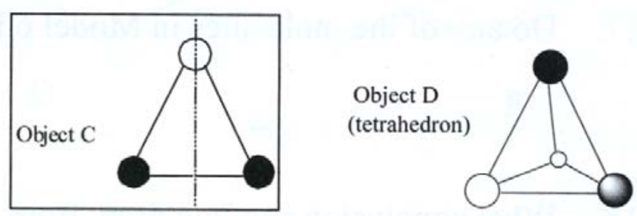
12. Object **C** has an obvious mirror plane, marked with a dotted line, and a not-so-obvious one. Assume the spheres are of equal size.

13. Where is the second mirror plane on **C**?

14. Draw the mirror plane on **D**.

15. Based on the definition of chiral, explain why an sp^3 carbon with four different groups attached *must* be chiral.

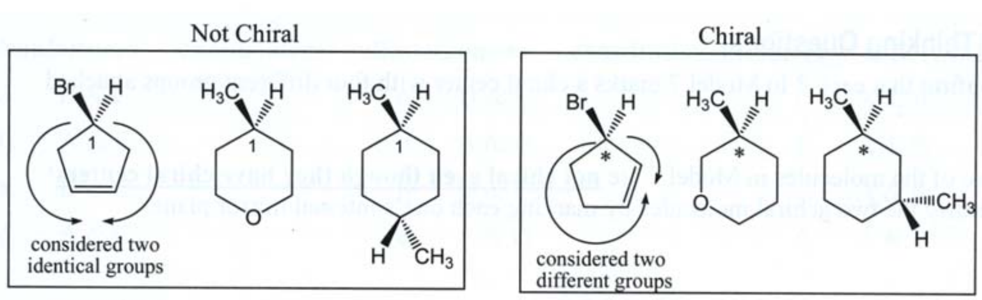




Ring Structures

16. Confirm that each ring structure in the "Not Chiral" figure has a mirror plane by drawing it on the structure.

17. Confirm that each ring structure in the "Chiral" figure does not have a mirror plane.



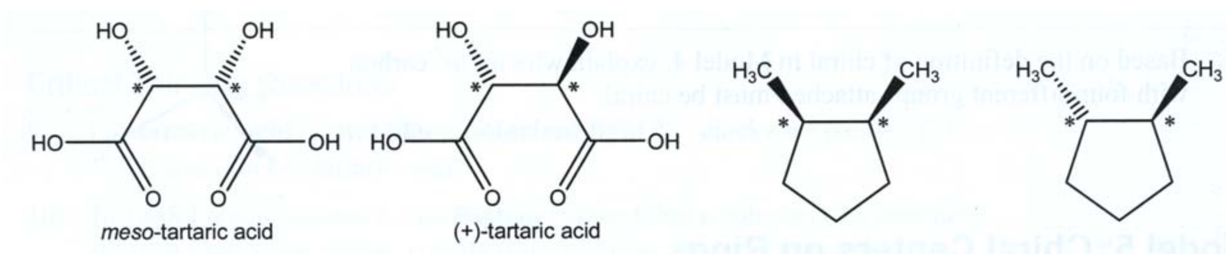
18. Write an explanation for why each carbon labeled “1” in the “Not Chiral” box is considered to have two identical groups attached.

19. Write an explanation for why each carbon labeled * in the “Chiral” box is considered to have four different groups.

20. Which box contains molecules that will superimpose on their mirror images? Explain how you know.

***Meso* Structures and Diastereomers**

21. Confirm that each stereocenter in the figures below marks a chiral center.



22. Two molecules above are achiral even though they have stereocenters. This is because they have planes of symmetry. Mark the planes of symmetry and identify the two structures that are achiral. These structures are called *meso* structures (structures that have stereocenters but also have an internal symmetry plane and are achiral).

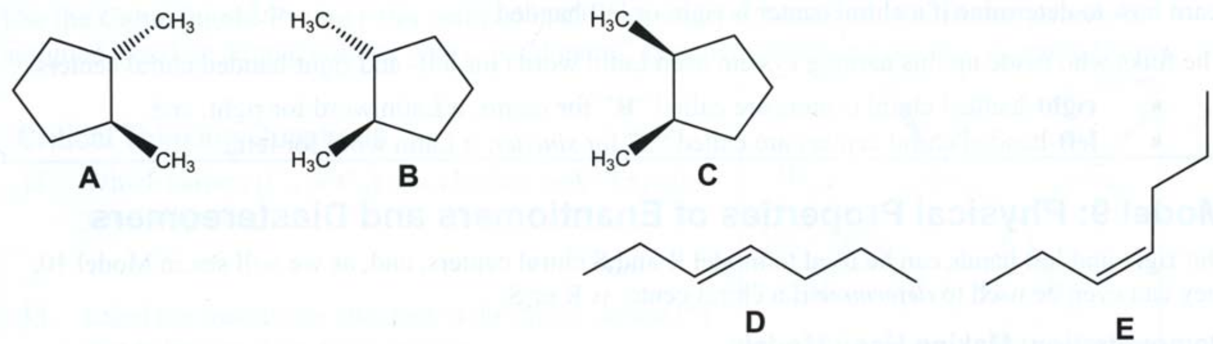
23. Look carefully at the first two structures. Explain why these structures (1) are stereoisomers of each other, but (2) are NOT mirror images.

24. Structures that are stereoisomers but not mirror images of each other are called *diastereomers*. Are the last pair of structures above diastereomers? Why or why not?

25. Complete the structures below (on C2 and C3) so that they are diastereomers of 2,3-dibromopentane.

Summary of Relationships Between Molecules

26. Label structures **A**-**E** with all of the following terms that apply: *cis*, *trans*, *meso*.



27. Are models **A** and **B** superimposable? (Make models if necessary.) Which of the following terms describes their relationship?

identical	conformers	enantiomers
diastereomers	constitutional isomers	unrelated

28. Which of the terms in #27 describes the relationship between the following pairs of structures?

a. **B** and **C**
b. **A** and **C**
c. **D** and **E**
d. **A** and **D**
e. **A** and **E**

Stereocenters: Right- and Left-Handedness

29. Previously we discussed priority rules with *E* and *Z* configurations. Priority is given based on atomic number of the atom directly attached to the double bond. When atoms are identical, you go out to the next set of atoms until a difference is found. Look at the example below.

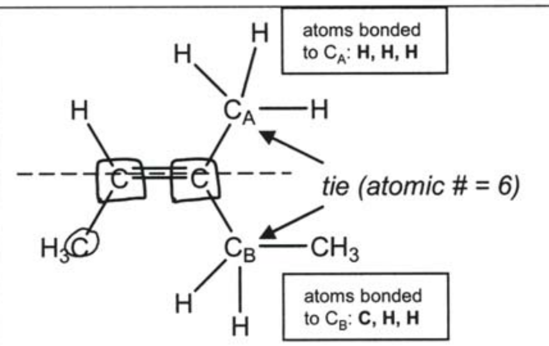
In the structure at right, carbons C_A and C_B are tied.

To determine which gets circled, look at the 3 atoms (other than the boxed carbon) that are bonded to each.

Think of these atoms as "cards."

- C_A's "cards" = H H H
- C_B's "cards" = H H **C**

High card wins, so C_B beats C_A, and the molecule is *Z*.

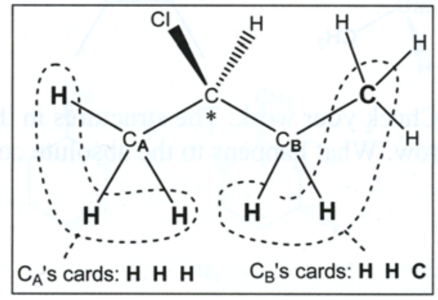


Additional Rules:

isotopes → the heavier atom wins (D beats H)

multiple bonds → double bond (e.g., C=O) counts the same as two single bonds to that atom (O-C-O)

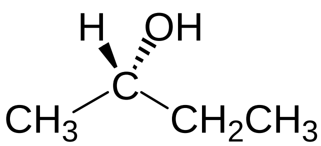
30. For stereocenters, we also use this idea of priority to help distinguish between the two possible 3-D structures that can exist. In this molecule which carbon—**A** or **B**—has the higher priority and why?

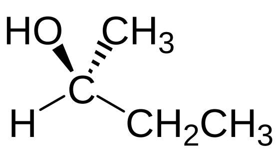


31. Label the priorities of the four groups attached to the stereocenter.

32. Since the lowest priority group is pointing away from you, draw an arrow from priority 1 to 2 to 3. If this arrow points to the right, then the stereocenter configuration is said to be ***R*** (Latin *rectus* = right). If the arrow points to the left, then the stereocenter is said to be ***S*** (Latin *sinister* = left). Confirm that this stereocenter in the molecule has the *R* configuration by drawing the arrow.

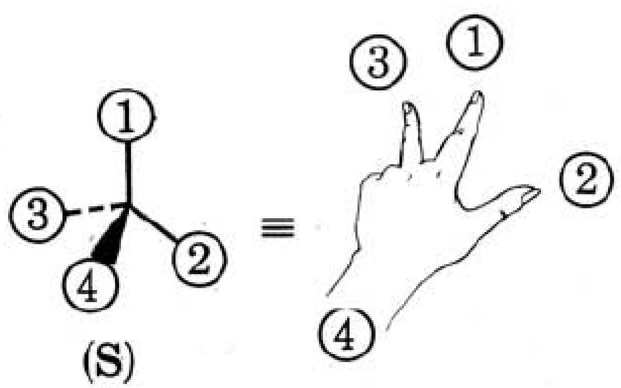
33. If the lowest priority group is NOT pointing away from you, you have to re-draw or mentally turn the molecule so that it does. Label the priorities of each group attached to the stereocenters in the molecules below, and re-draw the molecules so that the lowest priority group points away from you.



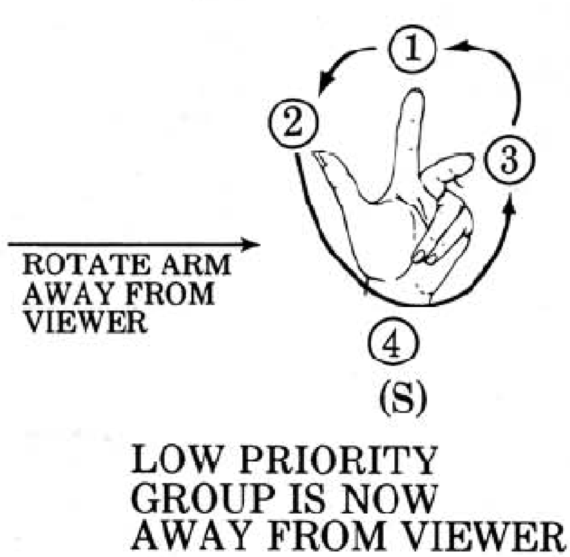


34. Label the stereocenters in the molecules above as *R* or *S*.

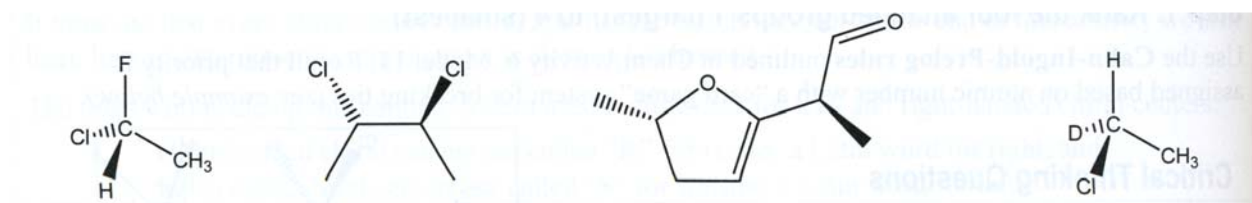
35. There is an easy method using your hand to determine if a structure is *R* or *S*. Let your wrist represent the position of priority group 4, and use your fingers to represent the positions of groups 1, 2, and 3. (If the #4 group is written on the right side of the molecule, it is easiest to use your right hand, and if it is on the left side of the molecule, it is easiest to use your left hand.)



36. Rotate your hand so that your wrist (#4 group) points away from you. Draw the arrow from 1 to 2 to 3, and assign the R or S configuration. For the molecule above, we get

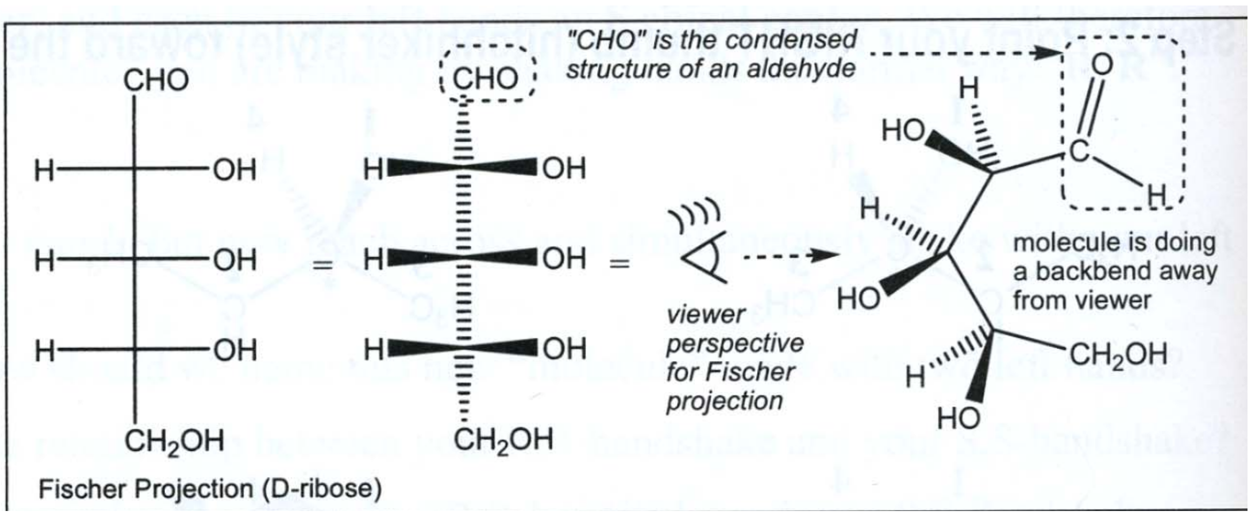


37. Use the hand method to determine the *R* or *S* configuration of each stereocenter below.



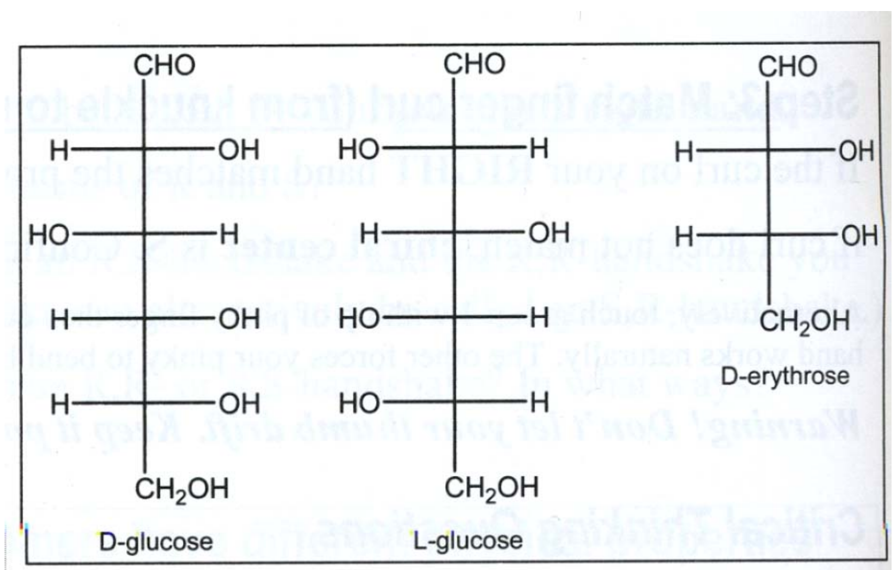
Fischer Projections

38. Fischer projections are a shorthand way of representing 3-D structures. In Fischer projections, horizontal bonds are wedge bonds (coming out towards you) and vertical bonds are dashed bonds (going away). The carbon backbone is written vertically for convenience.



39. Mark each chiral center on the Fischer projection of D-ribose (above) with its configuration (*R* or *S*).

40. Mark each chiral center on the Fischer projections below with *R* or *S*.



41. How many total stereoisomers exist for D-erythrose?

42. How many stereoisomers exist of D-glucose?

Predicting the Number of Existing Stereoisomers

43. The maximum number of stereoisomers that can exist for a molecule is given by the formula $\mathbf{2^n}$ where ***n*** = # stereocenters + # *E*/*Z* pi bonds (remember not all pi bonds have *E*/*Z* possibilities).

44. Do your answers in #41-41 agree with the answers predicted by the formula above? They should!

45. How many total stereoisomers exist for 4-chloro-2-pentene? What are their structures and names?

46. The total number of stereoisomers of 2,2-dibromobutane is three, not four as predicted by the formula. Draw the structures and explain why.

47. The total number of stereoisomers of 1,2-dimethylcyclopentane is three, not four as predicted by the formula. Why?

48. In what special case will the number of stereoisomers be less than $\mathbf{2^n}$?