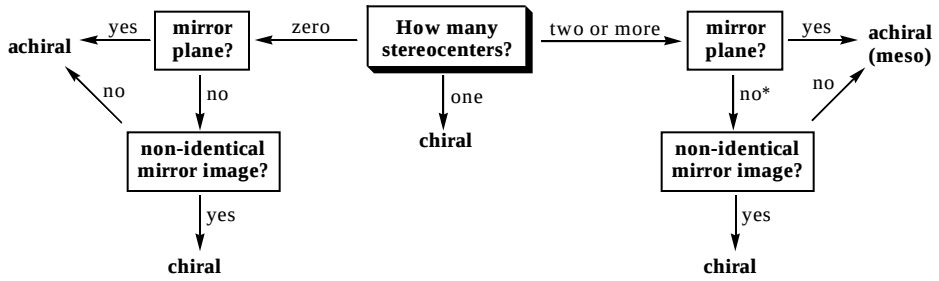
Handout #6, 5.12 Spring 2003, 2/28/03

Stereochemistry



stereochemistry: study of the spatial characteristics of a molecule
stereocenter: atom bonded to four different groups (has R or S configuration)
internal mirror plane: plane that divides molecule in such a way that two halves are identical

chiral (optically active): possessing a non-identical mirror image (an enantiomer)
achiral: superimposable on its mirror image

enantiomers: non-identical mirror images (same physical properties)
diastereomers: stereoisomers that are not enantiomers (different physical properties)
meso compound: achiral molecule that has stereocenters

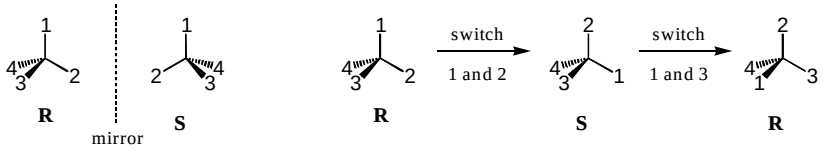
* If you can't find a mirror plane, it doesn't mean that there isn't one. **Compare mirror images!**

Assigning R/S Stereochemistry (Cahn–Ingold–Prelog)

- Every stereocenter can be assigned as **R** or **S**.
- A stereocenter is an atom attached to four **different** groups.

1. Assign each group a priority (1 = highest).
  a) Highest atomic number has priority.
  b) Heavier isotopes have priority (D > H).
  c) In a tie, move along the chain to the first point of difference.
  d) With multiple bonds, break each pi-bond and duplicate the atoms at each end.
2. Put the lowest priority group (4) in back and view along the bond from carbon to group 4.
3. Draw an arrow from 1 to 2 to 3.
  a) Clockwise = R (Your car turns **right**!)
  b) Counterclockwise = S (sinister means **left** in Latin)

Tricks:
1. Taking the mirror image of a stereocenter switches R and S. This means that, if a molecule is chiral, switching the R/S configuration of **every** stereocenter will give you the enantiomer.
2. Exchanging **any two** groups on a stereocenter switches R and S.



Fischer Projections

- Useful for comparing stereoisomers with more than one stereocenter.

The Rules:

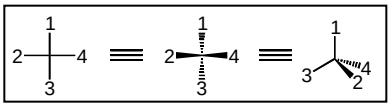
1. At every intersection, the vertical lines are pointed back (away from you) and the horizontal lines are pointed up (toward you).

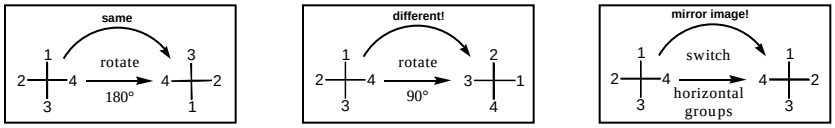
2. Draw the carbon backbone of a molecule as the vertical line with the most highly oxidized carbon on top.

a) You can think of oxidation as how many bonds carbon has to oxygen. So the ranking goes as follows: CO_2H > (CHO or CRO) > CH_2OH > CH_3

3. It is **legal** to rotate Fischer projections by **180° in the plane of the paper**.

4. It is **not legal** to rotate Fischer projections by **90°** or **out of the plane of the paper**.





Tricks:

1. Exchanging the horizontal substituents on a stereocenter switches R and S.

2. To take the mirror image, just exchange the horizontal substituents at **each** intersection. If the molecule is chiral, this will give you the enantiomer.

3. If you can draw a mirror plane through the Fischer projection, then the molecule is achiral.

Using the Lingo

- It is important that you use stereochemical terminology correctly. Here are the proper terms for describing each of the following:

an atom:

- an atom with four **different** groups attached is a stereocenter
- stereocenters are also called chirality centers, asymmetric centers, and stereogenic centers
- absolute configuration of a stereocenter is assigned using R/S nomenclature

a molecule:

- achiral or chiral (optically active)
- achiral molecules that contain stereocenters are called meso compounds
- optically active molecules can be labelled (+/–) or (d/l)

related molecules:

- enantiomers (non-identical mirror images)
- diastereomers (any stereoisomers that are not enantiomers)
- geometric isomers (a specific type of diastereomer)

samples of molecules:

- optically pure (only one enantiomer present in sample)
- racemate or racemic mixture (mixture containing equal amounts of each enantiomer)
- racemic mixtures are not optically active
- mixtures in between optically pure and racemic are described by their optical purity or enantiomeric excess (see section 5-7 in Wade)

Note: It is important not to confuse experimentally derived labels (+/– or d/l) with structurally derived labels (R/S). **They are not related!**