Assigning Stereochemistry using Fischer Projections:

Fischer projections can be used to assign stereochemistry. If the 4th (lowest) priority group is vertical the other three groups will show clockwise (R) or counterclockwise (S) rotation.





Assigning Stereochemistry V Multiple Stereocenters

Relationships between Stereoisomers (EDIM):

Stereoisomers can be compared to other isomers of the same structure and be related by their stereochemistry. Most relationships require comparison between two or more molecules.

- Enantiomers Non-superimposable and exact mirror images. Molecules that are enantiomers are chiral (have at least one stereocenter) and are exact reflections. They are nearly identical in properties but have opposite [α]_D and different properties in chiral environments. All stereocenters are exactly reversed when comparing enantiomers. (Left and right hands)
- Identical (chiral) molecules Superimposable and not mirror images. Molecules that are chiral and identical (have at least one stereocenter) and are identical in all ways. They are exactly the same and have exactly the same properties in all cases. This relationship does not have a fancy name, but it's important to realize when two stereoisomers really are the same thing. All stereocenters are exactly the same when comparing identical chiral molecules. (Two left hands)
- Diastereomers Non-superimposable and not mirror images. Molecules that are diastereomers must have multiple chiral centers and have completely different properties. They will be no more similar than any two constitutional isomers and will have different boiling or melting points, solubility, [α]_D etc. Some stereocenters are the same and some stereocenters are reversed when comparing diastereomers. (Left hand vs. right foot or left hand vs. left foot)
- Meso Superimposable and exact mirror images. The property of being meso is inherent to the molecule and doesn't depend on a comparison. Meso molecules are not chiral! They do have chiral centers but will have an internal mirror plane in at least one rotamer. Meso molecules must have multiple stereocenters and each stereocenter will have a paired center with the same four groups attached in the reverse stereochemistry (R/S pairs). All stereocenters are both the same and reversed (R,S). (Faces are meso, eyes are different from ears or mouths but the whole has a mirror place)



Example 1: Two Stereocenters with Different Substituents

*as pure compounds

If we had a mixture of the above compounds and picked out two random molecules we would get three different possibilities.

A/B and C/D are non-superimposible exact mirror images: ENANTIOMERS

A/C, B/C, A/D, B/D are non-superimposable but are not mirror images: DIASTEREOMERS

A/A, B/B, C/C, D/D are superimposable but not mirror images: IDENTICAL CHIRAL MOLECULES



Example 2: Two Stereocenters with the Same Substituents

If we had a mixture of the above compounds and picked out two random molecules we would get four different possibilities.

E/F are non-superimposible exact mirror images: ENANTIOMERS

E/G, E/G', F/G, F/G' are non-superimposable but are not mirror images: DIASTEREOMERS

E/E, F/F are superimposable but not mirror images: IDENTICAL CHIRAL MOLECULES

G/G', G/G, G'/G' are superimposable and are mirror images, this is a special case where two molecules are exactly the same and have an internal mirror plane and are MESO.

Relative vs. Absolute Stereochemistry

- *Absolute stereochemistry* Absolute stereochemistry is the exact relationship between atoms/chiral centers (the exact *R/S* assignments).
 - A molecule where absolute stereochemistry is assigned is a single isomer and will have an exact $[\alpha]_D$.
 - Alkenes do not have absolute stereochemistry.
 - Chiral molecules can have absolute stereochemistry.
- Relative stereochemistry Relative stereochemistry is the relationship between multiple chiral centers, but does not have exact *R/S* assignments.
 - A molecule where only relative stereochemistry is assigned is a racemic mixture ($[\alpha]_D = 0$).
 - Relative stereochemistry can give *cis/trans, syn/anti, E/Z,* or *erythro/threo* assignments
 - Molecules with only relative stereochemistry assignments will show dashes/wedges.
 - Alkenes have only relative stereochemistry.
 - o Achiral stereoisomers (meso) have only relative stereochemistry