SECTION 8 – STEREOCHEMISTRY – A DETAILED LOOK

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Section 8 = Stereochemistry - A Detailed Look.

- A compound that cannot be superimposed on its mirror image is "chiral".

- A compound that can be superimposed on its mirror image is "achiral".

- Non-superimposable mirror image stereoisomers are "enantiomers".

- A molecule with one stereogenic center is always chiral. 

```
\[ \begin{array}{c}
\text{mirror} \\
\text{H} \\
\text{C} \\
\text{F} \\
\text{Cl} \\
\end{array} \]
```

*ex:*

- Enantiomers → one compound cannot be superimposed on the other. Similar to a person's right hand and left hand.

```
\[ \begin{array}{c}
\text{mirror} \\
\text{H} \\
\text{C} \\
\text{F} \\
\text{Br} \\
\end{array} \]
```

*ex:*

- Achiral; same molecule; carbon does not have 4 different things attached.
- If a molecule contains an internal mirror plane ("plane of symmetry") in any conformation, it's achiral.

**Ex:**

\[
\text{achiral} \quad \text{achiral} \quad \text{plane of symmetry}
\]

**Enantiomers:**

- Have identical physical properties.
- Interact in identical ways with achiral molecules.
- Interact differently with chiral molecules.

\[
\text{Enantiomer 1: COOH} \quad \text{Enantiomer 2: COOH}
\]

- Mirror plane

**Enzyme:**

\[
\text{+ hog kidney (acylase)} \quad \text{No Reaction}
\]

- Chiral molecule

**Enantiomers** rotate the plane of polarized light in opposite directions.

\[
\text{Electric Field} \quad \text{end-view: plane-polarized light}
\]

\[
\text{oscillating E-vector}
\]
ordinary unpolarized light:

- So, how do enantiomers rotate plane-polarized light?

chiral compounds are said to be "optically active". 

if rotation (\(\alpha\)) is clockwise, compound is dextrorotatory (D) or (+)

if rotation (\(\alpha\)) is counterclockwise, compound is levorotatory (L) or (-)

observed rotation (\(\alpha\)):

\[ \alpha = [\alpha]c \lambda \]

where [\(\alpha\)] = specific rotation

\(c\) = concentration (g/ml)

\(\lambda\) = pathlength (1 dm = 10 cm)
- no simple relationship exists between the direction of rotation, (+) or (-), and the absolute configuration. 
  \[ \rightarrow \text{R or S designated compound.} \]

- achiral compounds do not rotate plane of polarized light; so they're "optically inactive".

- mixtures of equal amounts of enantiomers form racemic mixtures (or "racemates")

  \[ \rightarrow \text{optically inactive because one enantiomer's rotation of plane-polarized light cancels out the other enantiomer's opposite rotation.} \]

  \[ \text{ex: } (\pm) 2\text{-bromobutane} = 50\% \text{ (+)2-bromobutane} \quad 50\% \text{ (-)2-bromobutane} \]

---

**Specifying absolute configuration.**

1. Assign priorities (1, 2, 3, 4) to the 4 substituents attached to the C with the highest atomic wt./smallest atomic wt.

2. Orient the structure so the lowest priority substituent (#4) points away from you (dashed line \( \Rightarrow \) "into the pg.

3. If order of priority, 1 \( \rightarrow \) 2 \( \rightarrow \) 3 \( \rightarrow \) repeat, is clockwise, the configuration is \( \text{"R"} \) (rectus = right). If order of priority is counterclockwise, the configuration is \( \text{"L"} \) (sinister = left).

**ex:**

- \( \text{CH}_3 \) \( 3 \)
- \( \text{H} \) \( 4 \)
- \( \text{Br} \) \( 0 \)

\[ \text{1} \rightarrow \text{2} \rightarrow \text{3} = \text{counterclockwise, so left = "S"} \]

\[ (S) - 1\text{-bromo-1-fluoroethane} \]
**note**: Re-orienting carbon's 4 substituents by a cyclic permutation of 3 substituents by holding 1 fixed is possible, but don't switch just 2!!

- gives other enantiomer! (not desired).

**Compounds with Multiple Stereocenters**. denoted by (*)

- a compound with n stereocenters (chiral carbons) has a maximum of $2^n$ different stereoisomers.

**Ex**: $\text{CH}_3\text{CH}_2-\text{CH}-\text{CH}-\text{CH}_3$

- each stereocenter can be R or S; so a max. of 4 stereoisomers.

Note: if -H is not "going back" (dashed) as we'd like, but instead is "coming out" (wedge arrow), do your 1,2,3 to get S or R and switch it!
- Sometimes, compounds having 2 or more stereocenters (chiral carbons) can be achiral!!

- These compounds are called "meso-compounds".

**Example:** Tastaric acid

\[
\text{HO-C}^*\text{H-C}^*\text{H-C}^*\text{OH} \quad \text{OH} \quad \text{OH}
\]

\[
\text{HOOC} \quad \text{COOH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH}
\]

\[
\text{HOOC} \quad \text{COOH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH}
\]

\[
\text{HOOC} \quad \text{COOH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH}
\]

\[
\text{HOOC} \quad \text{COOH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH}
\]

- Enantiomers? No, because there's an internal plane of symmetry.

- These are the same compound (spin one of them 180° horizontally).

- A meso compound is achiral but has stereogenic centers.

- A compound is achiral if it has a plane of symmetry in any one conformation.

- Cyclic compounds ⇒ when determining stereoisomeric relationships, consider rings to be planar.

**Example:** Next page...
ex: trans compound:
\[
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\] \text{mirror enantiomers}
\[
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\]
\} \text{drawn "flat"}

ex: cis compound:
\[
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\]
\} \text{meso compound}
\[
\begin{array}{c}
\text{Cl} \\
\text{Cl}
\end{array}
\]
\} \text{internal line of symmetry} \Rightarrow \text{so achiral}

\Rightarrow \text{the cis compound is diastereomeric to the trans compound.}

\begin{array}{c}
\text{CH}_3 \\
\text{CH}_3
\end{array}
\]
\} \text{plane of symmetry in flat form, so achiral, even though the ring isn't really flat (chair)}

\text{Isomer Types - A Summary.}

1. **Constitutional Isomers** = different connectivities.
   \rightarrow "structural isomers"

2. **Stereoisomers** = same connectivities.
   a) **enantiomers** = non-superimposable mirror image compounds
   b) **diastereomers** = not mirror images; just plain different.
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