Section 8 = Stereochemistry - A Detailed Look.

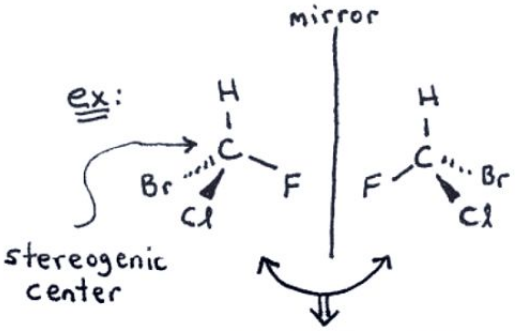
- a compound that <u>cannot be superimposed</u> on its mirror image is "<u>chiral</u>".

- a compound that <u>can be superimposed</u> on its mirror image is "<u>achiral</u>".

- <u>non-superimposable mirror image</u> stereoisomers are "<u>enantiomers</u>".

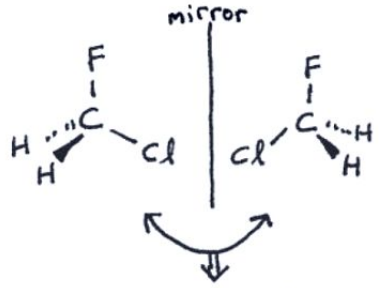
- a molecule with one <u>stereogenic center</u> is always <u>chiral</u>.
  ↳ = a carbon atom with 4 different things attached.

<u>ex</u>:



<u>enantiomers</u> → one compound cannot be superimposed on the other. Similar to a person's right hand and left hand.

<u>ex</u>:

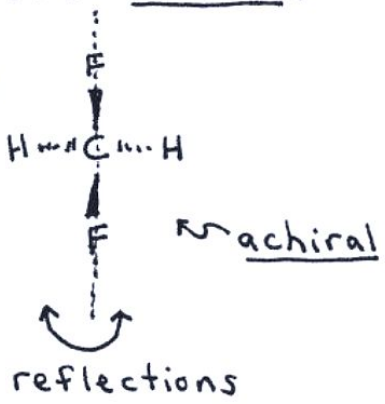


<u>achiral</u>; same molecule; carbon does <u>not</u> have 4 different things attached.

- if a molecule contains an internal mirror

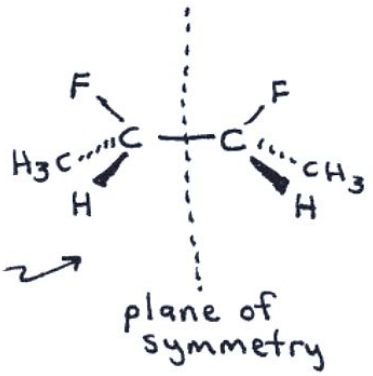
- if a molecule contains an <u>internal mirror plane</u> ("plane of symmetry") in any conformation, it's <u>achiral</u>.

ex:



achiral

ex:

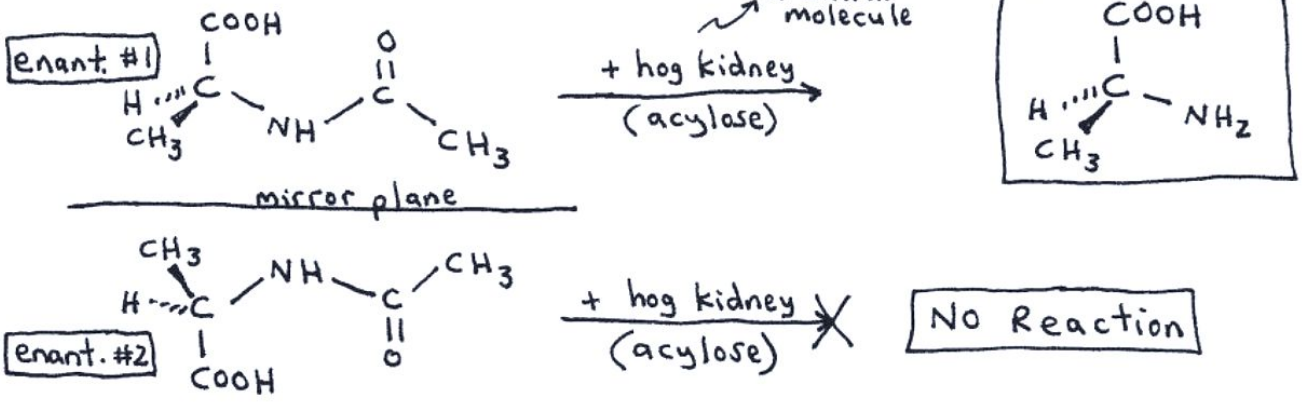


<u>achiral</u>

plane of symmetry

⊛ <u>Enantiomers</u>.

- have identical physical properties.
- interact in <u>identical</u> ways with <u>achiral</u> molecules.
- interact <u>differently</u> with <u>chiral</u> molecules.



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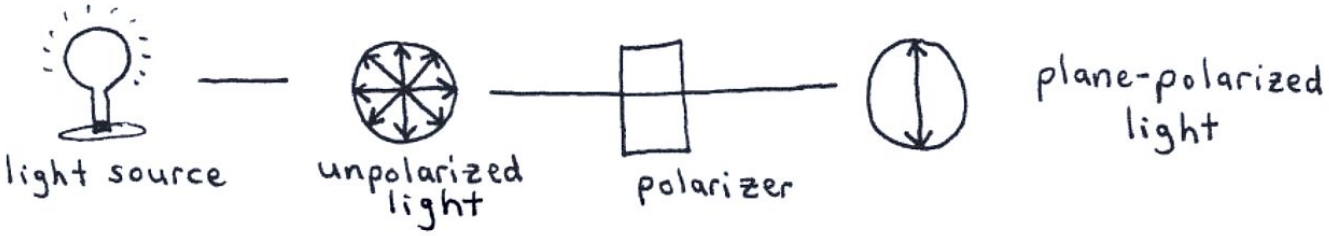
* <u>Enantiomers</u> rotate the <u>plane of polarized light</u> in opposite directions.

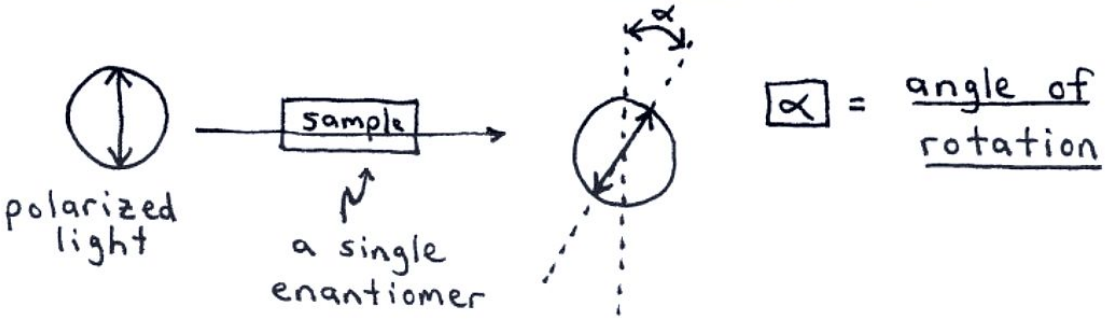
<u>end-view</u>:

plane-polarized light

↳ ordinary unpolarized light:



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



$[\alpha]$ = angle of rotation

⊛ chiral compounds are said to be "optically active".
↳ = rotate plane-polarized light

→ if rotation (α) is clockwise, compound is dextrorotatory (D) or (+)

→ if rotation (α) is counterclockwise, compound is levorotatory (L) or (−)

⊛ observed rotation (α):

$$\alpha = [\alpha] c \ell$$

, where $[\alpha]$ = specific rotation
c = concentration (g/mL)
ℓ = pathlength (1 dm = 10 cm)

- no simple relationship exists between the direction of rotation, (+) or (-), and the absolute configuration.
  ↳ 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")
  - → optically inactive because one enantiomer's rotation of plane-polarized light cancels out the other enantiomer's opposite rotation.
  - → ex: (±) 2-bromobutane = 50% (+)2-bromobutane, 50% (-)2-bromobutane

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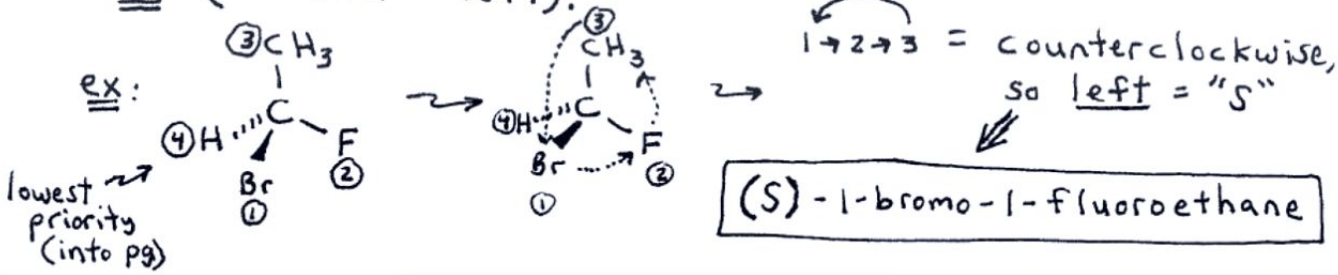
✱ Specifying absolute configuration.

① Assign priorities (1, 2, 3, 4) to the 4 substituents attached to the C. (high atomic wt. → 1; smallest atomic wt. → 4)

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

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

ex:

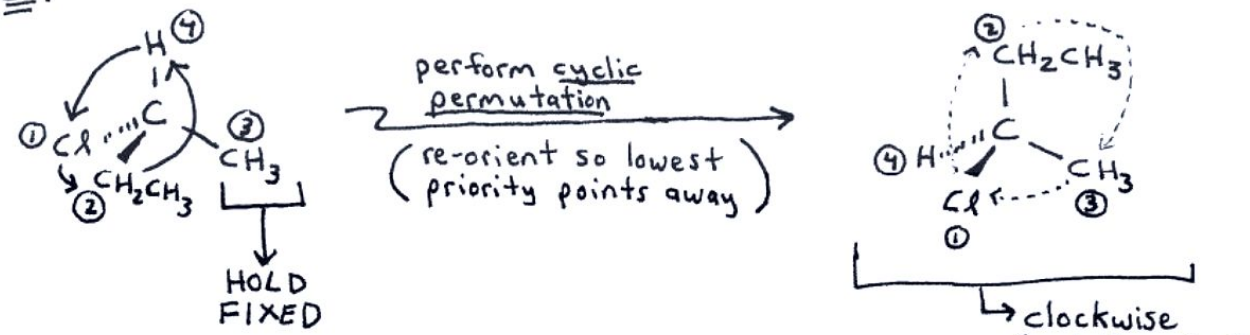


(S) - 1 - bromo - 1 - fluoroethane

** 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).

ex:



(R)-2-chlorobutane

⊛ Compounds with Multiple Stereocenters.

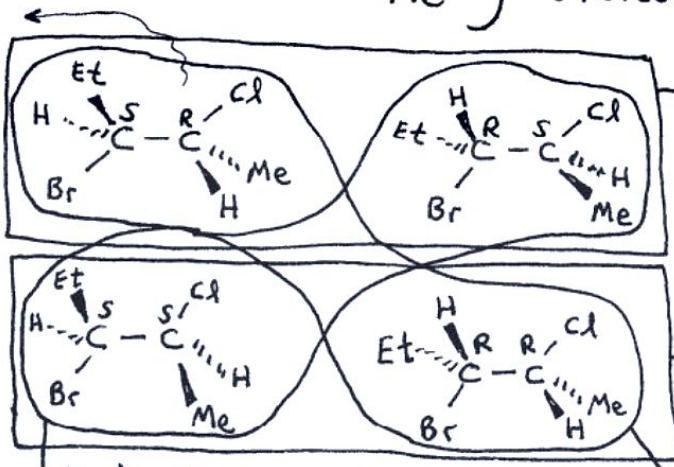
denoted by (*)

↳ a compound with [n] stereocenters (chiral carbons) has a maximum of [2^n] different stereoisomers.

ex: $CH_3CH_2-\overset{*}{C}H(Br)-\overset{*}{C}H(Cl)-CH_3$ (-Et, -Me)

} 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!



enantiomers = (S,R and R,S)

↳ have opposite configurations at every stereocenter.

enantiomers (S,S and R,R)

diastereomers (S,S and R,S)

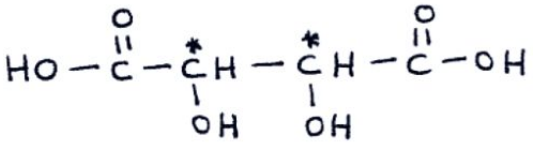
↳ stereoisomers that are not enantiomers.

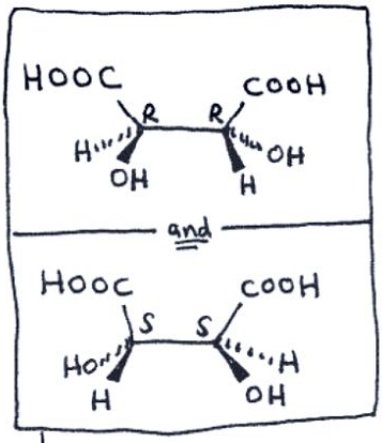
↳ have different chemical and physical properties.

diastereomers = (R,R & S,R)

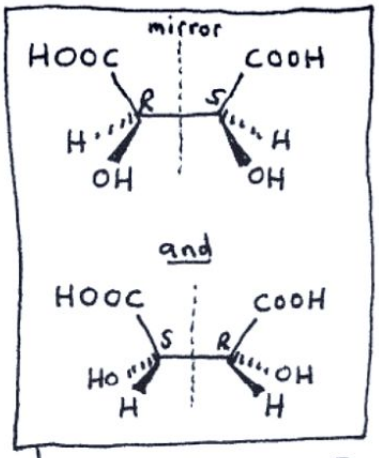
- sometimes, compounds having 2 or more stereocenters (chiral carbons) can be achiral !!
  ↳ these compounds are called "meso-compounds".

ex: tastaric acid ⇒





↳ enantiomers



→ enantiomers? NO, because there's an internal plane of symmetry.

→ these are the same compound (spin one of them 180° horizontally)

⇐ → achiral, meso compound ***

* 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.

ex: next page...

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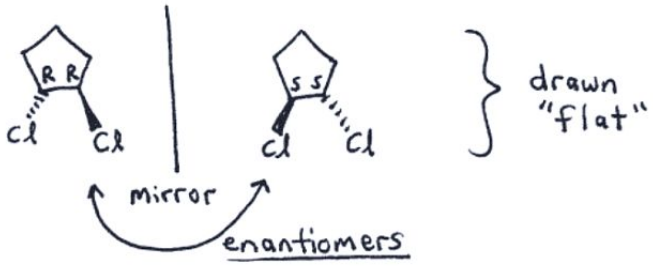
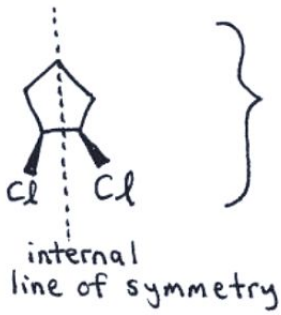
ex: trans compound:

} drawn "flat"

ex: trans compound :



ex: cis compound :

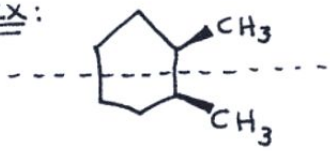


meso compound

⇒ so achiral

→ the cis compound is diastereomeric to the trans compound.

ex:



plane of symmetry in flat form, so achiral, even though the ring isn't really flat (chair)

⊛ Isomer Types - A Summary.

① Constitutional Isomers = different connectivities.
↳ "structural isomers"

② Stereoisomers = same connectivities.

a) enantiomers = non-superimposable mirror image compounds

b) diastereomers = not mirror images; just plain different.