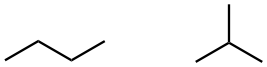
Stereochemistry: The study of properties of matter in 3D.

Constitutional isomers: Different compounds with the same molecular formula. For example, C_4H_{10} has two constitutional isomers:

n-butane *i*-butane



Stereoisomers: Two or more compounds with identical molecular formula and connectivity. However, they differ from each other in the spatial orientation of the groups they are connected to.

Stereogenic Center (or Stereocenter): a (carbon) center, axis or plane that is a focus of stereoisomerism, such that an interchange of two groups attached to this feature (carbon) leads to a stereoisomer.

Chiral Molecules (or objects) have on-superimposable mirror images.

Achiral Molecules have superimposable mirror images.

Chiral Center: A carbon that is bonded to four different groups of atoms (asymmetric center).

Specific Configuration: The arrangement in space of the four different groups about a chiral center.

Enantiomers: Mirror image stereoisomers.

Racemic Mixture (Racemate): An equimolar mixture of enantiomers.

Diastereomers: Non-mirror image stereoisomers.

Meso Compound: Achiral diastereomers of chiral stereoisomers. (Contain chiral centers).

Stereochem I: Stereochemistry at Tetrahedral Centers

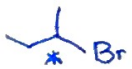
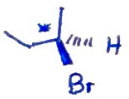
Constitutional isomers differ in connectivity

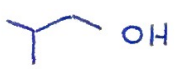
Stereoisomers differ in spatial arrangement

Consider the mirror image of your left hand
→ This image (your right hand) no longer looks like your left hand

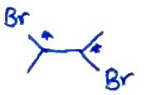
Chiral objects, and chiral molecules, have non-superimposable mirror images

Chirality arises from asymmetric/chiral centers: A carbon that is bonded to 4 different groups of atoms.

Ex:  in 3D: 

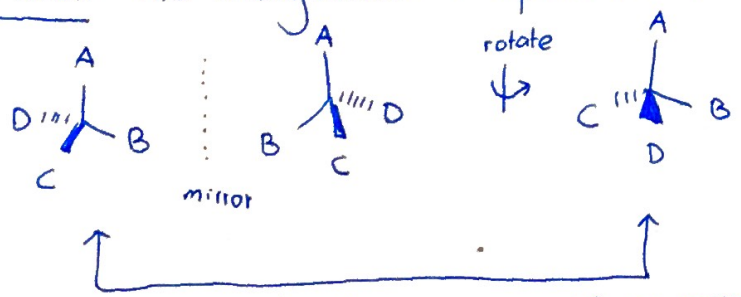
What about: 

no chiral centers
name?



name?

configuration: The arrangement in space of the four different groups about a chiral center



not same! not superimposable on mirror image

★ Enantiomers: mirror-image stereoisomers (the relationship between a pair of hands)

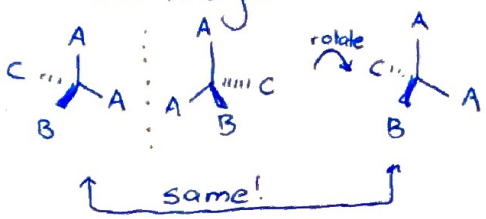
In organic chemistry, enantiomers have important properties, but all physical properties are the same. Except: ① optical properties (i.e. direction of rotation of polarized light)
② reactivity with other chiral molecules

In nature, all amino acids are Left-handed
and all sugars are Right-handed

Molecules are chiral, achiral, or racemic

superimposable on mirror image

↳ equimolar mixture of enantiomers



Specification of configuration at chiral centers: The R/S system

Cahn-Ingold-Prelog sequence rules:

① The atom with the highest atomic number gets priority (1, 2 etc)

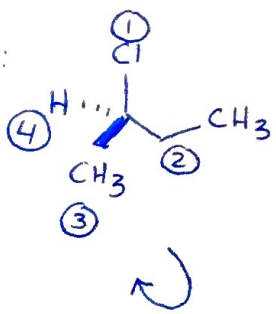
↑ atomic # → ↑ priority label

② If the four atoms attached to the chiral center are not all different, priority is determined at the first point of difference.

If same atomic #, move to difference point

③ If ⥮X, count as two ⊱X

Ex:



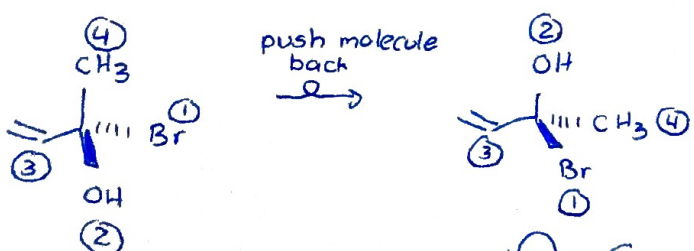
(R)-2-chlorobutane

Having made the assignments place the #4 group away from you and observe the sequence: 1 → 2 → 3

* If 1 → 2 → 3 is clockwise: R (rectus)

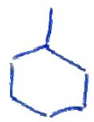
" counterclockwise: S (sinister)

Ex 2:



S configuration

How many chiral centers?



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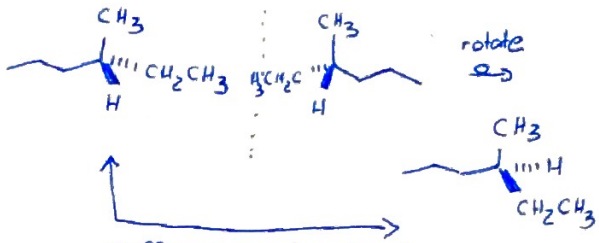
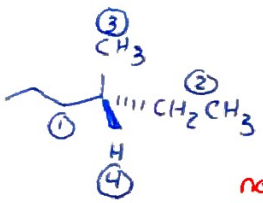
1

enantiomers?



Different molecules!
These two are enantiomers

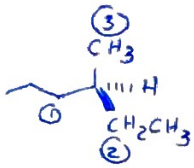
Names? R/S configuration?



need to put H back!

↷ = R

(R)-3-methylhexane

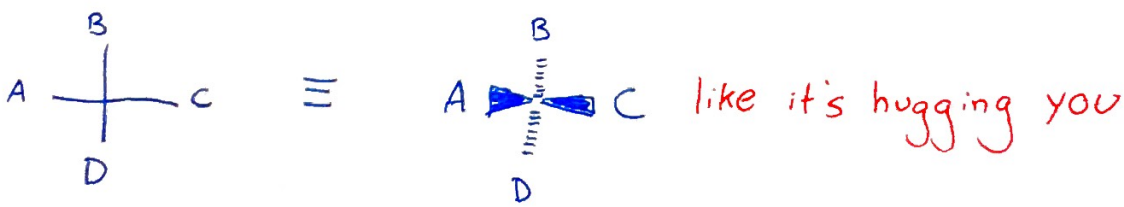


↶ = S

(S)-3-methylhexane

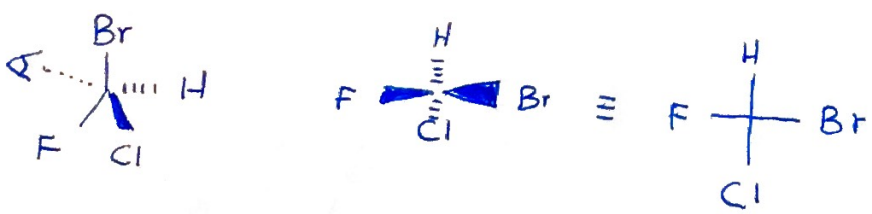
We also use Fischer projections to represent chiral centers

In general:



like it's hugging you

Ex:



Flowchart

Same Molecular Formula? — NO → NOT isomers (different compounds)

↓ Yes

Isomers

Same connectivity? — NO → **Constitutional**

↓ Yes

Stereoisomers

Interchangeable structures without Bond-breaking? — Yes → **Conformational**

↓ NO

Contain stereocenter (a stereogenic center) → **Configurational**

Mirror image stereoisomers? — Yes → **Enantiomers**

- contain chiral centers

↓ NO

Diastereomers

- cis/trans
- Includes alkenes

Note: All chiral centers are stereogenic centers, but not all stereogenic centers are chiral.

ex.