Course Chem 343 Lecturer Gellman (11 am)

Day Friday Date 10/14/2011

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Chapter 6: Stereochemistry

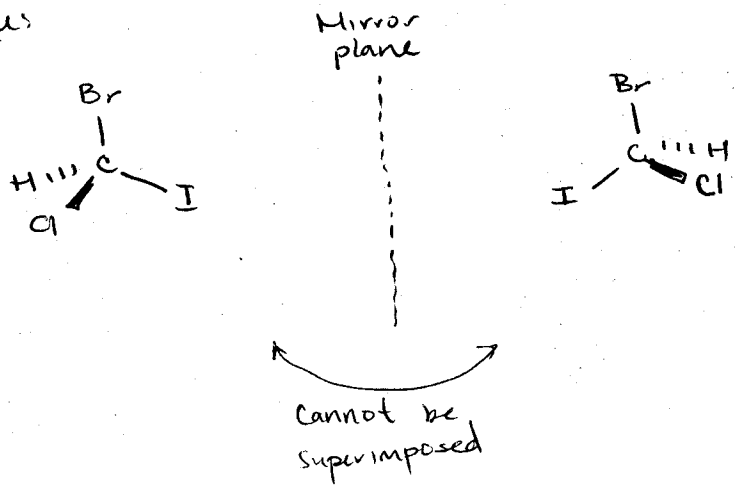
Rec. Problems: 1, 3-7, 8b, 9, 12-25, 27-42, 45-54.

Recall: "Stereoisomers" differ from one another in the spatial arrangement of atoms, but not in terms of bonding relationships (ex. E & Z isomers)

[Note: 23 & 24 & subsequent "sawhorse projections" (pg 257). Focus on other drawing conventions.]

Enantiomers: Mirror images that cannot be superimposed

Example:



Comments:

① If a molecule differs from its mirror image, it is "Chiral." Many molecules are identical to their mirror images (ex. Figure 6.1); These are "Achiral"

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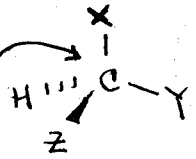
(2) A chiral molecule has only one enantiomer

An Achiral molecule has no enantiomers

(3) Most chiral molecules (organic molecules) have an sp^3 carbon with four different bonding partners.

ways to refer to these types of carbons:

"Stereocenter"
"Chiral center"
"Stereogenic center"



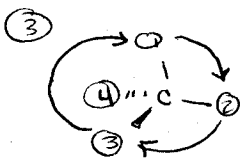
$X \neq Y \neq Z \neq H$

(4) However, some molecules that contain stereocenters are achiral and some chiral molecules do not contain an sp^3 carbon with 4 different binding partners.

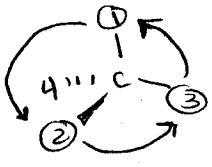
R,S nomenclature: Specifies configuration at sp^3 stereocenters

steps: (1) assign priority to 4 different bonding partners

(2) Orient molecules so that the lowest priority group points away from you



Clockwise
(R)



Counter-Clockwise
(S)

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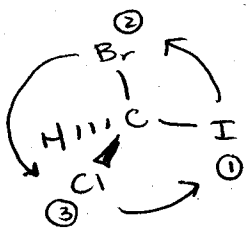
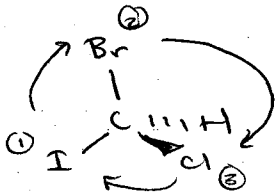
Recall example enantiomers:



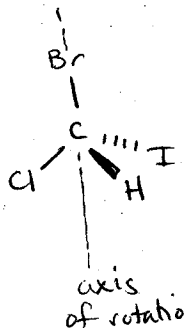
Clockwise arrangement of groups by priority
↳ [S] enantiomer



CCW arrangement of groups by priority
↳ [R] enantiomer

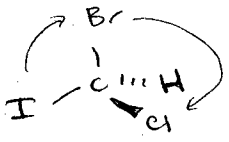
NOTE: Must be able to manipulate 3D representations of molecules on paper & in your head. Models will help!!

example:



in order to get this molecule into the proper orientation for assignment

spin about C-Br bond →



[R]

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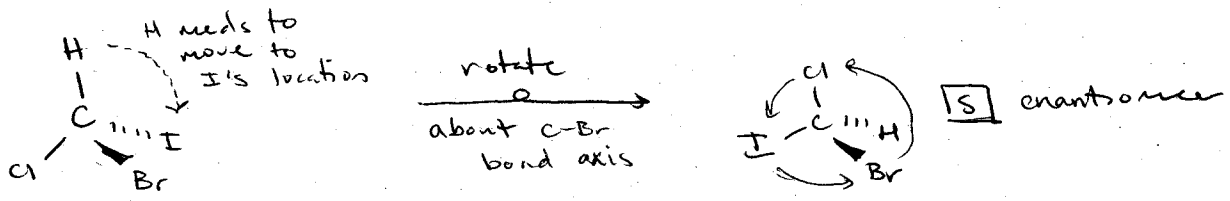


5 enantiomer

How do we distinguish enantiomers experimentally?

① Most physical properties are the same for enantiomers.
- Melting point, boiling point, ΔH_f°, density, etc.

Key Distinction!

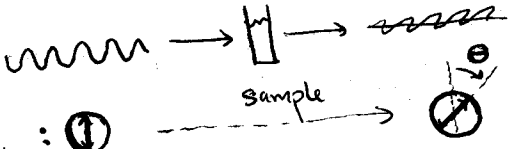
Optical Rotation: How the molecule interacts with (rotates) plane-polarized light.

electromagnetic (EM) wave (light) →

← light only has vertical polarization

↓

pass polarized light through a solution containing "enantiomerically pure" sample ⇒ plane of polarization will rotate in a characteristic way for each enantiomer



light polarization: ①

θ = theta = angle of rotation

[θ is defined for each enantiomer of a compound]

Key concept: clockwise rotation ($\theta > 0$)
counterclockwise rotation ($\theta < 0$)

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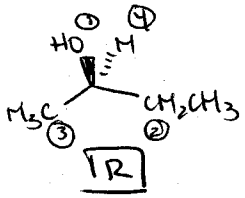
Example:

(1) 

$\Rightarrow$ Measure:

$[\alpha]_D^{20} = \sim 13.9°$

$[\alpha] \Rightarrow$ Specific rotation - value normalized for the concentration and path length of the sample

$20 \Rightarrow$ Measurement taken at 20°C

$D \Rightarrow$ Use the D-line from sodium vapor emission (589.3 nm)

So... terminology

(S)-(+)-2-butanol
(R)-(-)-2-butanol

** Note: (R & S) do NOT correlate with (+/-)

(R/S) specific to molecular structure as drawn

(+/-) - Empirically measured value for optical rotations

Phased differently:

→ R enantiomers can rotate light either (+) or (-) depending on the molecule

→ S enantiomers can rotate light either (+) or (-) depending on the molecule.