Essential Organic Chemistry
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Chapter 6

Isomers and Stereochemistry

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isomers

- constitutional isomers
- stereoisomers
  - cis–trans isomers
  - isomers that contain asymmetric centers
Review of Isomerism

- **Isomers** – Compounds that have the same molecular formula but do not have identical structures.

- **Constitutional Isomers** – differ in the way their atoms are connected.

- **Stereoisomers** – differ in the way their atoms are arrange in space.
Constitutional Isomers

Constitutional isomers:

- Ethyl alcohol: \( \text{CH}_3\text{CH}_2\text{OH} \)
- Dimethyl ether: \( \text{CH}_3\text{OCH}_3 \)
- 1-Chlorobutane: \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \)
- 2-Chlorobutane: \( \text{CH}_3\text{CH}_2\text{CHCH}_3 \)
6.1 Cis-trans isomers

Differ in the arrangement of their atoms in space (cannot interconvert) - *Alkenes*.
6.1 Cis-trans isomers

➢ Cyclic structure.

\[
\text{cis-1-bromo-3-chlorocyclobutane} \quad \text{trans-1-bromo-3-chlorocyclobutane}
\]

\[
\text{cis-1,4-dimethylcyclohexane} \quad \text{trans-1,4-dimethylcyclohexane}
\]
6.2 Chirality

- **Chiral** – Nonsuperimposable on its mirror image.

- **Achiral** – Superimposable on its mirror image.

- If a molecule (or object) has a mirror plane or an inversion center, it cannot be chiral.
right hand

left hand

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Chiral or Achiral?

- Brandy snifter

achiral
Chiral or Achiral?

➢ Shears

chiral
Chiral or Achiral?

➢ Beer mug

achiral
Chiral or Achiral?

➢ Hiking boot

chiral
Chiral or Achiral?

- Baseball glove

chiral
Chiral or Achiral?

➢ Boat propeller

chiral
Chiral or Achiral?

➢ Desk chair

achiral
Chiral or Achiral?

➢ School desk

chiral
Chiral or Achiral?

➢ *cis*-1,3-dimethylcyclopentane

achiral

mirror plane
Chiral or Achiral?

\(\textit{trans}-1,3\text{-dimethylcyclopentane}\)

[chiral]
Chiral or Achiral?

➢ *1,1-dimethylcyclohexane*

achiral
6.3 Asymmetric centers

- An asymmetric center is an atom that is bonded to four different groups.
Chiral or Achiral?

- 2-butanol

Asymmetric center

chiral

mirror image
Chiral or Achiral?

2-bromopropane

achiral
PROBLEM 4

Which of the following compounds have an asymmetric center?

a. $\text{CH}_3\text{CH}_2\text{CHCH}_3$  
   \[
   \text{Cl}
   \]

b. $\text{CH}_3\text{CH}_2\text{CHCH}_3$  
   \[
   \text{CH}_3
   \]

c. $\text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_2\text{CH}_3$  
   \[
   \text{Br}
   \]

d. $\text{CH}_3\text{CH}_2\text{OH}$

e. $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3$  
   \[
   \text{Br}
   \]

f. $\text{CH}_2=\text{CHCHCH}_3$  
   \[
   \text{NH}_2
   \]
6.4 Isomers with one asymmetric center

**2-bromobutane**

The two isomers of 2-bromobutane are enantiomers.
6.4 **Isomers with one asymmetric center**

- A chiral molecule
- Nonsuperimposable mirror image
- Enantiomers

- An achiral molecule
- Superimposable mirror image
- Identical molecules
Enantiomers

A chiral compound and its mirror image are called *enantiomers*.

2-butanol:

![enantiomers](image)
Enantiomers

Asparagine:

L-asparagine (from asparagus) bitter taste

D-asparagine (from vetch) sweet taste

enantiomers
Which of the compounds in Problem 4 can exist as enantiomers?
6.5 How to draw enantiomers

perspective formulas of the enantiomers of 2-bromobutane
Draw the enantiomers of each of the following compounds using perspective formulas:

a. CH₃CHCH₂OH  

b. ClCH₂CH₂CHCH₂CH₃  

c. CH₃CHCHCH₃

\begin{center}
\begin{align*}
\text{Br} & \quad \text{CH₃} \\
a. & \quad \text{CH₃CHCH₂OH} & b. & \quad \text{ClCH₂CH₂CHCH₂CH₃} & c. & \quad \text{CH₃CHCHCH₃} \\
\end{align*}
\end{center}
6.6 Naming enantiomers: the $R,S$ system

- This has the highest priority
- This has the lowest priority
- Clockwise = $R$ configuration
**Absolute Configuration**

- **R** and **S**
  - Assign priorities to the remaining groups based on atomic numbers.
  - Clockwise (highest to lowest priority) ⇒ **R**
  - Counterclockwise ⇒ **S**

(R)-2-butanol
Absolute Configuration

Assign priority:

- Atomic number of atom directly bonded.
- If the same atom is bonded, go to the next atom, etc.
- Groups containing multiple bonds are treated as though multiple atoms were attached:
Absolute Configuration

Determine the absolute configuration of the following compounds:

- \( \text{H}_3\text{C}-\text{C}-\text{Cl} \)
- \( \text{Br}-\text{S}-\text{Cl} \)
- \( (\text{CH}_3)_2\text{CHCH}_2 \)
- \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{S}-\text{Cl} \)
- \( \text{F}-\text{D}-\text{R}-\text{CH}_3 \)
- \( \text{O} \)
- \( \text{H}-\text{R}-\text{C}-\text{C}=\text{N} \)
Absolute Configuration

Determine the absolute configuration of the following compounds:
PROBLEM 8

Which of the following molecular models are identical?
the group with the lowest priority is bonded by a hatched wedge

(S)-2-bromobutane

(R)-2-bromobutane
what is its configuration?

this molecule has the $R$ configuration; therefore, the molecule had the $S$ configuration before the groups were switched.
PROBLEM 9

Assign relative priorities to the following groups:

a. \(-\text{CH}_2\text{OH} \quad \text{-CH}_3 \quad \text{-CH}_2\text{CH}_2\text{OH} \quad \text{-H}\)

b. \(-\text{CH}=\text{O} \quad \text{-OH} \quad \text{-CH}_3 \quad \text{-CH}_2\text{OH}\)

c. \(-\text{CH}(\text{CH}_3)_2 \quad \text{-CH}_2\text{CH}_2\text{Br} \quad \text{-Cl} \quad \text{-CH}_2\text{CH}_2\text{CH}_2\text{Br}\)

d. \(-\text{CH}=\text{CH}_2 \quad \text{-CH}_2\text{CH}_3 \quad \text{-C}=\text{CH} \quad \text{-CH}_3\)
PROBLEM 10

Indicate whether each of the following structures has the $R$ or the $S$ configuration:

a. \[
\begin{array}{c}
\text{H} \\
\text{Br} \\
\text{C} \\
\text{CH}_3 \\
\text{COOH}
\end{array}
\] 

b. \[
\begin{array}{c}
\text{H} \\
\text{OH}
\end{array}
\]
PROBLEM 11

Name the following compounds:

a. \[
\begin{array}{c}
\text{Br} \\
\text{H} \\
\text{C} \\
\text{CH}_2\text{CH}_3 \\
\text{CH}_3
\end{array}
\]

b. \[
\begin{array}{c}
\text{H} \\
\text{H}_3\text{C} \\
\text{C} \\
\text{CH}_2\text{CH}_2\text{Cl} \\
\text{Cl}
\end{array}
\]
Do the following structures represent identical molecules or a pair of enantiomers?

\[
\begin{align*}
\text{CH}_3 & \quad \text{and} \quad \text{OH} \\
\text{HO} & \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{H}
\end{align*}
\]

The easiest way to find out whether two molecules are enantiomers or identical molecules is to determine their configurations. If one has the \(R\) configuration and the other has the \(S\) configuration, they are enantiomers. If they both have the \(R\) configuration or both have the \(S\) configuration, they are identical molecules. Because the structure on the left has the \(S\) configuration and the structure on the right has the \(R\) configuration, we know that they represent a pair of enantiomers.

Now continue on to Problem 12.
PROBLEM 12

Do the following structures represent identical molecules or a pair of enantiomers?

a. \( \text{CH}_2\text{Br} \quad \text{and} \quad \text{Cl} \quad \text{CH}_2\text{CH}_3 \)
\( \text{H}_3\text{C} \quad \text{CH}_2\text{CH}_3 \quad \text{Cl} \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_2\text{Br} \quad \text{CH}_3 \quad \text{CH}_2\text{Br} \)

b. \( \text{CH}_2\text{Br} \quad \text{and} \quad \text{H} \quad \text{OH} \quad \text{CH}_3 \quad \text{HO} \quad \text{CH}_2\text{Br} \quad \text{CH}_3 \quad \text{CH}_2\text{Br} \)
6.7 Chiral compounds are optically active

- Plane-polarized light is produced by passing normal light through a polarizer.
Optical Activity

- When plane-polarized light passes through a solution of achiral molecules, the light emerges from the solution with its plane of polarization unchanged.
Optical Activity

However, when plane-polarized light passes through a solution of a chiral compound, the light emerges with its plane of polarization changed.
Optical Activity

- **Optical Activity** – The ability of a compound to rotate the plane of polarized light.

- A compound that rotates the plane of polarization is said to be *optically active*.

- **Chiral** compounds are *optically active* and **achiral** compounds are *optically inactive*.

- A *polarimeter* is used to make such measurements: