

5.S: STEREOCHEMISTRY AT TETRAHEDRAL CENTERS (SUMMARY)

CONCEPTS & VOCABULARY

5.1: Enantiomers and the Tetrahedral Carbon

- Every molecule is either **chiral** (not superimposable on its mirror image) or **achiral** (superimposable on its mirror image).
- **Chiral** molecules do not have a plane of symmetry, while **achiral** molecules have one or more **planes of symmetry**.
- **Stereoisomers** vary by spatial arrangement of atoms but have the same atom connectivity.
- **Stereoisomers** that are mirror images of one another but are not superimposable are called **enantiomers**.

5.2: The Reason for Handedness in Molecules - Chirality

- A Tetrahedral carbon atom bonded to four different substituents is an **asymmetric** carbon (also called a **stereocenter** or **chiral** carbon), which typically leads to a **chiral** molecule (meso compounds are the exception in section 5.7).

5.3: Optical Activity

- **Enantiomers** cause rotation of plane-polarized light in equal amounts in opposite directions. This is called **optical activity**. Clockwise rotation is called **dextrorotatory** (+) and counter-clockwise is called **levorotatory** (-).
- **Specific rotation** is the amount that a sample of a chemical rotates plane-polarized light. It can be used to calculate the purity of a mixture of **enantiomers** called the **enantiomeric excess**.
- **Resolution** is the separation of a mixture of **enantiomers**.
- **Racemates** are defined as a 50:50 mixture of **enantiomers**, resulting in a sample that is not **optically active**. The process of forming a **racemic** mixture is called **racemization**.

5.4: Pasteur's Discovery of Enantiomers

5.5: Sequence Rules for Specifying Configuration

- Use the CIP rules to determine the priority of each substituent attached to a **chiral** carbon to determine whether configuration is **R** or **S**. With the lowest priority group facing away from you, draw an arc connecting groups 1-2-3. If that arc is clockwise, the configuration is **R**. If counterclockwise, the configuration is **S**.

5.6: Diastereomers

- **Stereoisomers** that are not mirror images of one another are called **diastereomers**.
- **Diastereomers** have two or more **stereocenters**. The configurations of the **stereocenters** cannot be inverse of each other (example R,R and S,S) because that defines a pair of **enantiomers**.

5.7: Meso Compounds

- **Meso** compounds are **achiral** but have **chiral** centers. This is caused by having an internal **plane of symmetry** that allows the two molecules to be superimposable on one another and be **optically inactive**.

5.8: Racemic Mixtures and the Resolution of Enantiomers

- Each component of a **racemic** mixture rotates plane polarized light an equal amount in opposite directions, so there is no **optical activity**.
- **Racemic** mixtures can be separated into the component **enantiomers** by reaction with a **chiral** reagent, which will form **diastereomer** intermediates of the molecules which can then be separated. Following separation the **chiral** reagent is removed to yield the two pure **enantiomers**.

5.9: A Review of Isomerism

- There are several categories of **isomers** with the largest distinction between:
 - constitutional (structural) isomers that contain the same number of each atom but differ in connectivity
 - **stereoisomers** that have all the same atoms with the same connectivity, but only differ in how the atoms are arranged three dimensionally
- In addition to the **diastereomers** and **enantiomers** that have been discussed at length in this chapter, **stereoisomers** can also be:
 - cis/trans or E/Z isomers which differ by spatial arrangement around a double bond
 - conformational **isomers** (conformers) which occur due to free rotation of sigma bonds

5.10: Chirality at Nitrogen, Phosphorus, and Sulfur

- Nitrogen when bonded to three different atoms is **chiral**, however the lone pair of electrons moves freely between positions on the Nitrogen causing these molecules to become a **racemic** mixture.
- When bonded to four different atoms in quaternary ammonium salts, nitrogen atoms lead to **chiral** molecules.

- Organic phosphates with four different groups can also be **chiral**.

5.11: Prochirality

- When a carbon can be converted to a **chiral** center by changing only one of its attached groups, it is called **prochiral**.
- If a molecule has two hydrogens on the same atom and replacement of either one with deuterium would lead to **enantiomers**, the hydrogens are **enantiotopic**.
- Similarly if this replacement would lead to **diastereomer** molecules, the hydrogens are **diastereotopic**.
- If replacement of a hydrogen would not lead to a chiral center being created, they are termed **homotopic**.

5.12: Chirality in Nature and Chiral Environments

SKILLS TO MASTER

- Skill 5.1 Identify stereocenters in molecular structures.
- Skill 5.2 Identify whether two structures are identical (not meso), constitutional isomers, enantiomers, diastereomers or meso and identical.
- Skill 5.3 Explain how plane polarized light is used to show optical activity.
- Skill 5.4 Calculate specific rotation from experimental data.
- Skill 5.5 Calculate optical purity and enantiomeric excess from experimental data.
- Skill 5.6 Determine configuration of stereocenters as R or S.
- Skill 5.7 Draw the enantiomer and diastereomers of a given compound with one or more stereocenters.
- Skill 5.8 Identify planes of symmetry in meso compounds.
- Skill 5.9 Describe a process for separating a mixture of enantiomers.
- Skill 5.10 Explain why racemic mixtures are optically inactive.
- Skill 5.11 Explain the difference between constitutional and stereoisomers.
- Skill 5.12 Give an example of a chiral center that is not carbon.

MEMORIZATION TASKS

MT 5.1 Memorize the rules for determining R and S configuration.

MT 5.2 Memorize the types of isomers and how to identify them.

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