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## Introduction to the Structures and Isomerism of Simple Organic Molecules: Description and Modeling

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### Objectives

- **Part I:** To learn the structures of and construct models for simple organic molecules, and to draw their projection and perspective formulae.
- **Part II:** To classify, recognize and construct models of different types of isomers of organic compounds.

### Background

Almost all compounds that contain carbon are known as **organic compounds**. Most organic compounds also contain hydrogen. Organic compounds that contain only carbon and hydrogen atoms are classified as **hydrocarbons**. Structures and simple physical properties of hydrocarbons will be discussed in **Part I**. Some organic compounds also contain other nonmetals (referred to as heteroatoms) such as oxygen, nitrogen, the halogens, sulfur, and phosphorus. These compounds are known as **hydrocarbon derivatives**.

Based on their structures and properties, organic compounds are also classified according to groups of atoms within the molecule called **functional groups**. Each functional group is characterized by the type of bonds and/or heteroatoms it contains. The most common functional groups are the alkanes, alkenes, alkynes, aromatic hydrocarbons, organic halides, alcohols, aldehydes, ketones, esters, carboxylic acids, amines and amides. The first four of these functional groups contain only carbon and hydrogen atoms and therefore belong to the class of hydrocarbons.

Molecules that have the same molecular formula but are not identical are called **conformers** or **isomers**. Conformers differ only by the angle of rotation about a single bond(s) however isomers have different structural or spatial arrangements.

In **part II** different classes of conformers and isomers will be discussed and molecular models will be used to visualize their three-dimensional structures.

### Part I: Hydrocarbons

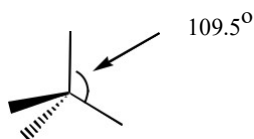
The four classes of hydrocarbons are alkanes, alkenes, alkynes and aromatic hydrocarbons. Alkanes and alkenes and alkynes are further classified as aliphatic hydrocarbons.

Names of hydrocarbons use a root name that indicates the number of carbon atoms. Then appropriate suffixes and/or prefixes are added to complete the name.

For example: heptane indicate a seven (hepta-) alkane (-ane). The number of carbon atoms in a chain or ring is indicated as follows:

Number of C atoms	Root Name	Number of C atoms	Root Name
1	meth-	7	hept-
2	eth-	8	oct-
3	prop-	9	non-
4	but-	10	dec-
5	pent-	11	undec-
6	hex-	12	dodec-

- **Alkanes** contain single bonds only. Each carbon in an alkane has a tetrahedral geometry with a bond angle of about  $109.5^\circ$ . Carbon atoms in alkanes are  $sp^3$  hybridized.



- The relationship between the number of carbons and hydrogens in alkanes is summarized by the general formula  $C_nH_{2n+2}$ , where  $n = \#$  of carbons.
- The structures and names of the straight chain alkanes containing one to six carbons are as follows:
  - Notice that their names end in -ane

CH<sub>4</sub> methane

CH<sub>3</sub>CH<sub>3</sub> ethane

CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> propane

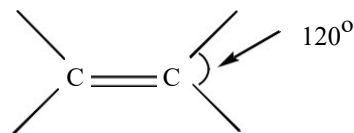
CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> butane

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> pentane

CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub> hexane

And so on....

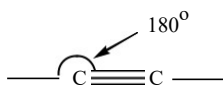
- **Alkenes** contain one or more double bonds. The geometry around the double bonded carbons is trigonal planar with a bond angle of  $120^\circ$  around the carbon. The double bonded carbons in alkenes are  $sp^2$  hybridized.



- The relationship between the number of carbons and hydrogens in alkenes is summarized by the general formula  $C_nH_{2n}$ ,  $n = \#$  of carbon atoms.
- The structures and names of the simplest straight chain alkenes (with one double bond between the first and the second carbons) containing two to six carbons are as follows:
  - Notice that their names end in -ene.

$\text{CH}_2=\text{CH}_2$  ethene  
 $\text{CH}_2=\text{CHCH}_3$  1-propene  
 $\text{CH}_2=\text{CHCH}_2\text{CH}_3$  1-butene  
 $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_3$  1-pentene  
 $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  1-hexene  
 And so on....

- **Alkynes** contain one or more triple bonds. The geometry around the triple bonded carbons is linear with a bond angle of  $180^\circ$ . The triple bonded carbons in alkynes are sp hybridized.



- The relationship between the number of carbons and hydrogens in alkynes is summarized by the general formula  $\text{C}_n\text{H}_{2n-2}$ ,  $n = \#$  of carbon atoms.
- The structures and names of the simplest straight chain alkynes (with one triple bond between the first and the second carbons) are as follows:
  - Notice that their names end in -yne

$\text{CH}\equiv\text{CH}$  ethyne

$\text{CH}\equiv\text{CCH}_3$  propyne

$\text{CH}\equiv\text{CCH}_2\text{CH}_3$  1- butyne

$\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$  1- pentyne

$\text{CH}\equiv\text{CCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$  1- hexyne

and so on.


- **Branched and cyclic hydrocarbons:**

Carbon atoms in organic compounds not only are arranged in a straight chain (each carbon is bonded to maximum of two other carbons) but can also be arranged in branched chain (each carbon can be bonded to three or four other carbons) or a cyclic chain (the carbons are arranged to form a ring).

Branched aliphatic hydrocarbons can be named using common (old) names (specially the small molecular weights) or are named systematically by following a set of rules for naming.

Cyclic aliphatic hydrocarbons are simply named by adding a prefix **cyclo-** in front of the name of their analogous open chain hydrocarbon.

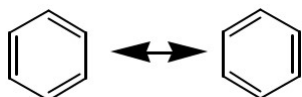
For example an alkane with 4 carbons can be arranged in:

- Straight chain:  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$   
butane
- Branched chain:  $\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ | \\ \text{CH}_3 \end{array}$   
isobutane (common name)
- Cyclic chain:  (in organic chemistry, carbons and hydrogens are often not shown explicitly, as is the case here)  
cyclobutane

**Aromatic hydrocarbons** refer to structures where carbons are bonded to each other forming a planar cyclic carbon chain (ring) and contain delocalized  $\pi$  (pi) bonds, as suggested by the resonance structures below. The most common aromatic compounds are benzene ( $\text{C}_6\text{H}_6$ ) and its derivatives (a benzene ring with substituent(s) attached to it). The carbons in aromatic hydrocarbons are  $sp^2$  hybridized and the C-C-C and C-C-H bond angles are  $120^\circ$ .

Benzenes derivatives are named by using their common names or named by using the name of the substituent + benzene (eg methylbenzene)

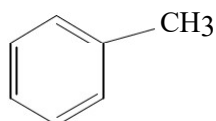
- Benzene



Also represented as:



- A benzene derivative:



Methylbenzene (toluene)

- **Saturated and unsaturated hydrocarbons** : Carbon can form a maximum of four single bonds in a compound. Since each carbon in an alkane contains four single bonds with maximum number of hydrogens possible, alkanes are called **saturated hydrocarbons**. However alkenes, alkynes and aromatic hydrocarbons contain  $\pi$ -bonded (double or triple bonds) carbons and contain less than the maximum number of hydrogens. Therefore they are called **unsaturated hydrocarbons**. The  $\pi$ -bonds in unsaturated organic compounds can be converted to single bonds by adding additional atoms to form saturated organic compounds.
- **Intermolecular force between hydrocarbons and physical properties**: The primary intermolecular forces between hydrocarbons are London dispersion forces. London forces are relatively weak for small molecules but increase in magnitude with increasing molecular size. Therefore at room temperature hydrocarbons containing four or less carbons exist as gases; hydrocarbons containing five to twelve carbons exist as liquids; hydrocarbons containing more than twelve carbons generally exist as solids.

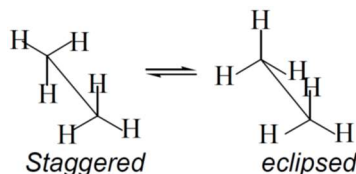
## Part II: Conformers and Isomers

Different orientations of the same molecule that differ only by the angle of rotation about a single bond or bonds are called **conformers**. Conformers look different, but are really the same compound since one can be converted to another simply by rotation about a single bond.

Different compounds with the same molecular formula that have different structural or spatial arrangements are called **isomers**.

### Conformers (conformational isomers)

The different arrangements of atoms can arise by *simple rotation* around single bonds. These different arrangements are said to be **conformations**. A conformation that is stable compared with the case with a slightly different rotation angle (i.e. at a “local energy minimum”) is called a **conformer**. The molecule will not spend a significant amount of in the form of a conformation that is at local energy maximum. For most molecules at room temperature there is sufficient thermal energy to convert one conformer (remember, those are the relatively stable conformations) into another by rotation around single bonds, because single bonds don't offer resistance to rotation around them (“free rotation”.) Sometimes sets of conformations for a particular molecule are given special names describing their orientations. The staggered and eclipsed conformations of ethane:

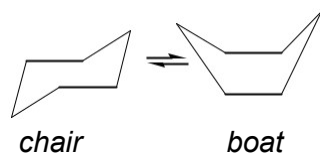


Staggered conformation is a “conformer” whereas the eclipsed conformation is just a “transition state” the molecule passes through when it switches between the stable staggered conformers.

Visit the following page for a more detailed explanation and interactive animation:  
[Conformations of ethane \(manchester.ac.uk\)](http://www.manchester.ac.uk)

[https://personalpages.manchester.ac.uk/staff/T.Wallace/20412tw2/1.2\\_anim\\_ethane.html#:~:text=Conformations%20of%20ethane.%20Experiments%20show%20that%20there%20is,%28staggered%20when%20viewed%20end-on%20in%20a%20Newman%20projection%29.](https://personalpages.manchester.ac.uk/staff/T.Wallace/20412tw2/1.2_anim_ethane.html#:~:text=Conformations%20of%20ethane.%20Experiments%20show%20that%20there%20is,%28staggered%20when%20viewed%20end-on%20in%20a%20Newman%20projection%29.)

- The chair and the boat conformers of cyclohexane.



## Isomers

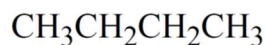
Different arrangements of atoms in a set of molecules that *cannot* be interconverted by simple rotation around a single bond are called **isomers**. Interconversion of isomers is much more restricted and takes much more energy than interconversion of conformers. Enough energy to break one or more  $\pi$  or  $\sigma$  bonds is needed for interconversion of isomers. Therefore, they are different compounds and exhibit different properties.

There are two main classes of isomers called **constitutional (structural)** isomers and **stereoisomers**. These types of isomers not only in organic compounds but also in inorganic compounds (coordination complexes) discussed in the second semester of general chemistry.

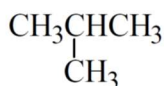
### Constitutional (Structural) Isomers

Isomers with different structural arrangements are called **constitutional** isomers. Constitutional isomers can differ from each other by their sequence of atoms, their sequence of bonds or their types of bonds. The following illustrate different types of constitutional isomers.

- Different sequence of atoms (same functional group).

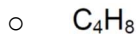


butane

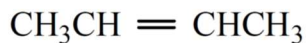


isobutane (methylpropane)

- Different sequence of bonds (different location of functional group)

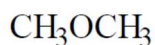
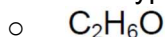


1-butene



2-butene

- Different types of bonds (different functional group)



dimethyl ether



ethanol

## Stereoisomers

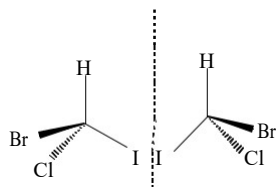
Isomers that differ from each other by the way their atoms are arranged in space are called **stereoisomers**. There are two classes of stereoisomers: enantiomers and diastereomers

- **Enantiomers (optical isomers)**

An object or a compound that does not contain a plane or a center of symmetry is said to be **chiral**. Chiral objects have the property that they are not superimposable (exactly overlap) on their mirror images. A common example of a pair of enantiomers are your hands. They are mirror images of each other, but are not superimposable. Thus, chiral compounds or object are said to exhibit “handedness”.

Just as certain objects are chiral, certain molecules and ions are also chiral. The most common chiral organic compounds contain at least one tetrahedral carbon that is bonded to four different groups. A tetrahedral carbon that contains four different groups is said to have a chiral or stereogenic center. In most cases, compounds containing chiral carbons are **not superimposable** on their mirror images. If the molecule or ion is chiral and therefore is not superimposable on its mirror image, then the molecule and its mirror image are said to be **enantiomers** (or optical isomers) of each other.

CHBrClI



Enantiomers have identical physical and chemical properties except for their effect on plane polarized light and their reactions with other chiral (asymmetric) compounds. A pair of enantiomers rotate plane polarized light in opposite directions. For this reason, enantiomers are also known as **optical isomers**. Biological molecules generally exhibit optical isomerism and this property can be very important in biological reactions. For example, different optical isomers can have very different tastes, odors and toxicities.

Objects or molecules that are identical to their mirror images and are therefore superimposable on their mirror images are said to be achiral (not chiral). Examples include  $\text{CH}_2\text{Cl}_2$ , or any tetrahedral carbon with at least two identical groups bonded to it.

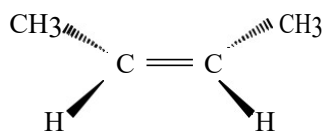
- **Diastereomers**

- i) Geometric isomers (also called cis/trans isomers)
- ii) stereoisomers that have two or more chiral centers but are not mirror images (optional)

- i) Geometric Isomers**

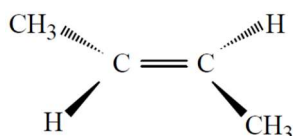
Geometric isomers in organic compounds have different orientations of atoms or groups across a double bond or a ring. If the same types of atoms or groups of atoms are attached to **the same side** of the double bond or a ring then the arrangement is referred as **cis-isomer**.

- *cis*-2-butene



If the same types of substituents are attached to the *opposite side* of the double bond or a ring then the arrangement is referred to as **trans-isomer**.

- *Trans*-2-butene



Geometric isomerism arises because there is no “free” rotation around a double bond or within the carbons in a ring. Bonds have to be broken to convert one isomer into the other.

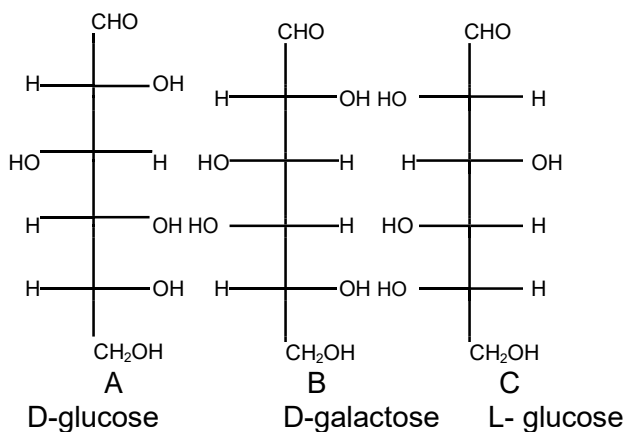
## ii) Stereoisomers that have two or more chiral centers but are not enantiomers (optional)

Different spatial arrangements around the chiral carbons can lead to stereoisomers that are not mirror images. Compounds that contain 2 or more chiral carbon atoms but that are not mirror images of each other are said to be **diastereomers**. Molecules that contain two or more chiral centers can therefore have both enantiomers and diastereomers. This type of isomerism is common in carbohydrate chemistry.

A projection diagram called a Fischer projection best represents molecules that have two or more chiral centers and their isomers. Fischer projections show three-dimensional arrangement of the bonds in a molecule. In Fischer projections bonds coming out of the plane are drawn with horizontal lines and bonds that are going into the plane are drawn with vertical lines. The tetrahedral carbons are represented by the intersection of the horizontal and vertical lines.

Fischer projections of D-glucose and D-galactose are shown below.

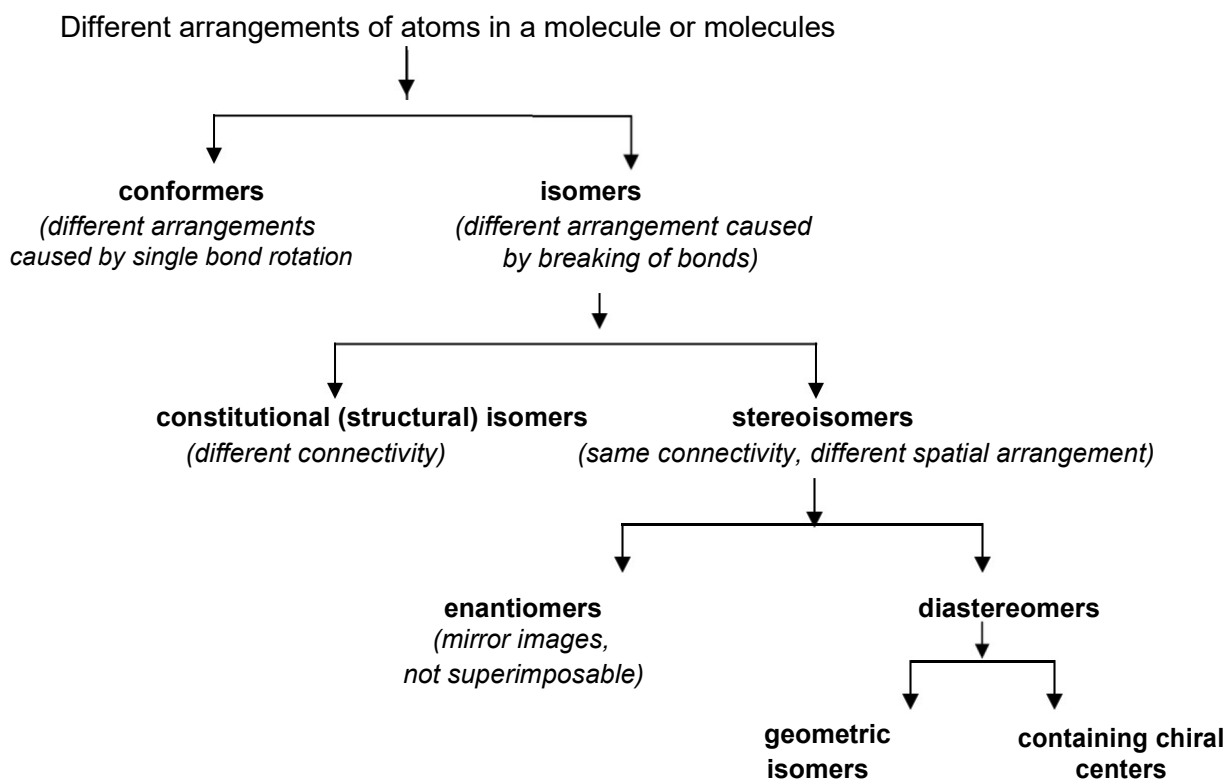
- A & B and B & C are diastereomers of each other. But A & C are enantiomers of each other.



Unlike pairs of enantiomers, diastereomers have different physical properties beyond their effects on plane polarized light.



## Summary of Conformers and Isomers



Molecular models will be used to illustrate the three-dimensional structures of simple hydrocarbons and different types of isomers. The model kits contain different colored balls and different size sticks. Three-dimensional models will be constructed from these balls and sticks.

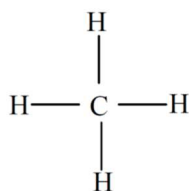
### Using Molecular Model Kits

Different colored balls represent different atoms. Commonly the black balls represent carbon atoms, white balls represent hydrogen atoms and red balls represent oxygen atoms. The halogens (chlorine, iodine, and bromine) are usually represented by the green balls. Blue balls represent nitrogen atoms. However it is also possible to determine which balls to use to represent an atom by just looking at the number of holes in the balls. The holes represent the number of bonds these atoms generally form. For example carbon forms four bonds and therefore to use a ball that has four holes is used, oxygen forms two bonds and therefore the red one that has two holes is used. Hydrogen forms one bond and therefore the white ball with the one hole is used. The halogens usually form one bond so the green balls with one hole are used. The blue ball that is used for nitrogen is an exception since it contains four holes and nitrogen usually forms three bonds. Therefore remaining hole can represent the lone pair on the atom.

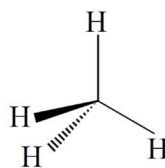
The plastic sticks in the kits represent bonds. There are two different sized sticks. The short, stiff sticks are used to represent single bonds and the long flexible sticks are used for double and triple bonds. In order to make one double bond two flexible sticks are needed to connect the two adjacent atoms and to make a triple bond three flexible sticks are used to connect the two adjacent atoms.

Molecular models will be constructed for each molecule. **Projection** structures as well as three dimensional perspective diagrams will be drawn. The projection structure is just the Lewis structure in which each pair bonding electrons is represented as a line. Three dimensional **perspective** drawings require a different drawing technique to identify bond orientation. A solid straight lines ( — ) represent bonds lying in the plane of the paper, a wedge-shaped line constructed of hatch marks ( ▨ ) represents bonds that project down into the paper, and solid wedge-shaped line ( ▴ ) represents bonds that project up out of the paper, toward the viewer.

- Projection and perspective diagram of CH<sub>4</sub>



projection



perspective

It is important to be able to visualize these three-dimensional structures in your mind without the aid of molecular models. If you need further practice with these models you can purchase them from the SMC bookstore or you can be creative and make home made models using materials that are available in your home.