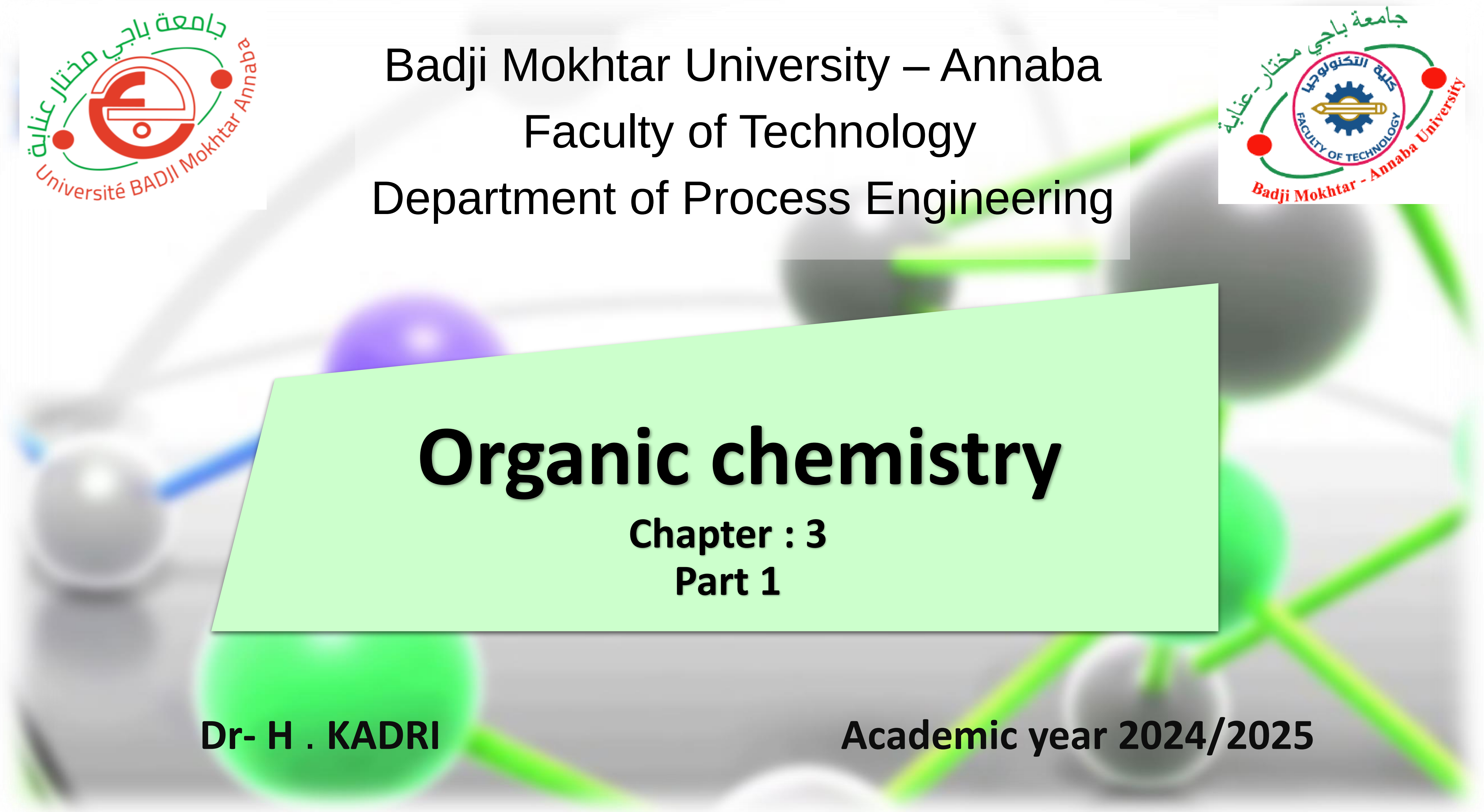

Badji Mokhtar University – Annaba
Faculty of Technology
Department of Process Engineering

Organic chemistry

Chapter : 3

Part 1

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Chapter 3 :
Concepts of Stereoisomerism

Chapter 3 : Concepts of stereoisomerism

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- 2- Plane isomerism : Definition
- 2-1- Chain isomerism
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1- Definition :

Compounds that have the same molecular formula **(CxHyOz)** but different structural formulas are called **‘isomers’**. They differ by the nature of the chemical bonds **(planar isomerism)** or by the spatial arrangement of the atoms **(stereoisomerism)**. As a result, these molecules will have different physical and chemical properties.

- Determination of molecular formula :

Consider a molecule A (Cx Hy Oz Nt) with a molar mass MA. The mass percentage of each constituent element of this molecule is given by the following relationship:

$$\% X = \frac{MC \times n}{\% MA} \times 100$$

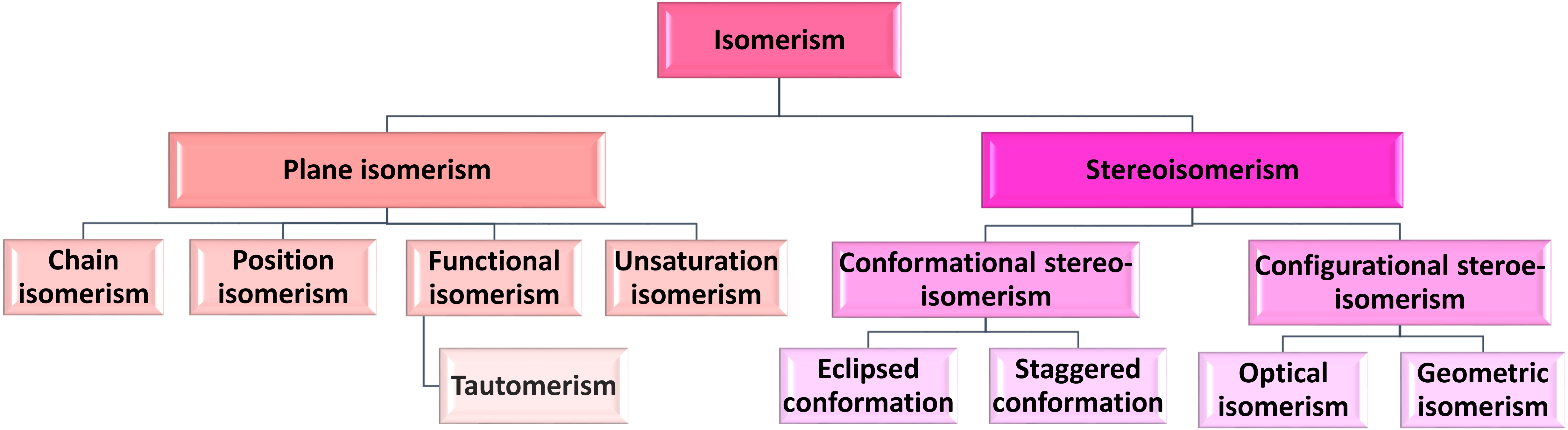
with: Mx = mass of the element X , n: number of atoms of X ⇒ $\frac{MA}{100} = \frac{MX \times n}{\% X}$

- Applying this relationship to all the other elements gives :

$$\frac{MA}{100} = \frac{MC \times x}{\% C} = \frac{MH \times y}{\% H} = \frac{MO \times z}{\% O} = \frac{MN \times t}{\% N} \Rightarrow \frac{MA}{100} = \frac{12 \times x}{\% C} = \frac{1 \times y}{\% H} = \frac{16 \times z}{\% O} = \frac{14 \times t}{\% N}$$

We distinguish two types of isomerism [2]:

- Plane isomerism (structural or constitutional)
- Steric isomerism or stereoisomerism



Isomerism

Plane isomerism

Stereoisomerism

Chain isomerism

Position isomerism

Functional isomerism

Unsaturation isomerism

Tautomerism

Conformational stereo-isomerism

Configurational steroe-isomerism

Eclipsed conformation

Staggered conformation

Optical isomerism

Geometric isomerism

[2] : cours de chimie organique par : A. SAFER , fac de chimie usto/ L2 GP

Isomerim

2- Plane isomerism :

Plane or constitutional isomerism corresponds to isomerism that designate different atomic arrangements. Constitutional isomers have only their molecular formula in common; they do not consist of the same chemical functions and can be represented by planar diagrams.

We distinguish four types of plane isomerism : **Chain isomerism; Position isomerism; Functional isomerism; Unsaturation isomerism**.

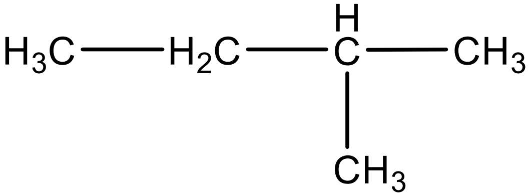
2-1- Chain isomerism:

In this case the order of the carbons is different

Example: **C_5H_{12}**

$H_3C-CH_2-CH_2-CH_2-CH_3$

pentane



$$H_3C-H_2C-\underset{\displaystyle CH_3}{\overset{\displaystyle H}{C}}-CH_3$$

1-methylbutane

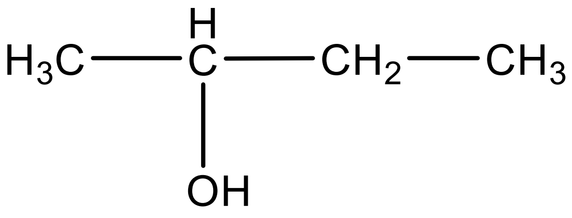
2-2- Position isomerism:

Positional isomers are molecules that differ by the position of the functional group on the carbon chain.
This means that it is the functional group that moves within the carbon skeleton.

Example : $C_4H_{10}O$

$H_3C—CH_2—CH_2—CH_2—OH$

butanol



$H_3C—\underset{\displaystyle OH}{\overset{\displaystyle H}{C}}—CH_2—CH_3$

butan-2-ol

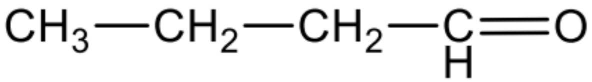
2-3- Functional isomerism :

If the isomers are different in terms of the chemical function present in the molecule, they are said to be functional isomers.

Example 1: The following three molecules all have the molecular formula **C_4H_8O**.

The first is an alcohol, the second an aldehyde and the third an ether oxide.

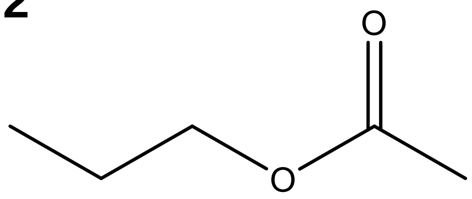
$CH_3—CH═CH—CH_2—OH$



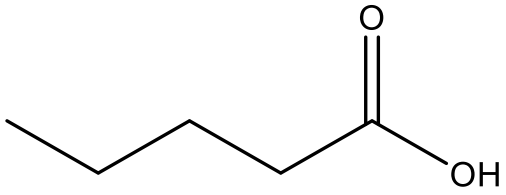
$CH_3—CH_2—CH_2—\underset{H}{C}═O$

$CH_2═CH—CH_2—O—CH_3$

Example 2 : **$C_5H_{10}O_2$**



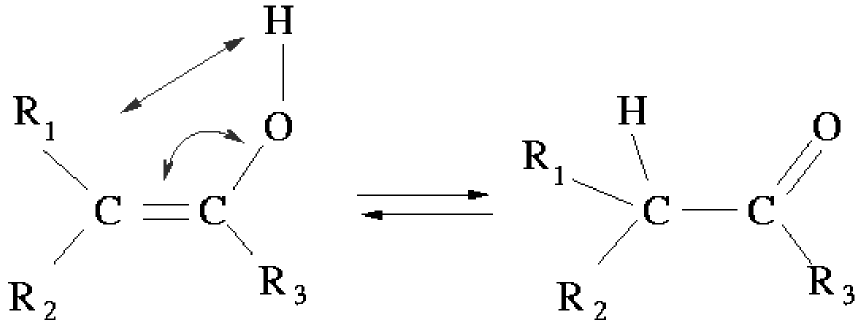
Ester : **propyl ethanoate**



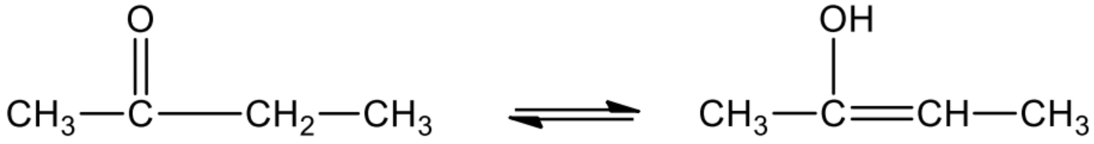
pentaoic acid

2-4- Tautomerism :

A special case of functional isomerism is tautomerism. This is the relationship between two tautomeric forms that are in equilibrium and involves the displacement or migration of a hydrogen atom and a π bond or the transposition of a functional group bond. Depending on physical and chemical conditions such as temperature, pressure, acid, neutral or basic environment, one structure is transformed into another and vice versa.

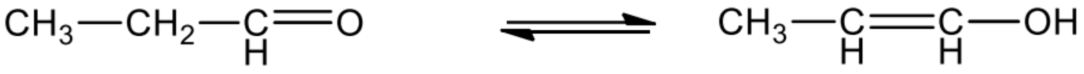


Example : The keto-enolic equilibrium is the most common example between a ketone or between an aldehyde and an enol.



$$CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH_3 \rightleftharpoons CH_3-\overset{\overset{OH}{|}}{C}=CH-CH_3$$

cétone énol



$$CH_3-CH_2-\underset{H}{C}=O \rightleftharpoons CH_3-\underset{H}{C}=\underset{H}{C}-OH$$

aldéhyde énol

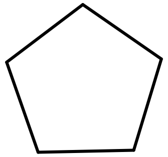
2-5- Unsaturation isomerism :

Unsaturation isomers are molecules with different unsaturations, which can be represented in different forms, either with a double bond or with a ring.

Example : **C_5H_{10}**

$H_2C{=}CH{-}CH_2{-}CH_2{-}CH_3$

Pent-1-ene



Cyclopentane

- Calculating the number of unsaturations :

Unsaturation can be defined as an π bond or a ring. To calculate the degree of unsaturation, apply the following relationship:

$$\boxed{N_i = (2n_C + 2 - n_H + n_N + n_X)/2}$$

With: N_i: the degree of unsaturation or ring; n_C: the number of carbon atoms; n_H: the number of hydrogen atoms; n_N: the number of nitrogen atoms; n_X: the number of halogen atoms.

- Note that the number of oxygen atoms is not taken into account in the calculation.

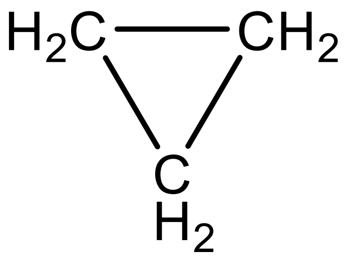
Example : C_3H_6

$$Ni = (2n_C+2 - n_H + n_N - n_X)/2$$

$$Ni = (2\times3+2 - 6)/2 = 1$$

Ni =1: This molecule can be represented in different ways: A molecule with a single double bond or a single ring.

$H_2C{=}CH{-}CH_3$



Note:

Chain and position isomers have slightly different properties, but functional and unsaturation isomers have very different physico-chemical properties ($T_{boiling}$, T_{melt}, density, etc.).

stereochemistry or stereoisometry

3- Stereoisometry:

Stereochemistry is the study of the arrangement (geometrical disposition) of atoms in three-dimensional space. Stereoisomers are molecules that have the same chain, the same position and the same function, but the configuration or geometry is different. These stereoisomeric molecules can be **configuration isomers** or **conformation isomers**.

3-1- Representation of molecules in space:

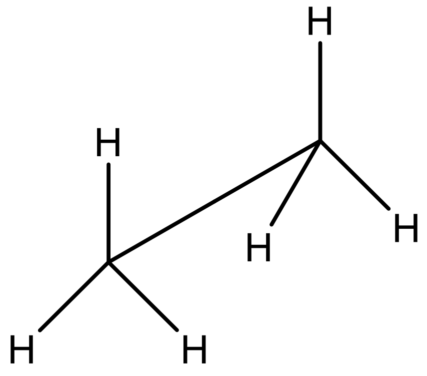
There are various geometric representations of molecules:

- Perspective representation (Oblique).
- Projective representation (Cram).
- Newman representation.
- Fischer representation.

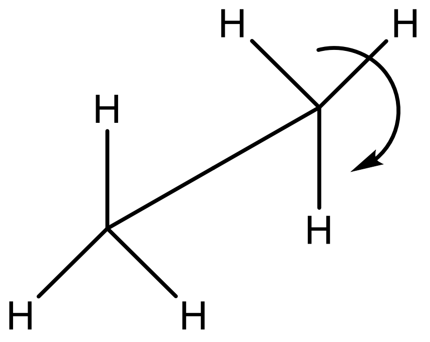
3-1-1- Perspective Representation (Oblique):

The oblique perspective is a method of representing an object in space using a two-dimensional figure.

An example of ethane C_2H_6 is represented in perspective as follows:



Eclipsed forme

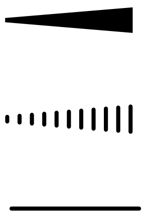


Staggered forme

3-1-2- Projective Representation (Cram) :

In projective representation or Cram projection, bonds are depicted either in the projection plane, in front of it, or behind it. They are represented as follows

:

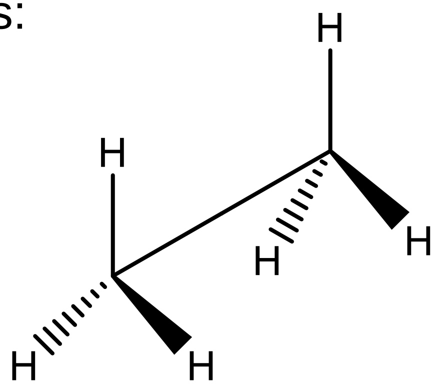


: In front of the plane

: Behind the plane

: In the plane

The ethane (C_2H_6) molecule is represented in projection as follows:



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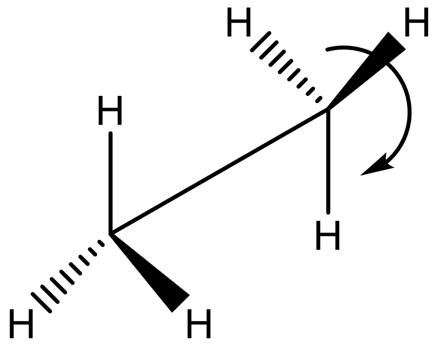
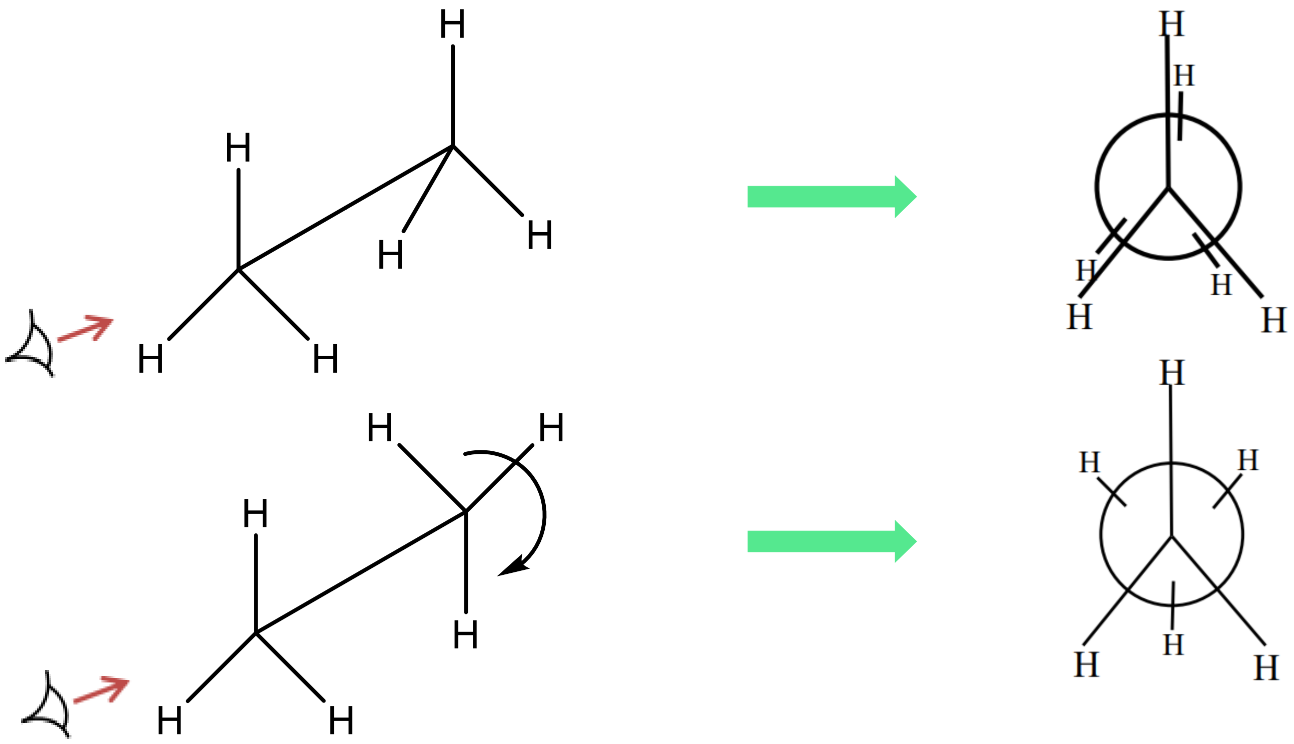


Staggered forme

3-1-3- Newman representation :

The Newman projection is a representation in which the molecule is viewed along the C-C axis, with a projection made onto a plane perpendicular to this axis. The first carbon atom encountered by the observer's eye is represented as a point, while the second carbon atom is represented as a circle.



Eclipsed forme

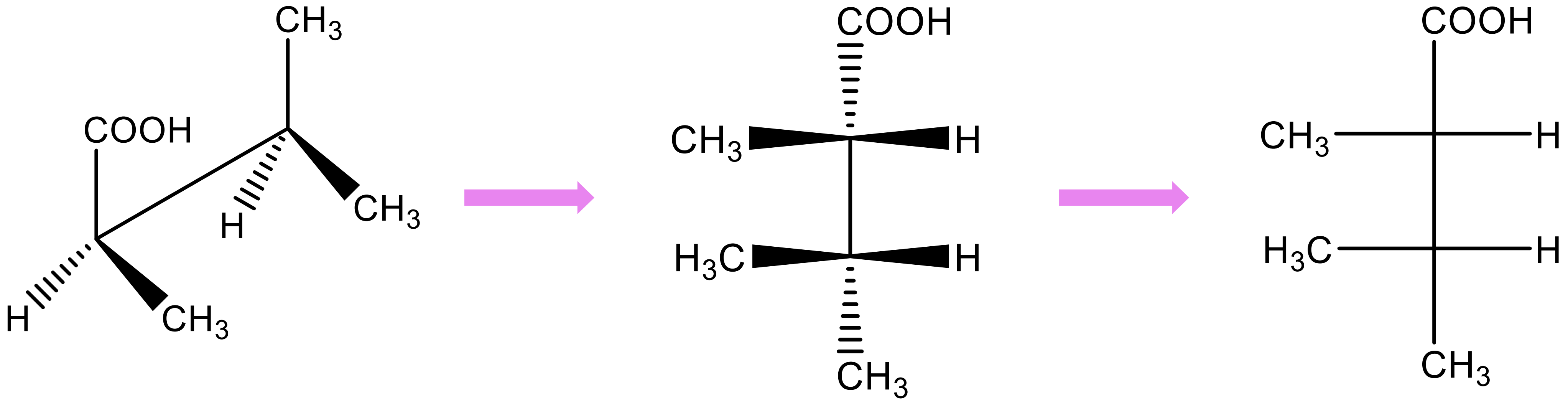
Staggered forme

3-1-4- Fischer representation :

This representation is widely used when the molecule has multiple carbon atoms with non-identical substituents. It is especially employed in the field of biochemistry, particularly for amino acids and carbohydrates such as sugars.

The most oxidized carbon (the one carrying oxygen atoms) **is always placed at the top** of the representation.

Example: **2,3-dimethylbutanoic acid**



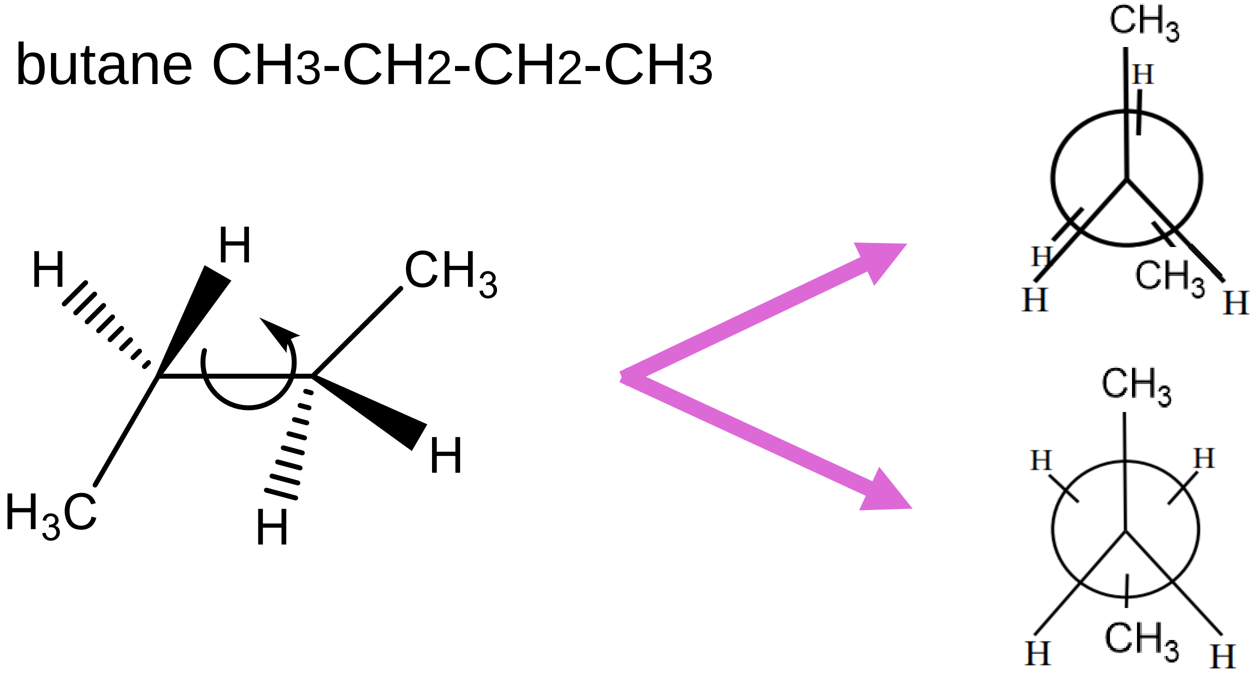
Note :

The **vertical substituents** (top and bottom) in the Fischer representation are considered to be substituents represented **behind the plane**. The **horizontal substituents** in Fischer's representation are considered to be substituents represented **in front of the plane**.

3-2- Conformational isomerism :

Two conformers represent the same molecule in different spatial arrangements and energy states. The change from one conformation to another is made by simple rotation around a single bond (σ bond), without breaking the bond.

Example 1 : butane $CH_3-CH_2-CH_2-CH_3$

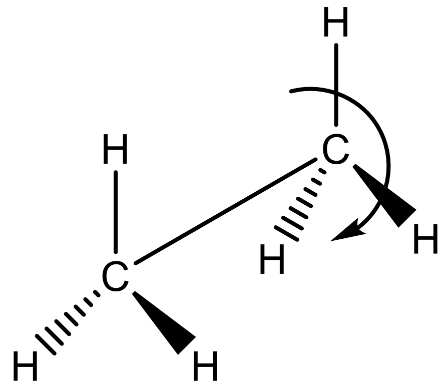


Conformation Eclipsed

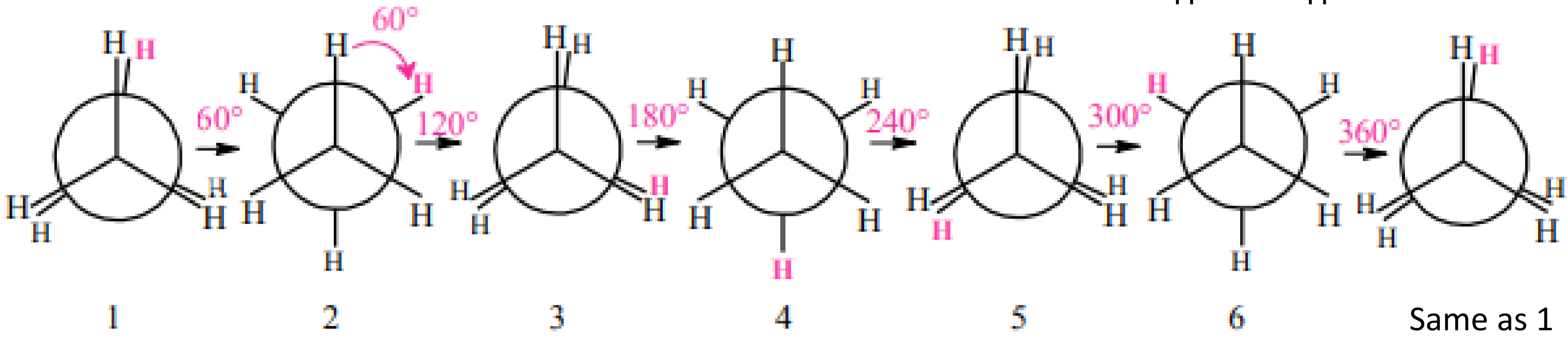
Conformation Staggered

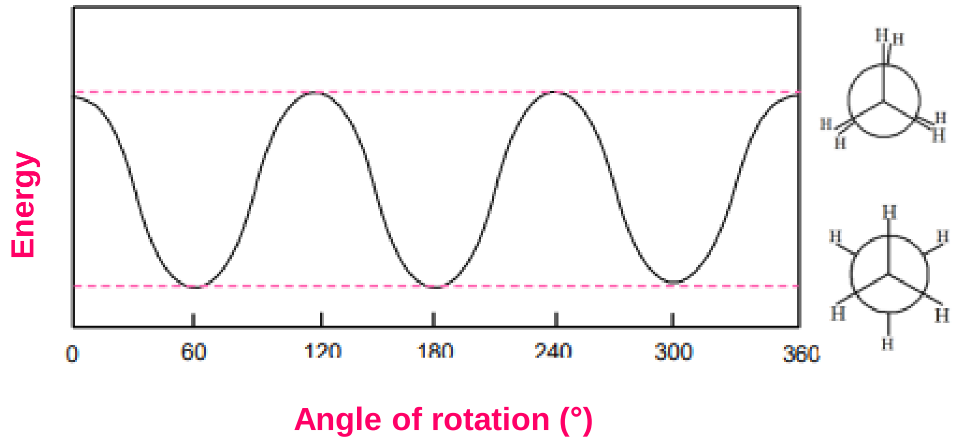
Eclipsed conformation: masking of the 2C substituents.
Staggered conformation: maximum distance between the 2C substituents.

Example 2 : ethane CH_3-CH_3



Here are the different conformations obtained:





The **staggered** conformation is much **more stable** than the **eclipsed** conformation. To draw the energy diagram as a function of the angle of rotation, we indicate the energy levels of each shape.

The **energy level** of the **most stable** ‘‘staggered‘‘ shape is **lower than** that of the least stable ‘‘eclipsed‘‘ shape.

Part 2