

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



Organic chemistry

Chapter : 3 Part 2

Dr-H.KADRI

Academic year 2024/2025

Chapter 3. part 2:

3-3- Configurational isomerism :

The configuration of a molecular entity is the spatial arrangement of its atoms or groups of atoms.

- A carbon is said to be asymmetric, chiral center, or stereo center when its four substituents are different.
- A group of atoms consisting of a double bond with its substituents can give rise to E and Z geometric isomerism.

A large number of molecules (those with asymmetric carbons or those with a double bond) exist in a specific configuration (two types of configurational isomerism: **optical isomerism** and **geometric isomerism**). The determination of this configuration requires knowledge of the **Cahn, Ingold**,

and Prelog sequential rule.

- Cahn, Ingold, and Prelog (CIP) Sequential Rules :

The atoms of the substituents carried by the asymmetric carbon (in optical isomerism) or the ethylenic carbon (in geometric isomerism) are classified according to their degree of distance from these carbons and according to a priority sequence.

Rule I: The priority sequence is based on the atomic number of the first atom encountered on the considered substituent. The atom with the higher atomic number is given priority over the one with a lower atomic number.

Thus in the following substituents comprising one or more atoms we have the following sequence of decreasing priority.

Rule II: When the atoms directly bonded to the asymmetric or ethylenic carbon are identical, the atoms located at the furthest distance are compared and rule I is applied.

Rule III: Multiple bonds are considered as single bonds and each atom involved in a multiple bond will be written as many times as it carries bonds.

3-3-1- Optical isomerism :

This type of isomerism is found in compounds with an asymmetric carbon and four different substituents, often denoted by C*.



Organic molecules containing one or more tetrahedral carbon atoms linked by four single bonds, carrying four different substituents, are called **chiral**, which comes from the Greek 'kheir' meaning hand.

It exist in two forms that are mirror images of each other and cannot be superimposed. It form a pair of enantiomers.

Enantiomers: are two molecules that are the image of each other in a mirror and cannot be superimposed: they are in fact chiral.

The most concrete example of chirality is that of a right hand that cannot be superimposed on a left hand.



Optical activity: :

In enantiomers or optical inverses, the term optical indicates that these two configurations have the physical property of deviating the plane of polarization of polarized light in a plane, which is measured using a polarimeter.

- If the molecule turns the light of the lamp to the **right** (clockwise) we say that the molecule is **dextrorotatory** from the Latin (dexter: right and gyre: to turn), by convention we designate it by 'd' or '+'.
- If the molecule causes the light from the lamp to turn to the left (anti-clockwise), the molecule is said to be **levorotatory** from the Latin (laevus: left and gyre: to turn), conventionally referred to as 'l' or '-'.
- If we have a mixture made up of 50% dextrorotatory molecules and 50% laevorotatory molecules, this
 mixture is called a racemic. Its rotatory power is zero, and the racemic mixture is said to be optically
 inactive.

- Specific rotatory power of an enantiomer : :

When an optically active substance is passed through by plane polarized light, it causes the plane of polarization of this light to rotate by an angle α that can be easily measured with an analyzer.

$$\left[\alpha\right]_{\lambda}^{t} = \frac{\alpha}{l \cdot c}$$

[α]: the specific rotatory power in $dm^{-1} g^{-1}cm^3$.

α: angle of rotation of the plane of polarization of the light in degrees, counted positively for a clockwise rotation when looking at the beam coming towards you.

I: length of the cell containing the solution in decimeters.

- c: concentration of the solution expressed in grams per cm^3 ..
- t: temperature of the medium,
- λ : the wavelength of the light beam.

- Absolute configuration ('R' and 'S'):

To identify optical isomers, it is necessary to define a nomenclature system that describes the spatial arrangement of asymmetric carbon atoms, i.e. to find out their absolute configuration.

The asymmetric carbon is viewed in such a way that the fourth-ranked substituent is on the opposite side to the observer.

If: 1 2 3 turns to the right, the carbon is said to have the absolute configuration 'R', from the Latin 'Rectus': right. If 1 2 3 turns to the left, the carbon is said to have the absolute configuration 'S', from the Latin 'Sinister': left.



According to the CIP rule: **OH > COOH > CH3 > H** The representation of the two enantiomers according to Cram and Fischer is as follows:



- Optically active compounds with two asymmetric carbons



Each of these 2 C* can be found, independently of the other, in the (R) configuration or in the (S) configuration. There are therefore 4 stereoisomers corresponding to the 4 possible combinations: (2 R, 3 R) stereoisomer I; (2 S, 3 S) stereoisomer II; (2 R, 3 S) stereoisomer III and (2 S, 3 R) stereoisomer IV.

These 4 stereoisomers can be grouped into two pairs of enantiomers (R,R) and (S,S) on the one hand, and (R,S) and (S,R) on the other.



- Case of cyclic molecules :

Taking cyclohexane as an example, if we respect the 120° angles for each sp3 carbon, we will have a twodimensional design where certain bonds are parallel. The same logic also applies to the three-dimensional representation,

$$\bigcirc = (\bigtriangleup \not \rightarrow (\checkmark) \not \rightarrow (\checkmark)$$

All that remains is to place the substituents on the 'chairs'. Once again, we need to maintain parallelism: six positions will be called axial and the other six, equatorial.



To move from a two-dimensional to a three-dimensional representation, it's a good idea to number the carbons first in both representations. You then simply need to respect the orientation of the substituents (upwards or downwards) on the corresponding carbons. If they are drawn vertically, the atoms are in an axial position. The others, on the other hand, are in an equatorial position.

Given a molecule with 'n' asymmetric carbon atoms, to calculate the number of stereoisomers that exist, we apply the following law : Number of stereoisomers = n^2 n : number of asymmetric carbons in the molecule .

There are two types of relationship between these stereoisomers:

□ Enantiomers : are the molecule and its image in the mirror, provided that these two molecules are not superimposable.

Diastereoisomers : are molecules which have the same sequence of atoms, but which are neither superimposable nor the image of each other in a mirror.

Hence we can deduce the following relationships in stereoisomerism:



Nomenclature: 'erythro', 'threo' and 'meso':

To designate pairs of diastereoisomers, we often use a particular nomenclature ('erythro', 'threo'), which shows whether the substituents are on the same or different sides of the carbon chain.

- In the Fischer projection, the substituents are arranged in descending order according to the Cahn Ingold Prelog rules.
- \Box If the substituents are on the same side \rightarrow it is said to be 'erythro'.

 \Box If the substituents are not on the same side \rightarrow it is called 'threo'.



- In Newman's projection, we classify in decreasing order according to the rules of Cahn - Ingold - Prelog. If the directions of rotation are identical on each carbon atom (C1 and C2), the compound is said to be 'erythro'; if they are in opposite directions, the compound is said to be 'threo'.



To designate a pair of enantiomers, another special nomenclature is used (meso), if the two enantiomeric molecules are identical and represent the same molecule (if the molecule is rotated in the plane). The meso form has a symmetry plane and is an **achiral** (not chiral) molecule that does not have optical activity, despite containing asymmetric carbons.



Example : The following molecules, indicating the erythro, threo or meso forms.



3-3-2- Geometric isomerism :

This type of isomerism is found in compounds with a double bond or a ring. It results from the blocking of rotation around the double bond (or ring). These molecules are said to be rigid.



This type of isomerism can only exist if R1 \neq R2 and R3 \neq R4: the **priority** according to the **highest atomic mass** of the substituents, the isomer is said to be **cis** in (A) and **trans** in (B).

In the case of the non bonding pair of nitrogen : it is **considered as the 4th substituent**. When the R and R' groups are on the same side of the double bond, the corresponding isomer is said to be "**syn**", otherwise it is said to be "**anti**". These are therefore the equivalents of the terms cis and trans used only for ethylenics.



The terms cis, trans, syn and anti are now obsolete and replaced by the Z and E terms defined below



To give an unambiguous name to a given configuration, a new Z or E nomenclature is introduced. It is based on a classification of substituents based on the atomic numbers of the successive atoms making up each substituent, i.e. :

On each double-bonded carbon atom, the priority substituent is determined.

- If the **two priority groups** are **on the same side** of the double bond, we have the **Z** isomer (Z for Zusammen: means 'together' in German; but sometimes the term cis is also used).

- If the **two priority groups** are **not** on the same side of the double bond we have the **E** isomer (E for Entgegen: means 'contrary to' in German; but sometimes the term trans is also used).

- Case of cyclic molecules :

In cycloalkanes, if the two substituents are on the same side of the plane of the molecule, the geometric configuration is called 'cis'; if the two substituents are on opposite sides of the plane of the molecule, the geometric configuration is called 'trans'.

Examples:



Applications:

- Cyclopropane



Chiral molecule 1 asymmetric carbon No symmetry plane No symmetry center



Achiral molecule 2 asymmetric carbons Symmetry plane **Meso compound**



CH₃

Н

Chiral molecule 2 asymmetric carbons No symmetry plane No symmetry center

Chiral molecule 2 asymmetric carbons No symmetry plane No symmetry center



Achiral molecule No asymmetric carbon



Achiral molecule 2 asymmetric carbons Symmetry plane **Meso compound**

- Cyclobutane



Achiral molecule No asymmetric carbon 2 symmetry planes



Chiral molecule 4 asymmetric carbons No symmetry plane No symmetry center



Achiral molecule No asymmetric carbon Symmetry center



Achiral molecule No asymmetric carbon 2 symmetry planes - Cyclohexane 1,2-disubstituted



If A = B or $A \neq B$: chiral compound, 2 asymmetric carbons

- Cyclohexane 1,3-disubstituted



If A = B: achiral compound, 2 asymmetric carbons, meso forme If $A \neq B$: chiral compound, 2 asymmetric carbons



Equivalent forms , if : A=B

If A = B or $A \neq B$: chiral compound, 2 asymmetric carbons No symmetry plane No symmetry center - Cyclohexane 1,4-disubstituted



If A = B or $A \neq B$, cis or trans: Achiral compound, symmetry plane

- Naphtalene:



Chapter 4 :

