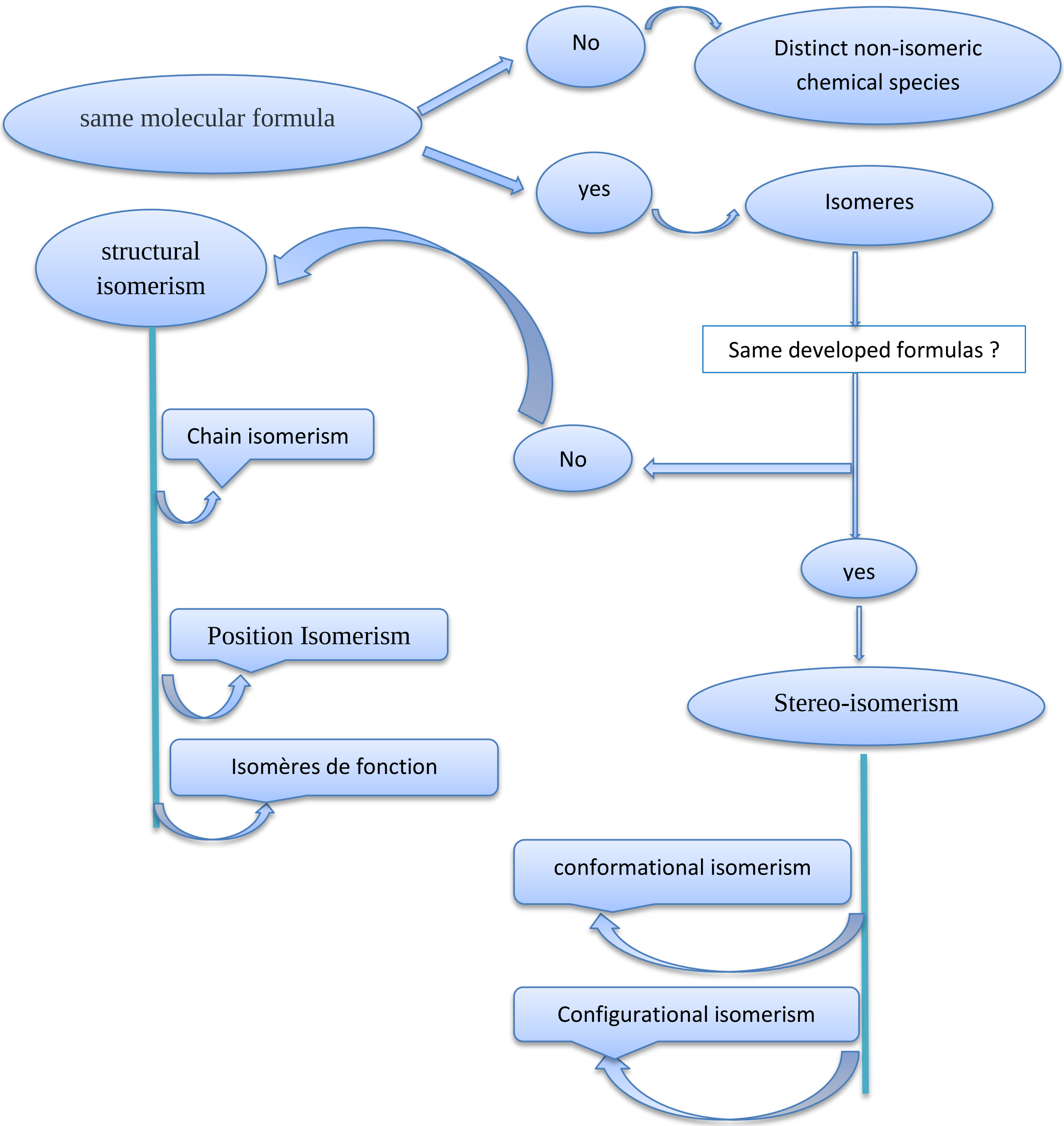
STERREO-ISOMERIE

I. Isomérism :

Isomerism in organic chemistry is a phenomenon shown by two or more organic compounds having the same molecular formula but different properties due to difference in arrangement of atoms along the carbon skeleton (structural isomerism) or in space (Stereo isomerism). The chart summarizes the types of isomerism.



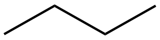
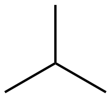
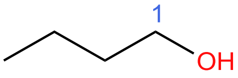
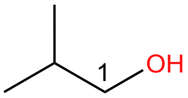
I.1. structural isomerism (plane isomerism):

The structural isomers are the compounds that have the same molecular formula but different in to arrangement of atoms within the molecule. For this type of isomerism, there are: chain (skeleton), position or functional isomers and tautomers

a. Chain (skeleton) isomers :

Chain isomers have the same molecular formula but differ in the order in which the carbon atoms are bonded to each other

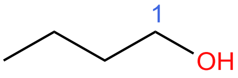
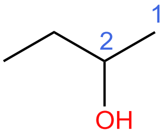
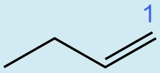
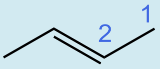
Examples :

C_4H_{10}		
$C_4H_{10}O$		

b. position isomers :

Position isomers have the same molecular formula but differ in the position of a functional group on the carbon chain

Examples

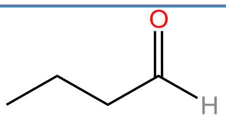
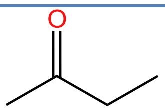
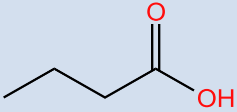
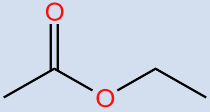
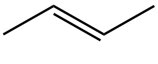
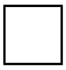
$C_4H_{10}O$		
C_4H_8		

The positional isomerism may also be extended to alkanes andalkynes which differonly in the position of the double or triple bond in their molecules. Thus the molecular formula C_4H_8 stands for two butenes,in which the double bond is different.

c. functional Isomers :

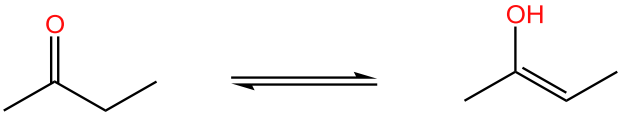
functional lisomer have the same molecular formula but different functional groups

Examples :

C_4H_8O		
$C_4H_8O_2$		
C_4H_8		

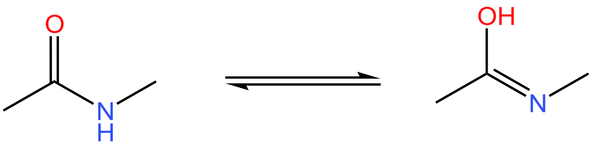
Cas particulier (tautomérie) :

It is aspecial type of functional isomerism in which the isomers are in dynamice quilibrium with each other.



Cétone
Butan-2-one

énol
but-2-én-2-ol



Amide

Imino-alcool

A carbonyl compound with a hydrogen atom on its carbon rapidly equilibrates with its corresponding enol (*eneol :* unsaturated alcohol) isomer. This spontaneous inter conversion between two isomers, usually with the change in position of ahydrogen, is called *tautomerism*, from the Greek *tauto*, meaning “the same”, and meros, meaning “part”. The individual keto and enol isomers are called tautomers.

I.2. Stereoisomerism :

The stereoisomers have the same structural formulas but differ in arrangement of atoms or groups in space. In other words, stereo isomerism is exhibited by such compounds which have identical molecular structure but different configurations. Configuration refers to the 3-dimentional arrangement of atoms that characterizes a particular compound.

Stereo isomerism can be further classified as :

1. Conformational isomerism
2. Configarational isomerism : (geometrical isomerism and optical isomerism)

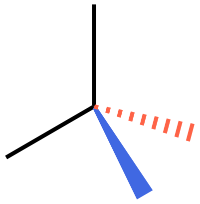
I.2.1. Representation of three dimensional molecules

The *sp3* hybridized tetrahedral carbon is three dimensional in nature. Generally it is very difficult to represent a three dimensional structure in a two dimensional plane paper. There are many methods have been developed for two dimensional representation of a three dimensional structure. Out of them **the flying-wedge, Fischer representation, sawhorse formula and newman projection** methods are most commonly used for two dimensional representation of a three dimensional structure.

a. Flying-wedge or wedge-dash projection

The Flying-Wedge Projection is the most widely used three dimensional representation of a molecule on a two dimensional surface (paper). This kind of representation is usually done for molecule containing chiral centre. In this type of representation three types of lines are used.

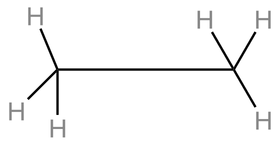
- liaison dans le plan de la feuille : —
- A solid wedge or thick line, it represents bond projection
  Towards the observer or above the plane of paper : 
- A dashed wedge or broken line, it represents bond projection
  away from the observer or below the plane of paper : 



b. Sawhorse formula

The sawhorse formula indicates the arrangement of all the atoms or groups on two adjacent carbon atoms. The bonds between the two carbon atoms are drawn diagonally and of relatively greater length for the sake of clarity. The lower left hand carbon is taken as the front carbon or towards the observer and the upper right hand carbon as the back carbon or away from the observer. e.g. ethane

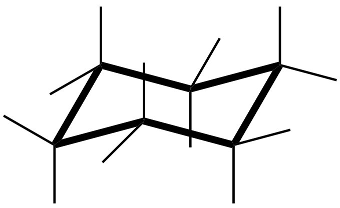
éclipsed



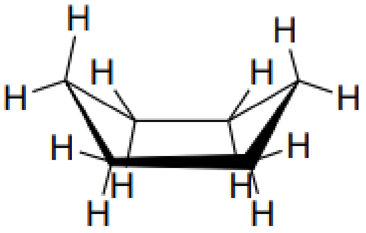
staggered

All parallel bonds in sawhorse formula are eclipsed and all anti parallel bonds are opposite or scattered. Gauche representation is that in which bulky groups are nearer to each other at 600 angles.

La molécule de cyclohexane :



Chair Conformation
of cyclohexane

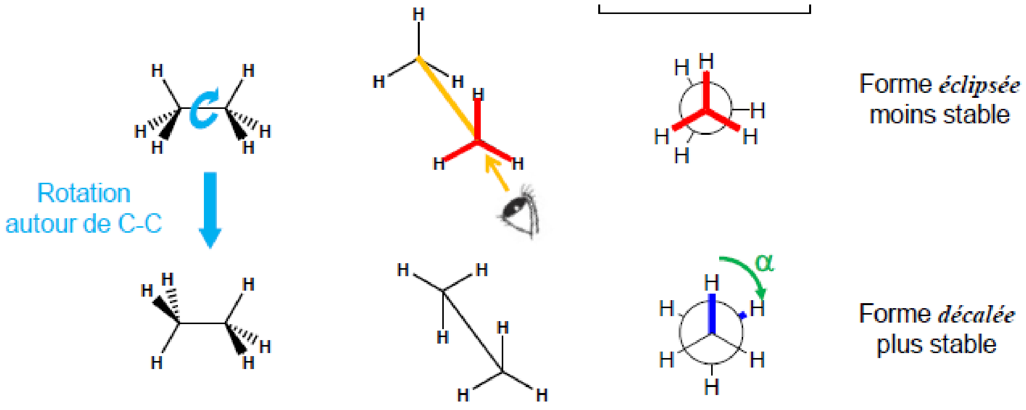


Boat Conformation
of cyclohexane

c. Newman projection :

Newman devised a very simple method of projecting three dimensional formulas on two dimensional paper which are known as Newman projection.

- In these formulae the molecule is viewed from the front or along the axis of a carbon-carbon bond.
- The carbon nearer to the eye is represented by a point and the carbon atom towards the rear by circle.
- The three atoms or groups on the carbon atoms are shown as being bonded to dot or circle by an angle of 1200 to each other.
- In Newman formula all parallel bonds are eclipsed or all anti parallel or opposite bonds are staggered.

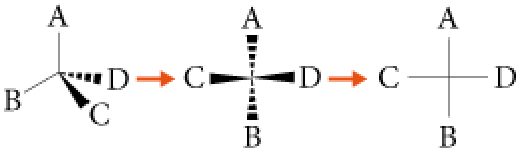


e- Fisher projection :

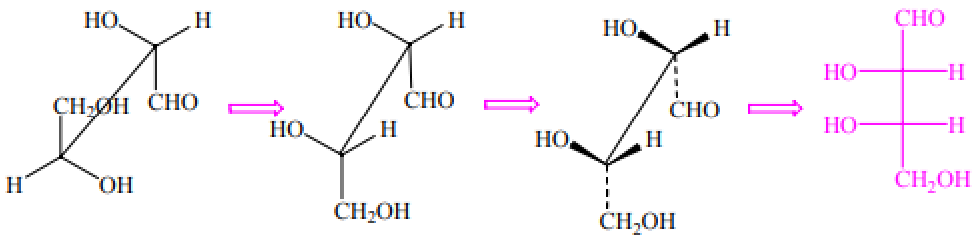
Fischer projection provide an easy way to draw three dimensional molecule on two dimensional paper and all the bonds are drawn as solid lines around asymmetric carbon atom. The Fischer rules for showing the arrangement around asymmetric carbon.

- The carbon chain of the compound is projected vertically, with the **most oxidized carbon** at the top or place the carbon number one at the top (as defined by nomenclature rule).
- The chiral carbon atom lies in the plane of the paper and usually omitted. The intersection of cross lines represents asymmetric carbon.
- The horizontal bonds attached to the chiral carbon are considered to be above the plane of paper or point towards the observer.
- The vertical bonds attached to the chiral carbon are considered to be below the plane of paper or point away from the observer.

Cette représentation est très utilisée, en particulier pour représenter les différents diastéréoisomères des oses et des acides aminés.



Exemple :



Usually the Fischer projection formula is drawn so that the longest carbon chain in the molecule is vertical with the highly oxidized group on the top.

I.2.2. Conformational Isomerism:

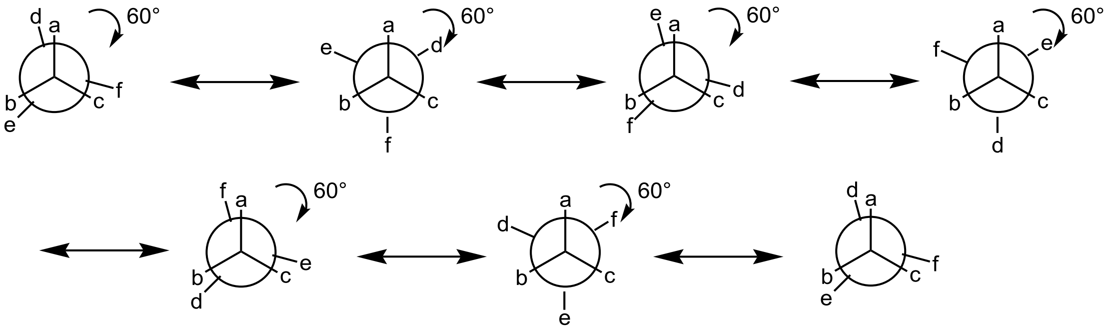
are different spatial arrangements of a molecule that are generated by rotation about single bonds. One molecule may have many different conformations. Some may be low in energy, others high. Some may be required for reactivity, while others may be completely inert. So, it is important to understand how conformations influence the properties of a molecule.

Conformer:

A conformer (or conformational isomer) is a compound with a particular conformation. Different conformers can have vastly different energies and the relative proportion of each conformer is related to the energy difference between them **Conformational isomers can be represented by :** Sawhorse representations or Newman projections

A. Conformations of acyclic hydrocarbons

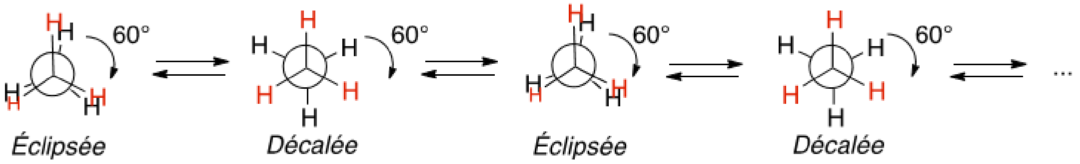
Conformers will be of different energy due to strain Sources of strain. Eclipsed is higher in energy than staggered due to increased torsional strain. Further rotation will convert eclipsed conformation back to staggered



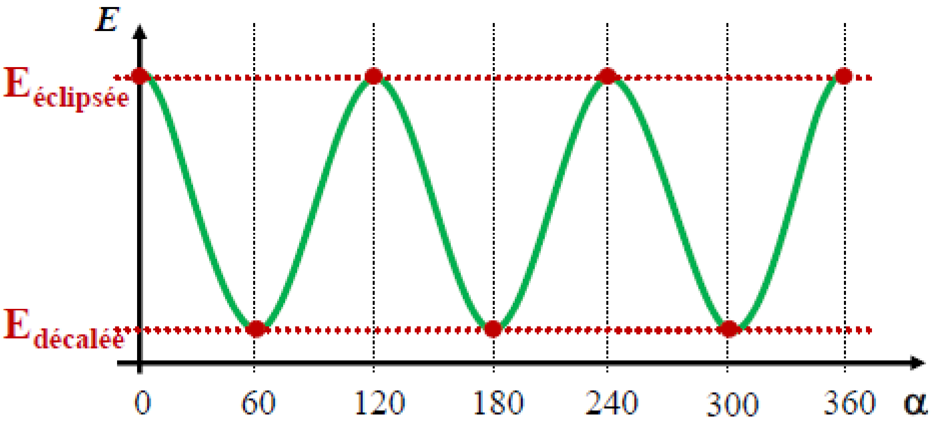
Conformations de l’éthane CH_3-CH_3 :

The different conformations of ethane are not equally stable. The staggered form in which the hydrogen atoms are ‘perfectly staggered’ (dihedral angle is 60°) is the most stable conformation. This is because, in this conformation the all carbon hydrogen (C-H) bonds are located at maximum possible distance to each other, and hence they feel minimum repulsive energy from each other. In eclipsed conformation of ethane, the hydrogen atoms attached to each carbon are directly opposing to each other. This result the minimum separation of the atoms or groups, and hence they feel maximum repulsive energy from each other. The eclipsed conformation therefore, of highest energy and has the lowest stability. A graph plot for the energy profile for various conformations of ethane is shown on figure 4. The relative stability of various conformations of ethane is

Staggered >> Eclipsed

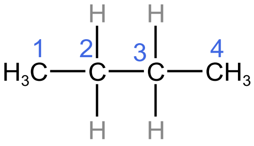


- Energy profile diagram of conformational isomer of ethane :



Conformational analysis of *n*-butane:

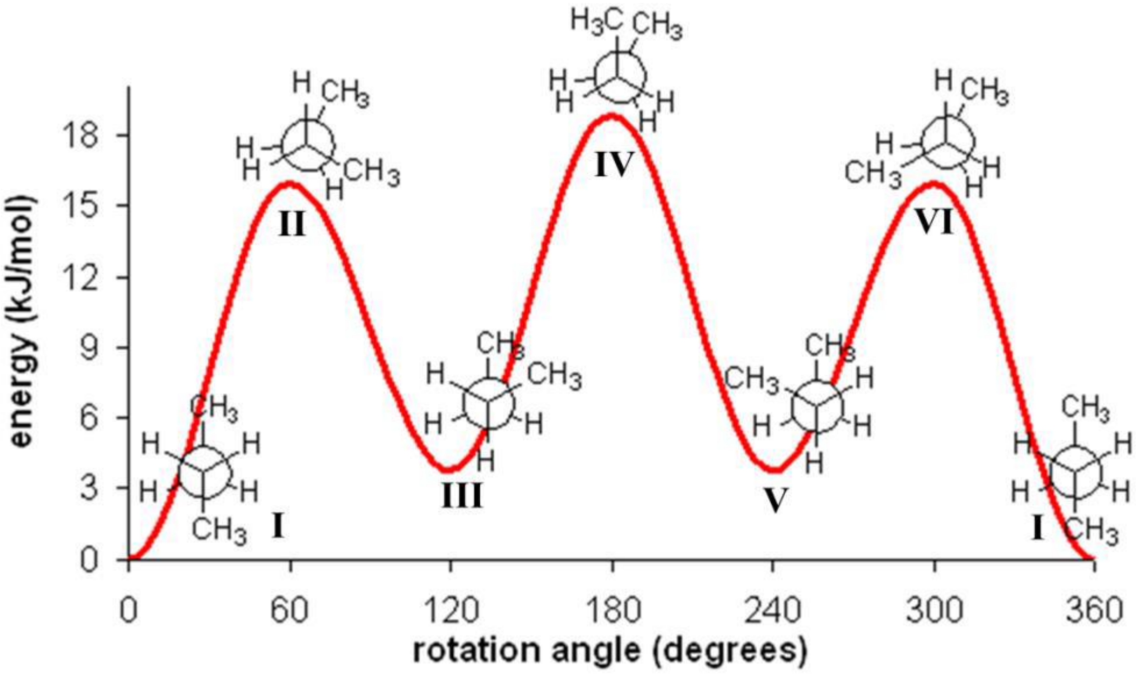
n-Butane (C_4H_{10}) has three carbon-carbon single bonds ; therefore the molecule can rotate about each of them. The rotation about C2 and C3 bond will provide the symmetrical conformations. To study the conformational analysis of *n*-butane, we must consider it as a derivative of ethane molecule, where one hydrogen at each carbon of ethane is replaced by methyl group (-CH3).



$H_3C-CH_2-CH_2-CH_3$

n- Butane molecule

Various conformation of *n*-butane can be obtained by rotation about C2 and C3 bond are shown in following figure :



Energy profile diagram of conformational isomer of *n*-butane

From this figure, we can see that *n*-butane has three staggered conformations (**I, III** and **V**). Conformer **I**, in which two methyl groups are as far as possible, and hence is more stable than other two staggered conformers (*i.e.* **III** and **V**), because conformer **I**, has minimum repulsive energy. As you can see from figure 3; in conformer **I,** both the methyl groups are located opposite to each other. The most stable conformer of *n*-butane, in which both the methyl groups are located opposite to each other is called the *anti-conformer*, whereas other two staggered conformers (*i.e.* **III** and **V**) are called *gauche conformer*. Due to difference in steric strain (repulsion between dihedral atoms/groups) the repulsive energy of *anti* and *gauche* conformers are also different. Three eclipsed conforms (**II**, **IV** and **VI** in figure 6) are also exits for *n*-butane, in which the dihedral atoms/groups are in front of each other (*i.e.* dihedral angle is 0°). The fully eclipsed conformer **IV,** in which the two methyl groups are closest to each other, has maximum steric strain; hence it is of higher energy than the other eclipsed conformers (**II** and **VI).**Thus the relative stabilities of the six conformers of *n*-butane in their decreasing order is given as follows:

Anti > Gauche > Eclipsed > Fully eclipsed

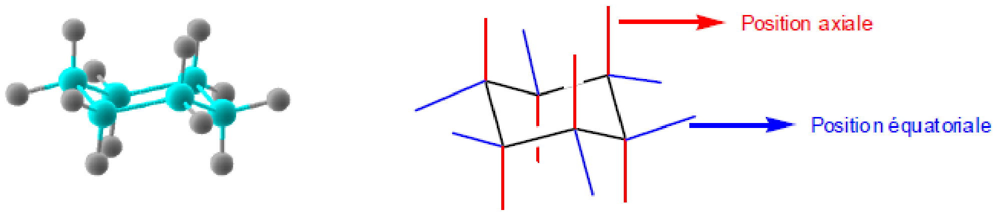
I III and V IV II and VI

b- Conformations of cyclic hydrocarbons :

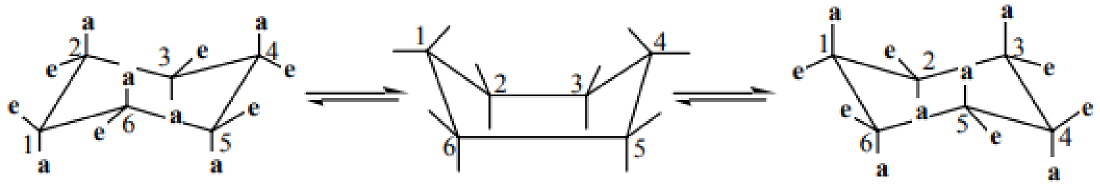
Conformation of cyclohexane:

It is known to you that in cycloalkane, all the ring carbons are *sp3* hybridized, hence must have tetrahedral geometry with all bond angles of 109.5°. But to sustain its cyclic structure the cycloalkane could not be able to maintain the bond angle of 109.5°. As a result there is a deviation from the normal tetrahedral bond angle. This deviation leads the development of strain in the molecule. Thus the cycloalkanes exhibit angle strain, due to which cycloalkanes are not as stable as their non-cyclic homolog. To minimize the angle strain the structure of cycloalkane is keep on changing from one cyclic form to another which are readily interconvertible by rotation about single bond. This is the reason why cyclohexane and larger rings are non-planar.

Cyclohexane exists in two readily interconvertible forms which are called the chair and boat conformations of cyclohexane



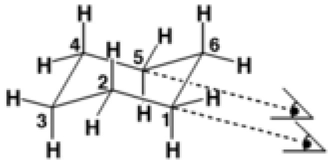
Chair Conformation
of cyclohexane

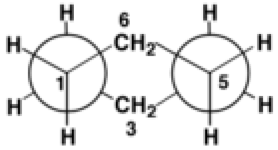


Boat Conformation
of cyclohexane

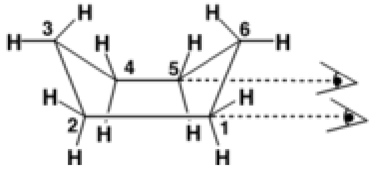
It is possible to represent in Newman the passage from a cyclohexane in the chair conformation to the boat conformation and to switch to another chair conformation using the two representations :

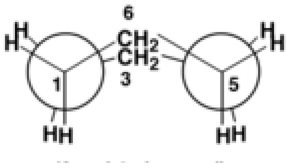
- Newman's representation of the chair conformation :

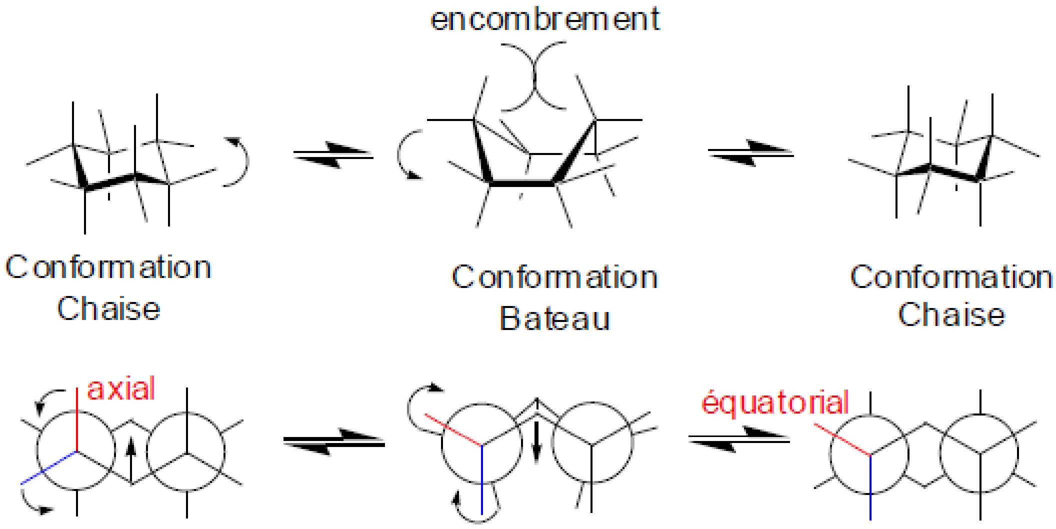




Newman's representation of the boat conformation :







I.2.3. configurational isomerism

Stereoisomerism is arises due to the difference in arrangement (configuration) of atoms or groups in space. When two or more than two isomers have the same structural formulae but having difference in the arrangement (configuration) of atoms in space are called **stereo-isomer** and the phenomenon is called **stereo-isomerism.**

Stereo-isomerism can be further classified as

- Geometrical (*E/Z* or *cis/trans*) isomerism
- Optical isomerism

A large number of molecules (those that have asymmetric carbons or those that have a double bond) appear in a given configuration. The determination of this configuration requires knowledge of the sequential rule of CAHN, INGOLD AND PRELOG

a. Cahn-Ingold-Prelog (C.I.P.) reules :

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

Reule I : Each atom is assigned a priority. Priority is based on atomic number; higher the atomic number, the higher the priority:

Priorité

$$I > Br > Cl > F > O > N > C > H > :$$

$$53 > 35 > 17 > 9 > 8 > 7 > 6 > 1 > 0$$

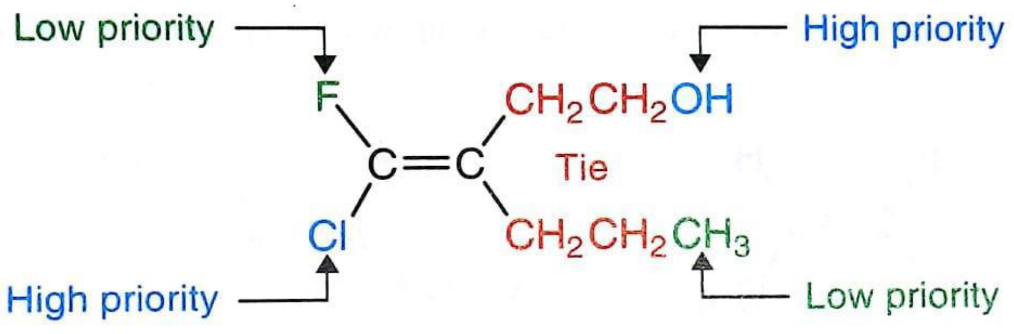
Numéro
atomimiqu

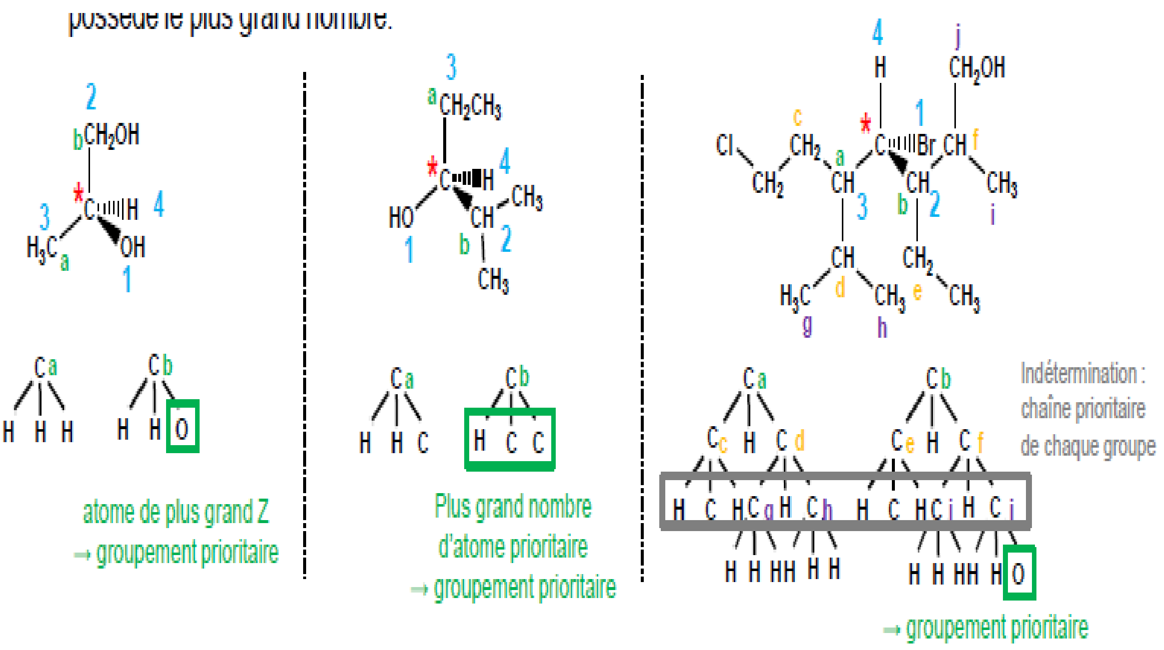
Reule 2 : For isotopes, the higher the atomic mass the higher the priority. For example : T (tritium) > D (deutérium) > H.

Highest Priority $^{18}O > {}^{17}O > {}^{16}O > {}^{14}C > {}^{13}C > {}^{12}C > {}^{3}H > {}^{2}H > {}^{1}H$ Lowest Priority

Reule 3 : if two or more of the atoms directly bonded to the chiral carbon are identical, the atomic number of the next atom is used for priority assignment. If these atoms also have identical atoms attached to them, priority is determined at the first point of difference along the chain. The atom that has attached to it an atom of higher priority gets the higher priority.

Highest Priority $\overset{(17)}{-CH_2Cl} > \overset{(8)}{-CH_2OH} > \overset{(7)}{-CH_2NH_2} > \overset{(6)}{-CH_2CH_3} > \overset{(2)}{-CH_2D} > \overset{(1)}{-CH_2H}$ Lowest Priority





atome de plus grand Z → groupement prioritaire

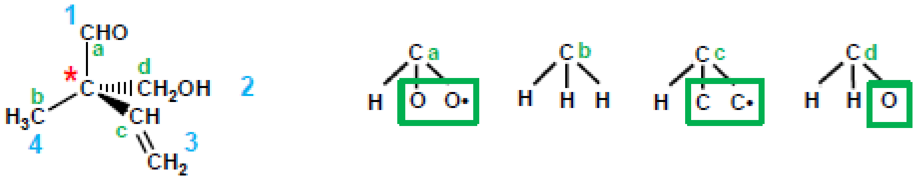
Plus grand nombre d'atome prioritaire → groupement prioritaire

Indétermination : chaîne prioritaire de chaque groupe

→ groupement prioritaire

*Reule **4** :* In the case of double or triple bonds, atoms participating in the double or triple bond are considered to be bonded to an equivalent number of similar atoms bysingle bonds, that is, atoms of double and triple bonds are replicated.

Multiple (double or triple)bonds are assumed to have the same number of single-bonded atoms..



a. Geometric isomerism:

Geometrical isomers occurs as a result of restricted rotation about a carbon-carbon bond. This is also called cis-trans isomerism.

This isomerism exhibited by variety of compounds such as compound containing double bond C=C, C=N, N=N, compound containing cyclic structure or compound containing restricted rotation due to steric hindrance.

- assigning configuration to alkenes:

Two systems such as **cis/trans system and E/Z system** can be used to designate the configurations of alkenes

E/Z system : This system can be used to specify the configuration about any carbon-carbon double bond unambiguously by using a set of priority rules. This system is devised in 1964 by **R.S.Cahn, C.K.Ingold and V.Prelog.**

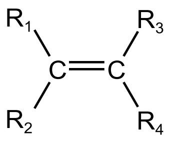
Z derived from German ,zusammen = together, whereas, **E** from German, entgegen = opposite

- *E*-alkenes have the groups of highest priority on the opposite sides
- *Z*-alkenes have the groups of highest priority on the same sides.

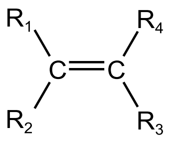
The E/Z system is based on a set of "**priority rules**", which allow you to rank any groups.

The general strategy of the E/Z system is to analyze the two groups at each end of the double bond. At each end, rank the two groups, using the CIP priority rules. Then, see whether the higher priority group at one end of the double bond and the higher priority group at the other end of the double bond are on the same side (Z, from German zusammen = together) or on opposite sides (E, from German entgegen = opposite) of the double bond.

A compound of formula R1R2C=CR3R4 is in fact common to two stereoisomers. Indeed, unlike the single bond, the double bond C=C does not allow rotation. The 2 alkenes below are therefore distinct and different molecules, which are therefore not in equilibrium.

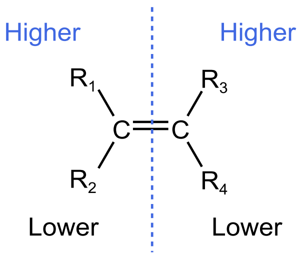


stéréo-isomère 1

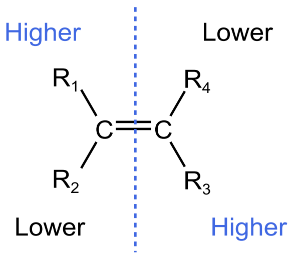


stéréo-isomère 2

To assign E/Z system, first determine the groups of highest priority on each carbon. If the two highest priority groups are on the same side of the double bond, the configuration is Z. If they are on opposite side of the double bond then the configuration is E.

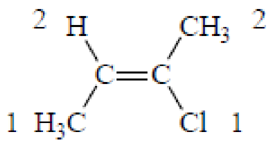


Z- stereo-isomer

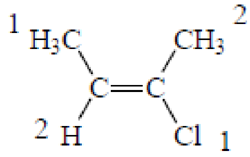


E-stereo-isomer

Exemples :

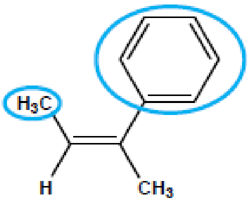


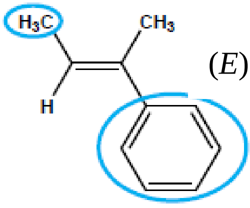
(Z)-2-chlorobut-2-ène



(E)-2-chlorobut-2-ène

(*Z*)-2-phenylbut-2-ene





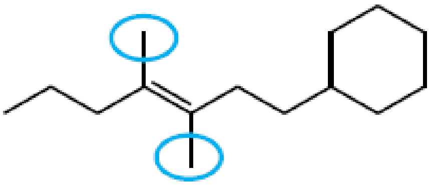
(*E*)-2-phenylbut-2-

Note: *The cis/trans notation can optionally be used to designate the stereochemistry of a double bond (it nevertheless remains less general than the Z/E notation since it can only be applied if the two carbons of the double bond have identical substituents).*

Examples :

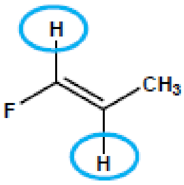
cis

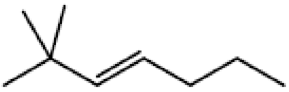
trans



trans

trans



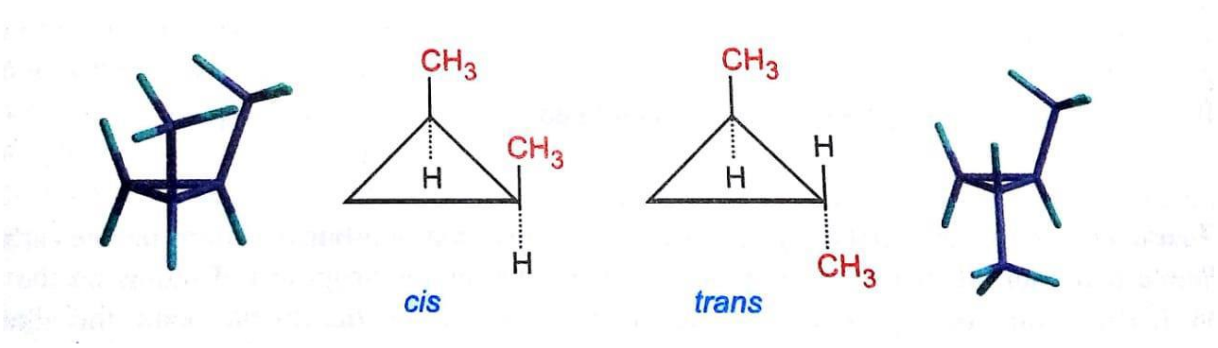


trans

- **Cis/Trans Isomerism in cyclic compounds :**

Geometric isomerism is also possible in cycloalkanes. There can be no rotation about carbon-carbons ingle bonds forming a ring because rotation would break the bonds and break the ring.

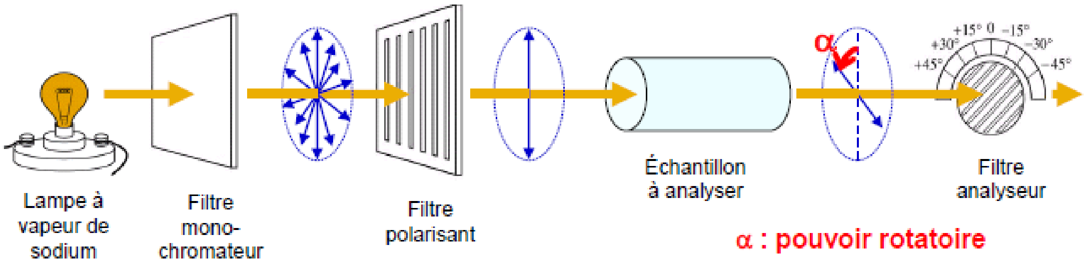
For example 1,2-dimethyl cyclopropane exist in two isomeric forms



b. Optical (configurational) isomerism:

Activité optique :

We know that ordinary lights are composed of rays of different wavelengths vibrating in all directions perpendicular to the path of its propagation. These vibrations can be made to occur in a single plane by passing ordinary light through the polarizing Nicol prism. Such light whose vibrations occur in only one plane is called plane polarized light



Compounds which rotate the plane of polarized light are called optically active compounds and this property is known as optical activity. Rotation of plane of polarized light can be of two types.

- **Dextrorotatory** : If the compound rotates the plane of polarization to the right(clockwise) it is said to be dextrorotatory (Latin: dexter-right) and is denoted by (+), or ‘d’.
- **Laevorotatory** : If the compound rotates the plane of polarization to the left(anticlockwise) it is said to be laevorotatory (Latin: laevus-left) and is denoted by (-) or ‘l’

The change in the angle of plane of polarization is known as optical rotation. The optical rotation is detected and measured by an instrument called polarimeter. The measurement of optical activity is reported in terms of specific rotation [α], which is given as,

$[\alpha]\ \lambda\ t = \alpha/lc$

$[\alpha]$= specific rotation

t = temperature of measurement

λ=wavelength of the light used

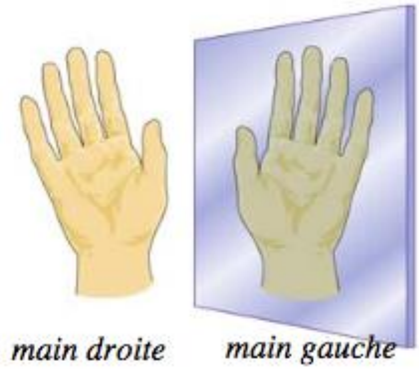
α= observed angle of rotation

l= length of sample tube in decimeter

c=concentration of the sample in g/mL of solution

- Chiralité :

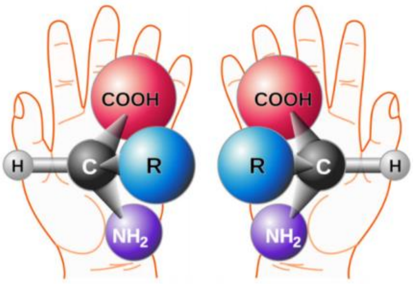
The word chiral **(**Greek word Chier,meaning hand) is used for those objects which have right-handed and left-handed forms, i.e., molecules which have “handedness” and the general property of “handedness” is termed chirality. An object which is not superimposable upon its mirror image is chiral.



The term Achiral :

Object and molecules which are superimposable on their mirror images is achiral. Achiral molecule has internal plane of symmetry, a hypothetical plane which bisects an object or molecule into mirror-reflactive halves. An object or molecule with an internal plane of symmetry is achiral.

The term Asymmetric center and chiral center : Three terms are used to designate, a carbon atom bonded tetrahedrally to four different substituents in a chiral molecule: Asymmetric atom, chiral center or stereocenter.

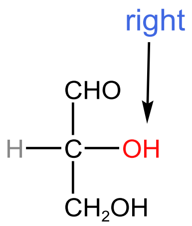


NOMENCLATURE OF OPTICAL ISOMERS

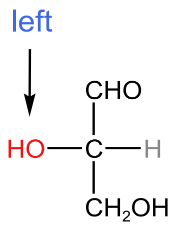
Following three nomenclatures are used for optically active compounds:

- ***Relative configuration :*** d/ l system of nomenclature

This nomenclature is mainly used in sugar chemistry or optically active polyhydric carbonyl compounds. This is a relative nomenclature because all the configurations described with respect to glyceraldehydes.

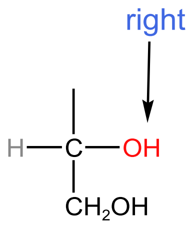


D-(+)-glyceraldehyde



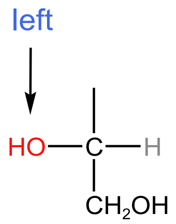
L-(+)-glyceraldehyde

All sugars whose Fischer projection formula shows the OH group on the right hand side of the chiral atom belong to the D-series.



D-series.

Similarly, if OH is on the left hand side, then the sugar belongs to the L-series.



L-series

- It must be noted that there is no relation between sign of rotation and (+, - or *d,l*) and configuration (D and L).
- Any compound that can be prepared from, or converted in to D(+) glyceraldehydes will belong to D-series and similarly any compound that can be prepared from, or converted in to L(-) glyceraldehydes will belongs to the L-series.

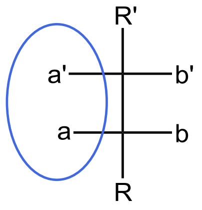
Erythro and *threo* system of nomenclature

This nomenclature is mainly used only in those compounds which have only two chiral carbons and the following structures:

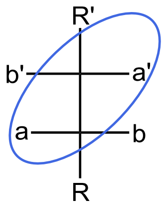
R’-Cab-Cab-R’’ or R’-Cab-Cbc-R’’

i.e. out of six substituent on two asymmetric carbons, at least one should be same in both the carbons.

When two higher groups in fisher projection formula are drawn on the same side of vertical line, the isomer is called *erythro* form; if these are placed on the opposite sides the isomer is said to be *threo* form.

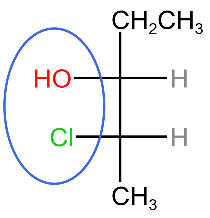


erythro form

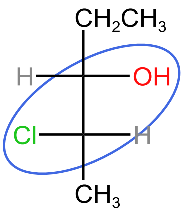


threo form

Example :



erythro-2-chloropentan-3-ol



threo-2-chloropentan-3-ol

R/S Nomenclature :

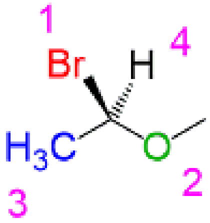
The order of rearrangement of four groups around a chiral carbon is called the absolute configuration around that atom. System which indicates absolute configuration was given by three chemists R.S. Cahn, C.K. Ingold and V. Prelog. This system is known as (*R*) and (*S*).

- *R :* comes from the Latin rectus (means right) **clockwise**
- *S :* comes from the Latin sinister (means left) . **counterclockwise**

The R, S nomenclature involves two steps:

Step I: The four ligands (atom or groups) attached to the chiral centre are assigned a sequence of priority a **priority based on** rules the Cahn-Ingold-Prelog system.

Eg :

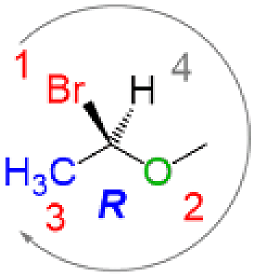


Step 2:

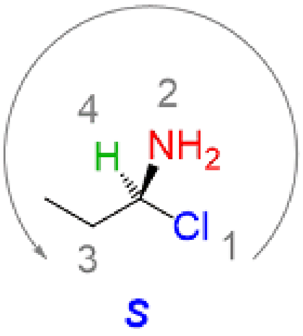
Draw an arrow starting from priority one and going to priority two and then to priority 3:

- **R and S When the lowest priority is a** dashed **(away from the viewer)**

If the **arrow goes clockwise,** like in this case, the absolute configuration is ***R***.

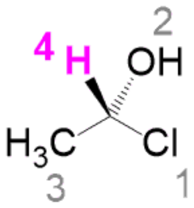


As opposed to this, if the arrow goes **counterclockwise** then the absolute configuration is ***S***.

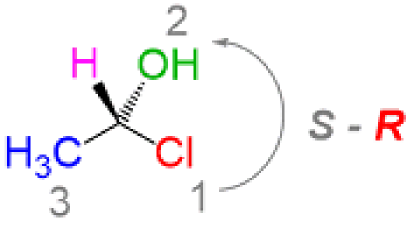


- **R and S When the lowest priority is a wedge :**

Group four pointing forward



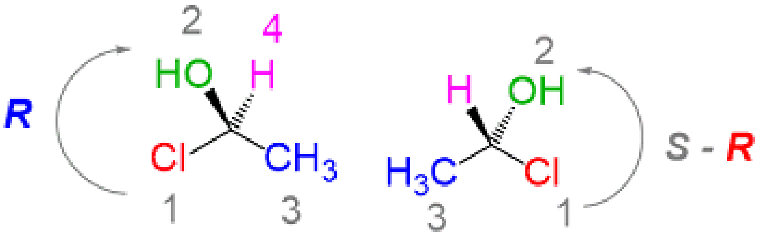
Here, you leave the molecule as it is with the **hydrogen pointing towards you**. Continue as you would normally do by assigning the priorities and drawing the arrow.



The only thing you have to do at the end is change the result from *R* to *S* or from *S* to *R*.

In this case, the arrow goes counterclockwise but because the **hydrogen is pointing towards us, we change the result from *S* to *R***.

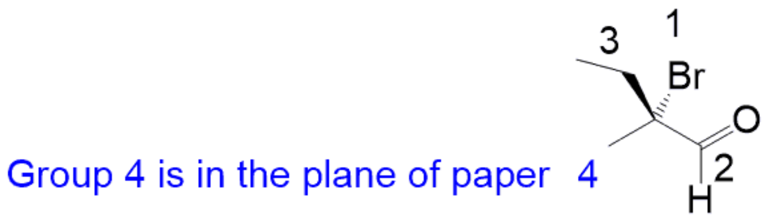
Of course, either approach should give the same result as this is the same molecule drawn differently.



R and S When the lowest priority is not a Wedge or a Dash

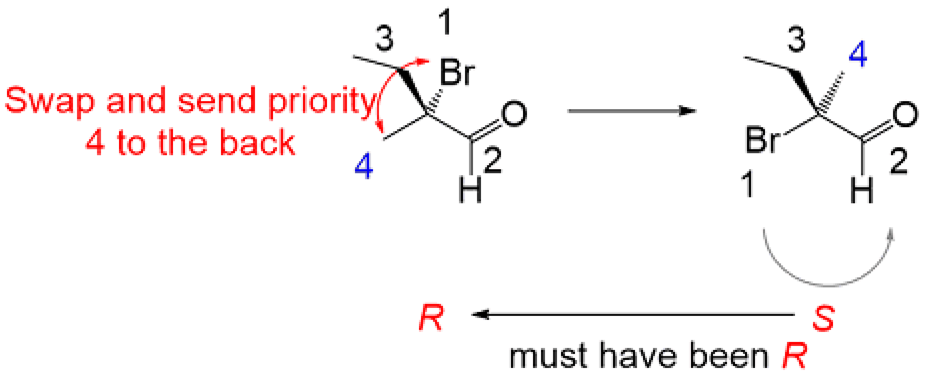
There is a third possibility for the position of group 4 and that is when it is neither pointing away or towards you. This means we cannot determine the configuration as easily as if the lowest priority was pointing towards or away from us, and then switch it at the end as we did when group 4 was a wedge line.

As an example, what would be the configuration of this molecule?



For this, there is this simple yet such a useful trick making life a lot easier. Remember it:

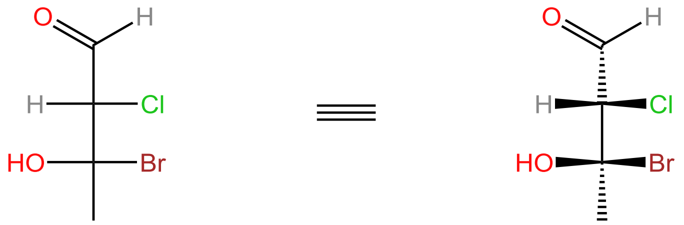
The **lowest priority group is in the drawing plane**, so what we can do is swap it with the with the one that is pointing away from us (Br). After determining the *R* and *S* we switch the result since swapping means changing the absolute configuration and we need to switch back again.



The arrow goes counterclockwise indicating *S* configuration and this means in the original molecule it is *R*.

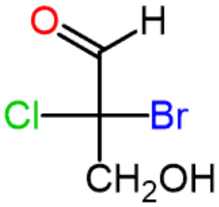
R and S configuration on Fischer projection :

To determine the *R* and *S* configuration of the chiral carbon atoms in a Fischer projection, we need first recall the concept of the Fischer projection. And that is; the **horizontal groups are pointing towards the viewer (wedge)**, and the groups on the **vertical axis are pointing away from the viewer (dash)** even though all the bonds are shown in plain lines.

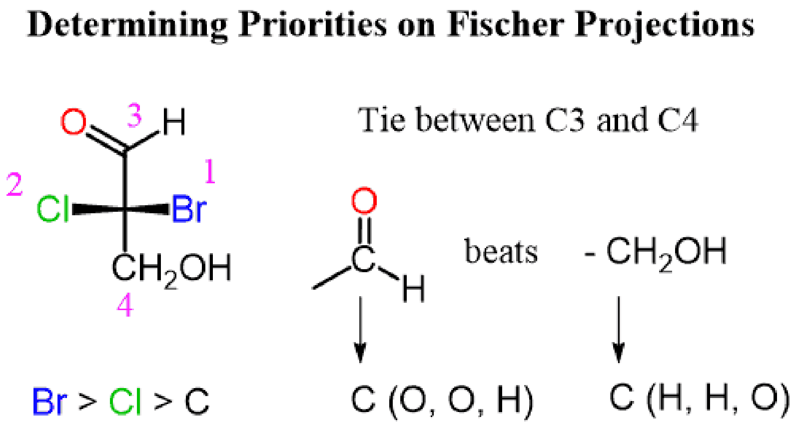


The rules for determining the absolute configurations are all the same that we learned in wedge and dash representation

For example, lets determine the configuration of the chiral carbon in the following Fischer projection:

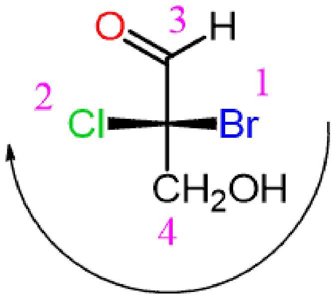


Step 1 : Assign the priorities of the four groups:

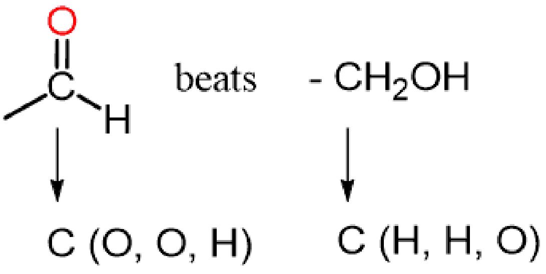


Notice that the aldehyde group has a higher priority than the alcohol because the C=O double is counted as if the carbon is connected to two oxygen atoms.

Step 2 : Determine the direction of the arrow; if the lowest priority is pointing away from you (vertical position), then the configuration is as it should be: clockwise (CW)-*R*, counterclockwise (CCW)-*S:*



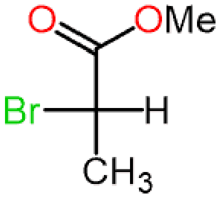
CW - *R*



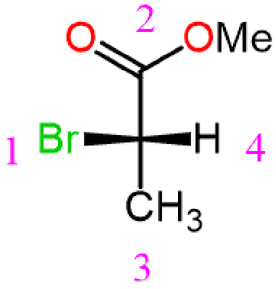
Priority #4 is pointing back ✓

In this case, the CH_2OH group is the lowest priority and pointing away from us therefore, the configuration is based on the direction of the arrow.

Let's now consider an example where the lowest priority is on a horizontal position (wedge line):

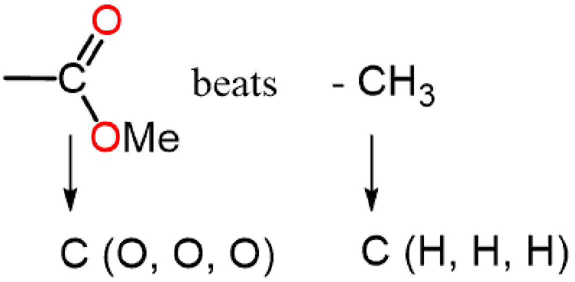


Step 1 : Assign the priorities:

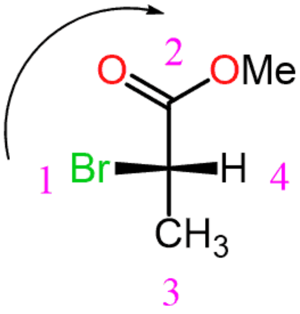


Br > C

Tie between C2 and C3



Step 2 : Determine the direction not the arrow and change the result (*R* to *S* or *S* to *R*) because the lowest priority is pointing towards as:



H is pointing forward -
R and *S* must be switched

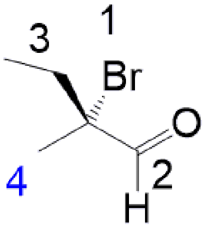
CW - *R*, but **must be switched to *S*** ✓

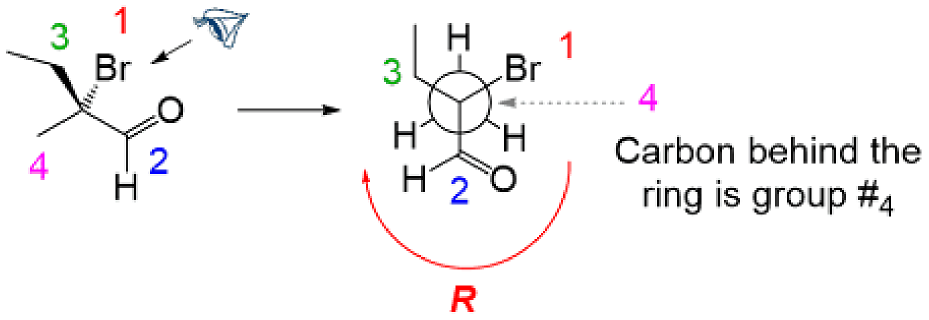
- **determined the *R* and *S* configuration of a chiral carbon in Newman projections :**

To determine the ***R* and *S* configuration** of a chiral carbon in Newman projections, we need to look through the bond such that the lowest priority group is pointing back.

Example :

Group 4 is in the plane of paper



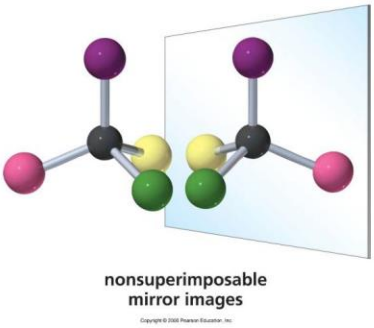


The lowest priority group is pointing back and therefore, the **clockwise direction** of the arrow indicates an ***R* configuration**.

Enantiomers and Diastereoisomers :

Stereoisomers : Isomers having the same molecular formula but different spatial arrangement of their atoms are known as stereoisomer. They are of following types:

- **Enantiomers**: Stereoisomers which are non superimposable mirror images of each other are called enantiomers. Chirality is necessary and sufficient condition for existence of enantiomers. These always exist as discrete pairs.


nonsuperimposable mirror images

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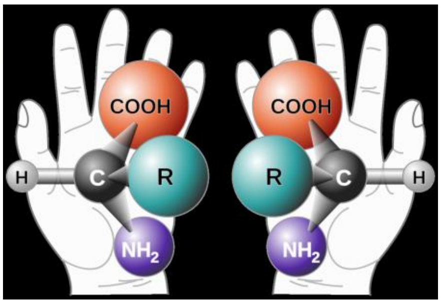
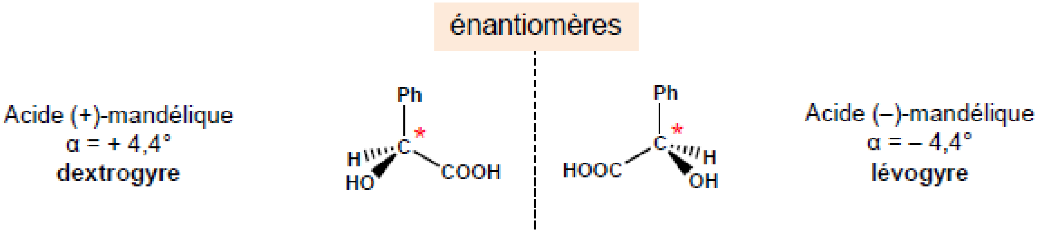


Properties of enantiomers:

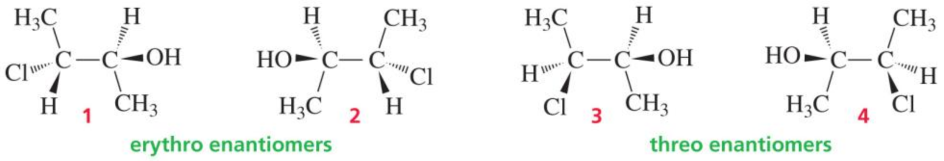
The main properties of enantiomers are given as follow

- Enantiomers always exist in pair
- Enantiomers are non-super imposable mirror image to each other
- Enantiomers have same physical properties (like boiling point, melting point, solubility, density, viscosity, refractive index etc.)and chemical properties in achiral environment
- Each enantiomers have opposite behavior with respect to plane polarized light, if one of them will rotate the plane polarized light towards right hand direction then definitely the other will rotate the plane polarized light towards left hand direction.
- Each enantiomers shows the same chemical reactivity with achiral reagent; however they have different reactivity with chiral reagent.

Example



- **Diastereomers:** Stereoisomers that are not mirror images of each other are called diastereomers.



perspective formulas of the stereoisomers of 3-chloro-2-butanol (staggered)

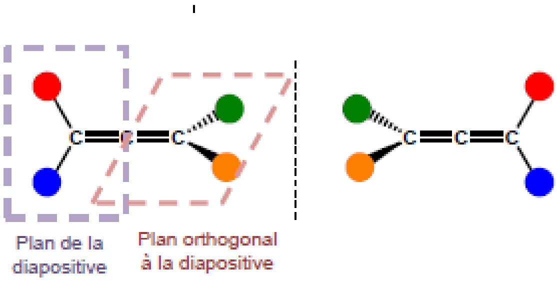
- **Properties of diastereomers:**

The main properties of diastereomers are given as follows:

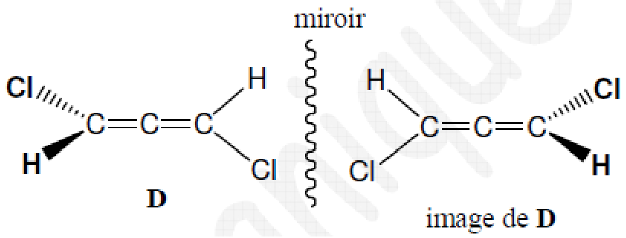
- All the stereoisomers except enantiomers are diastereomers.
- Diastereomers have different physical properties like boiling point, melting point, density, solubility, density, viscosity, refractive index etc.
- Diastereomers have different chemical properties like rates of reactions, reactivity even in achiral reaction medium.
- This difference in physical and chemical properties of diastereomers is very useful in the separation of enantiomers from their mixture.

Note : nembre of stereoisomere = 2^n / n : nembre of C*

- **Stereochemistry of Allenes :** When three or more adjacent carbon atoms in a molecule are bonded by double bonds, the compounds is called cumulene or said to have cumulative double bonds. Allene is the simplest example of this class. Allenes are chiral and they have nonsuperimposable mirror images and exist as enantiomers although they have no chiral centre.

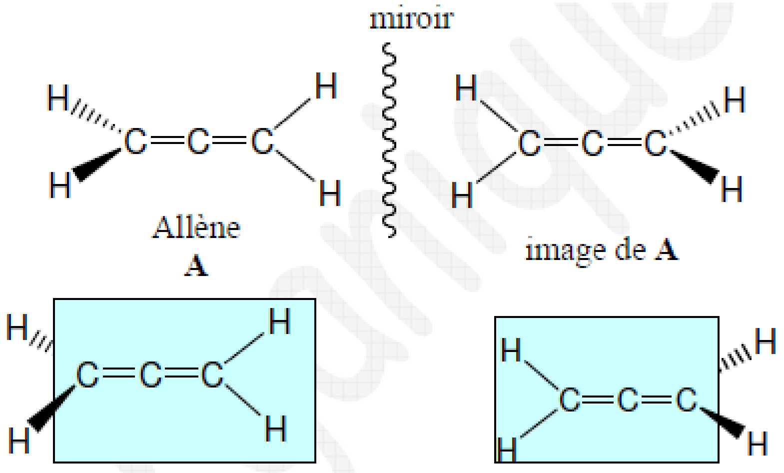


Example 1 : 1,3-dichloroallene ClCH=C=CHCl :



D image de **D**

Example 2 : Allene: $CH_2=C=CH_2$:



Allène **A** image de **A**

Racemic mixture (racemates)

A Racemic mixture is an equimolar mixture of a pair of enantiomers. The racemic mixture or racemates are optically inactive due to mutual or external compensation of two enantiomeric constituents. Racemic mixture in liquid and vapor phase shows physical properties (like boiling points, density, refractive index etc.) identical to those of pure enantiomers. However, the solid phase enantiomeric mixtures have some properties different from the pure enantiomers.

Remember: *Racemic mixture is not a meso compound; since both are optically inactive. The racemic mixture is an equimolar mixture of two enantiomers whereas meso is a single compound. Meso compounds are optically inactive because of the internal compensation; however, the racemic mixtures (racemates) are optically inactive because of the external compensation.*