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AT QENA

Stereochemistry of carbon compound

اعداد

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العام الجامعي

٢٠٢٢-٢٠٢٣

Constitutional isomer

Stereoisomer

Geometrical isomer

Geometrical isomer in unsaturated compound

Geometrical isomer in oxime compound

Geometrical isomer in carboxylic acid

Geometrical isomer in cyclic compound

Determination of the conformation of the geometrical isomer

Optical isomer

Conformational isomer

Stereochemistry

Stereochemistry, study the relative spatial arrangement of [atoms](#) that form the structure of [molecules](#) . The study of stereochemistry focuses on [stereoisomers](#), which by definition have the same molecular formula and sequence of bonded atoms (constitution), but differ in the three-dimensional orientations of their atoms in space.

Stereochemistry

Definition of isomers :-

Isomers are compound that have the same molecular formula but different in chemical structure .

(isomers can divided into two type)

stereoisomers isomer

constitutional isomer

→ 1- optical isomers

→ 2- conformational

→ 3- Geometrical

→ isomers

→ 1- skeletal isomers

→ 2- positional isomers

→ 3-functional group

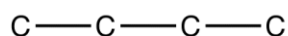
→ 4-tautomers isomers

Constitutional isomer

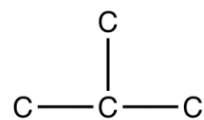
1- Skeletal isomer:-

Skeletal isomers are constitutional isomers that have the same functional groups but differ from each other in the connectivity of the carbon skeleton.

Stereochemistry

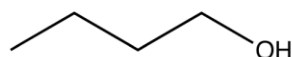


carbon skeleton
of 1

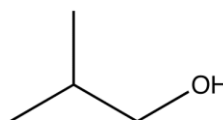


carbon skeleton
of 2

Example (1):- Butyl alcohol (1) and isobutyl alcohol (2) are constitutional isomers containing the same functional groups, namely the alcohol group.



1



2

Example (2):- (1) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$ | (3) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$

1-chlorobutane

Cl

(2) $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{Cl}$

2-chlorobutane

CH₃

CH₃

1-chloro-2-methylpropane

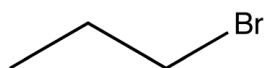
(4) $\text{CH}_3\text{CCl}(\text{CH}_3)_2$

CH₃

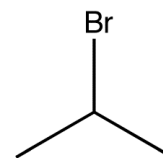
tertiary butyl chloride

- **Positional isomers :-**
- **Positional isomers** are constitutional **isomers** that have the same carbon skeleton and the same functional groups but differ from each other in the location of the functional groups on or in the carbon chain. eg. Propyl bromide (1) and isopropyl bromide (2)

Stereochemistry

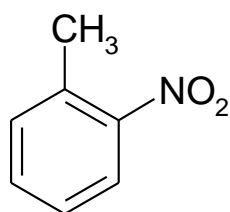


1

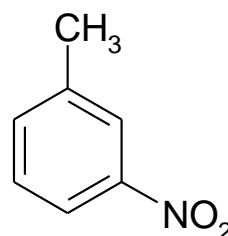


2

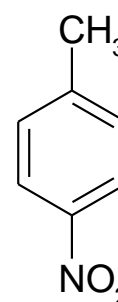
Example (2) :- also in aromatic compound



o-nitrotoluene



m-nitrotoluene

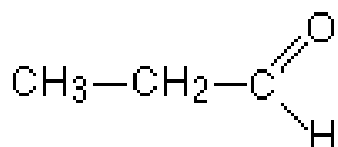


p-nitrotoluene

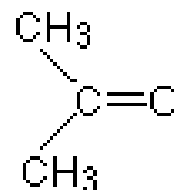
Functional group isomers :-

In this variety of structural isomerism, the isomers contain different functional groups - that is, they belong to different families of compounds (different homologous series). For example, a molecular formula C₃H₆O could be either propanal (an aldehyde) or propanone (a ketone).

Stereochemistry



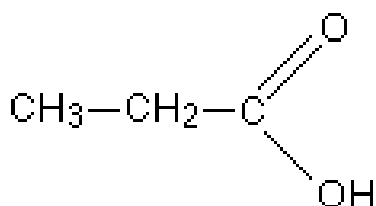
propanal



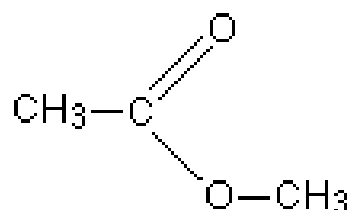
propanone

Example :-

- Another common example is illustrated by the molecular formula $\text{C}_3\text{H}_6\text{O}_2$. Amongst the several structural isomers of this are propanoic acid (a carboxylic acid) and methyl ethanoate (an ester).



propanoic acid



methyl ethanoate

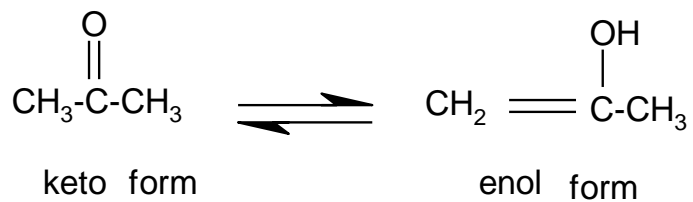
- **Tautomerism**

Tautomers are isomers of a compound which differ only in the position of the protons and electrons. The carbon skeleton of the compound is unchanged. A reaction which involves simple proton transfer in an intramolecular fashion is called a tautomerism. Keto-enol tautomerism is a very common process,

Stereochemistry

- Typically the 'keto' form of the compound is more stable, but in some instances the 'enol' form can be the more stable.

examples :-



2. Hybridization of carbon

Before studying the stereochemistry it must be regards to the hybridization.

2.1 Carbon sp^3 Hybridization:

When a hydrogen atom becomes part of a molecule, it uses its $1s$ atomic orbital for bonding. The situation with the carbon atom is different. Carbon atom has six electrons two electrons in the $1s$ orbital. There are four atomic orbitals at the second energy level: one $2s$ and three $2p$. However, the four remaining electrons will be distributed as two electrons in $2s$ orbital and two electrons in $2p$ orbitals. Hence, the carbon atom in this situation should be a divalent, but in fact the carbon atom has four equivalent orbitals ready to bond with 4 hydrogen atoms and the bond angle between each C-H bond is 109.5° .

These four equivalent orbitals arise from complete hybridization (one $2s$ orbital and three $2p$ orbitals) to yield four equivalent sp^3 orbitals. For this to be accomplished of the $2s$ electrons must be promoted to the empty $2p$ orbital. This promotion requires energy (96 Kcal/mole).

The four sp^3 orbitals have equal energies slightly higher than that of the $2s$ orbital, and slightly lower than that of the $2p$ orbitals. Each one of the sp^3 orbitals contains one electron for bonding (Fig. 2.1).

Stereochemistry

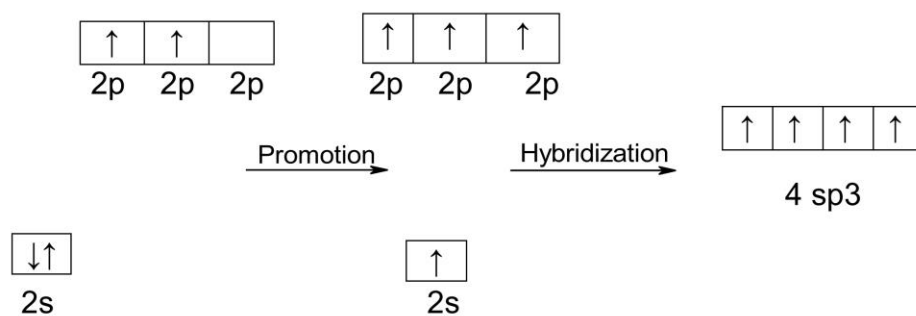
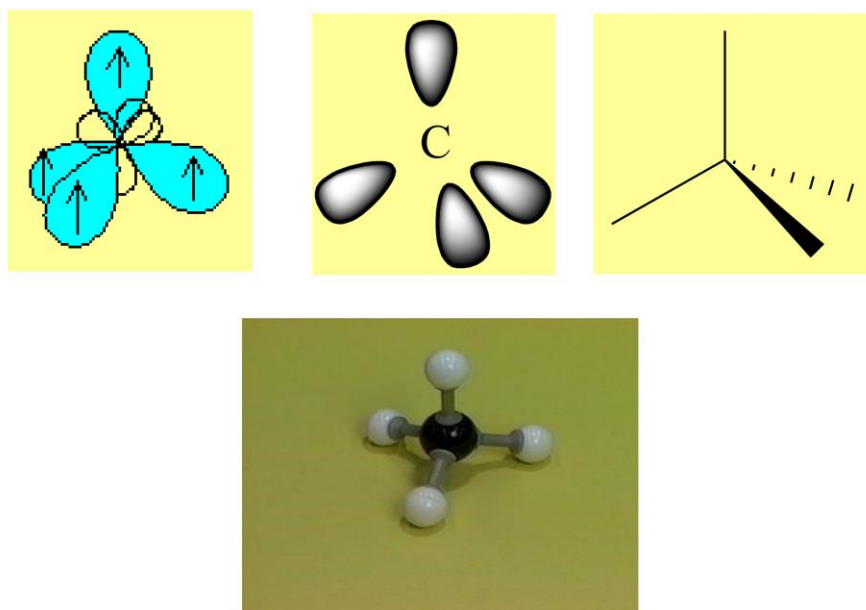


Fig. 2.1

Ex: In methane (CH₄):

Each **sp³** orbital of carbon overlaps with **1s¹** orbital of hydrogen atom to form four **sp³** (σ) sigma bonds and represented as a regular tetrahedron. (Fig. 2.2)



Tetrahedron structure for sp³ carbon

Ball and Stick Model of Methane to Emphasize Bonding

Fig. 2.2

2.2 Carbon sp² Hybridization:

Stereochemistry

When carbon atom is bonded to another atom by a double bond, the carbon atom is in the sp^2 -hybrid state.

To form sp^2 bonding orbitals, carbon hybridizes its $2s$ orbital with only two of its $2p$ orbitals. One p orbital remains unhybridized on the carbon atom. Because three atomic orbitals are used to form the sp^2 orbitals (Fig. 2.3).

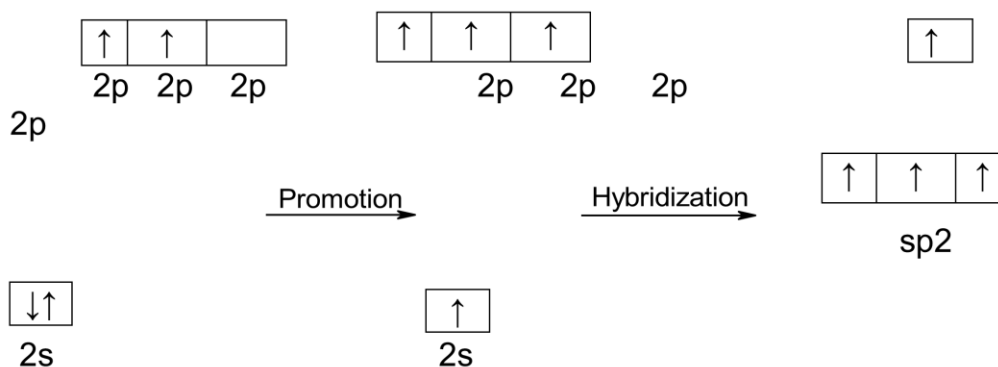


Fig. 2.3

The sp^2 orbitals have a shape similar to that of sp^3 orbitals and lie in the plane with angle of 120° between them and each sp^2 orbital contains one electron for bonding. An sp^2 hybridized carbon atom is said to be a trigonal. the one unhybridized p orbital, which is perpendicular to the sp^2 plane (Fig. 2.4).

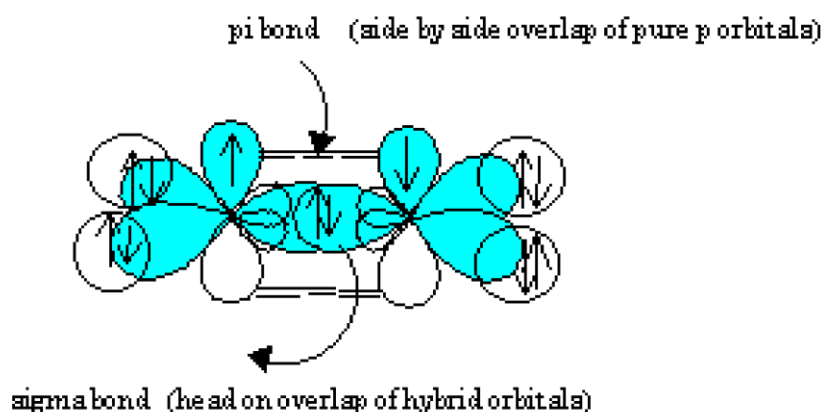


Fig. 2.4

Ex: In ethylene ($\text{CH}_2=\text{CH}_2$):

Two sp^2 carbons are joined by (σ) sigma bond formed by the overlap of one sp^2 orbital from each carbon atom. Each carbon atom still has two sp^2 orbitals left for bonding with hydrogen. Each p orbital contains one electron, since the two p orbitals overlap side-to-side to yield π (π) bond and locate above and below the plane of the (σ) sigma bonds. The (π) bond is the second bond of the double. (Fig. 2.5)

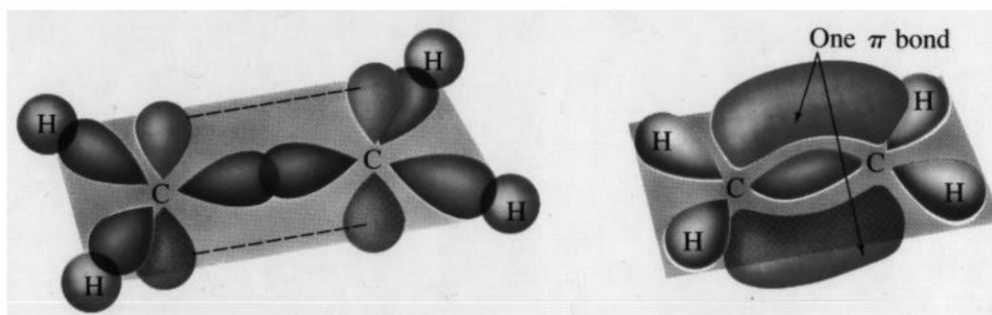


Fig. 2.5

2.3 Carbon sp Hybridization:

When a carbon atom is joined to only other atoms, as in acetylene ($\text{CH}\equiv\text{CH}$), its hybridization state is sp . One $2s$ orbital with only one $2p$ orbital to form two sp -hybrid orbitals and two unhybridized $2p$ orbitals remain, each with one electron. (Fig. 2.6)

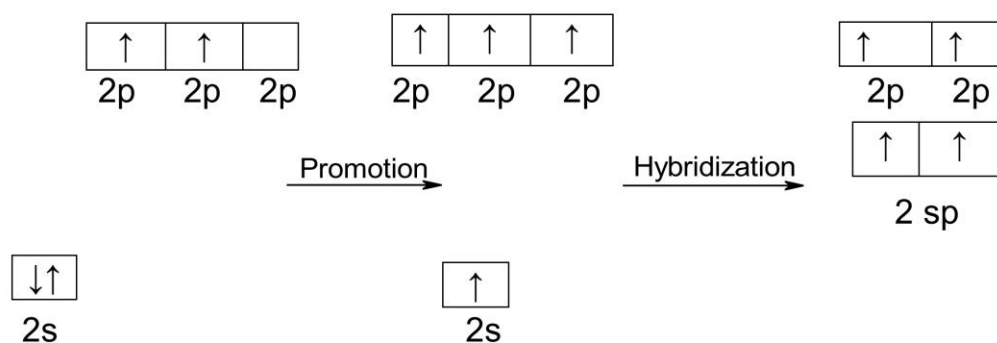


Fig. 2.6

Stereochemistry

The two sp orbitals lie in a straight line with an angle of 180° between them. The two p orbitals are perpendicular to each other and to the line of sp orbitals.

Ex: In acetylene ($\text{CH}\equiv\text{CH}$):

The two carbon atoms are joined by an $sp-sp$ (σ) bond. Each carbon is also bonded to a hydrogen atom by an $sp-s$ (σ) bond. The two p orbitals of one carbon then overlap with the two p orbitals of the other carbon to form two (π) bonds. (Fig. 2.7)

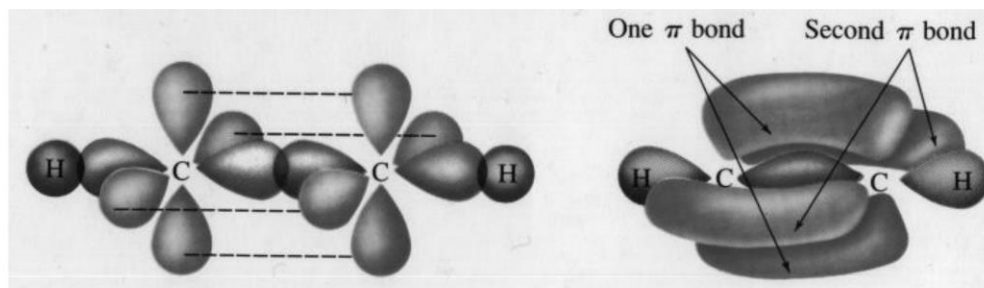


Fig. 2.7

Activities: Draw in space the following molecules in three dimensions according to the hybridization angles;

a- CH_3COOH b- $\text{CH}_3\text{-C}\equiv\text{C-CH}_2\text{-NH}_2$ c- $\text{CH}_2=\text{CHCOCH}_3$

Summary

- **Carbon sp^3 Hybridization:** in which 4 equivalent orbitals arise from complete hybridization (one $2s$ orbital and three $2p$ orbitals) to yield four equivalent sp^3 orbitals have equal energies with angle of $109^\circ 28'$ and each one contains one electron for bonding.
- **Carbon sp^2 Hybridization:** in which 3 equivalent orbitals arise from complete hybridization (one $2s$ orbital and two $2p$ orbitals) to yield 3 equivalent sp^2 orbitals with angle of 120° and one p orbital remains unhybridized .

- **Carbon sp Hybridization:** in which 2 equivalent orbitals arise from complete hybridization (one 2s orbital and one 2p orbitals) to yield 2 equivalent sp orbitals with angle of 180° and two p orbitals remain unhybridized .

Geometrical isomers in carbon-carbon double bond

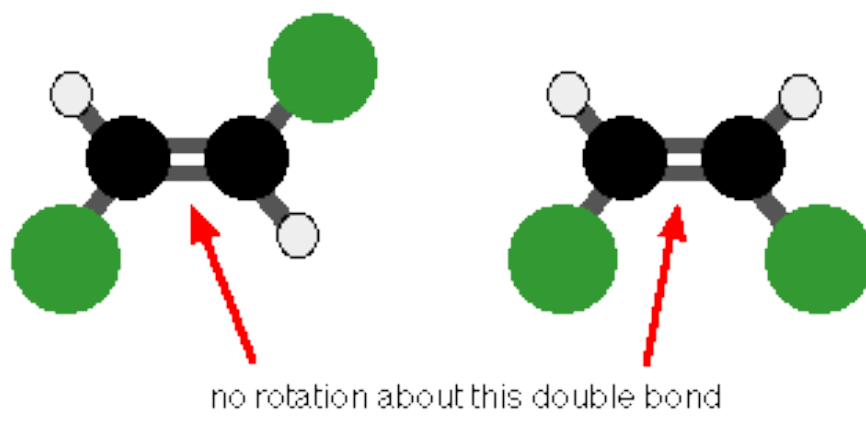
** Geometric isomers have **similar structural formulas but differ** in the arrangement of groups at a single atom, at double bonds, or in rings.

The carbon-carbon double bond won't rotate and so you would have to take the models to pieces in order to convert one structure into the other one. ... Drawing structural formulae for the last pair of models gives two possible isomers

Geometric (cis / trans) isomerism:-

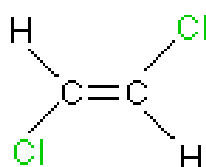
These isomers occur where you have restricted rotation somewhere in a molecule due to found carbon –carbon double bond .

Stereochemistry

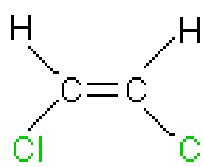


the two chlorine atoms are locked on opposite sides of the double bond. This is known as the trans isomer. (trans : from latin meaning "across" - as in transatlantic).

In the other, the two chlorine atoms are locked on the same side of the double bond. This is known as the cis isomer. (cis : from latin meaning "on this side")



trans-1,2-dichloroethene

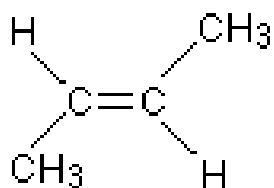


cis-1,2-dichloroethene

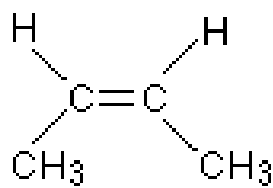
Example (1):-

- but-2-ene. In one case, the CH₃ groups are on opposite sides of the double bond, and in the other case they are on the same side.

Stereochemistry



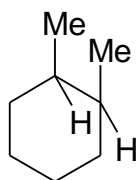
trans-but-2-ene



cis-but-2-ene

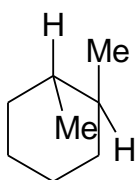
Example (2) :-

in cyclic compound .



(1)

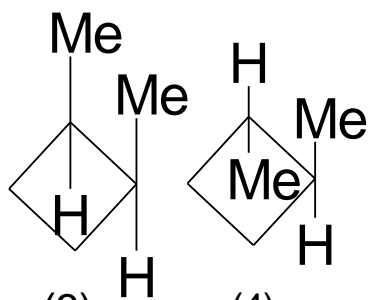
cis form



(2)

trans form

Example (3):-



(3)

cis form

(4)

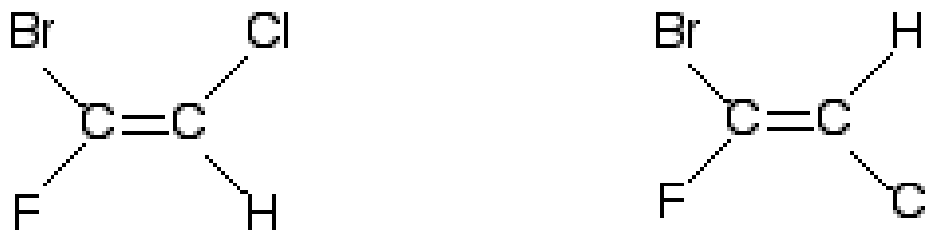
trans form

The symbols (E) and (Z)

The problem with the cis-trans system for naming geometric isomers

Stereochemistry

Consider a simple case of geometric isomerism, but There are problems as compounds get more complicated; Because everything attached to the carbon-carbon double bond is different.



How the E-Z system works

You look at what is attached to each end of the double bond in turn, and give the two groups a "priority" according to a set of rules.

Decreasing priority



Atoms: I, Br, Cl, S, P, F, O, N, C, H, lone-pair electrons.

Groups: -OCOR, -OR, OH.

-NO₂, -NR₂, -NHCOR, -NHR, -NH₂.

-COCl, -COOR, -COOH, -CONH₂, -COR, -CHO.

-C(R)₂OH, -CH(R)OH, -CH₂OH.

-CN, -C₆H₅, -C≡CR, -C≡CH, -C=CH₂, -CH(CH₃)₂.

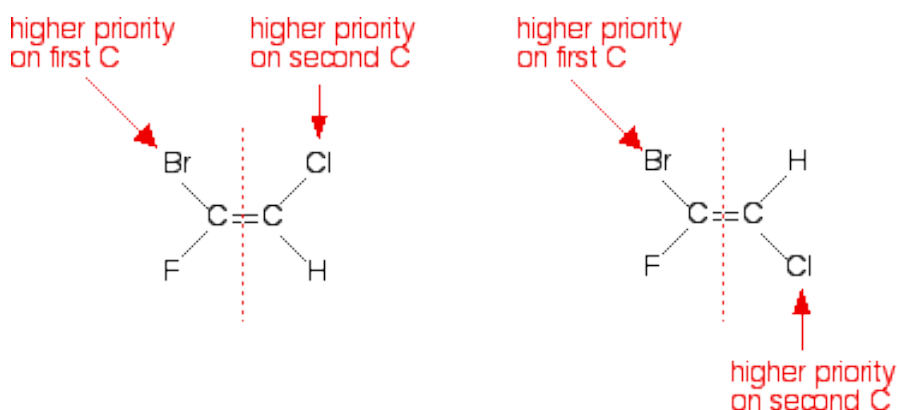
-C(R)₃, -CH(R)₂, -CH₂R, -CH₃.

Stereochemistry

group	Equivalent for priority

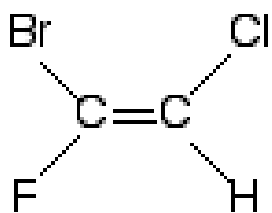
Stereochemistry

- In the example, at the left-hand end of the bond, it turns out that bromine has a higher priority than fluorine. And on the right-hand end, it turns out that chlorine has a higher priority than hydrogen.
- If the two groups with the higher priorities are on the same side of the double bond, that is described as the (Z)- isomer. So you would write it as (Z)-name of compound. The symbol Z comes from a German word (zusammen) which means together.

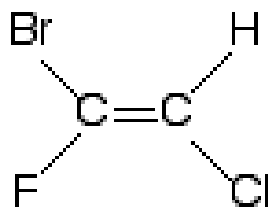


If the two groups with the higher priorities are on opposite sides of the double bond, then this is the (E)- isomer. E comes from the German (entgegen) which means opposite.

Stereochemistry

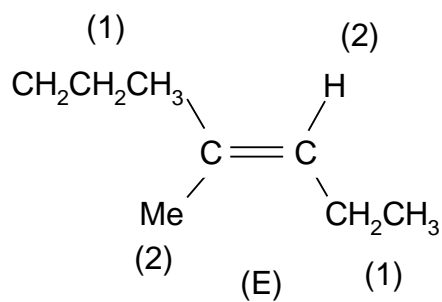
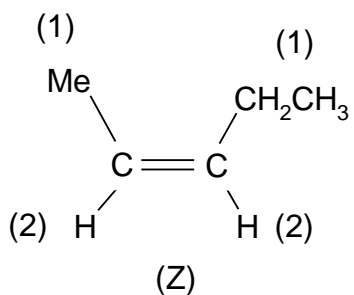


(Z)-rest_of_name



(E)-rest_of_name

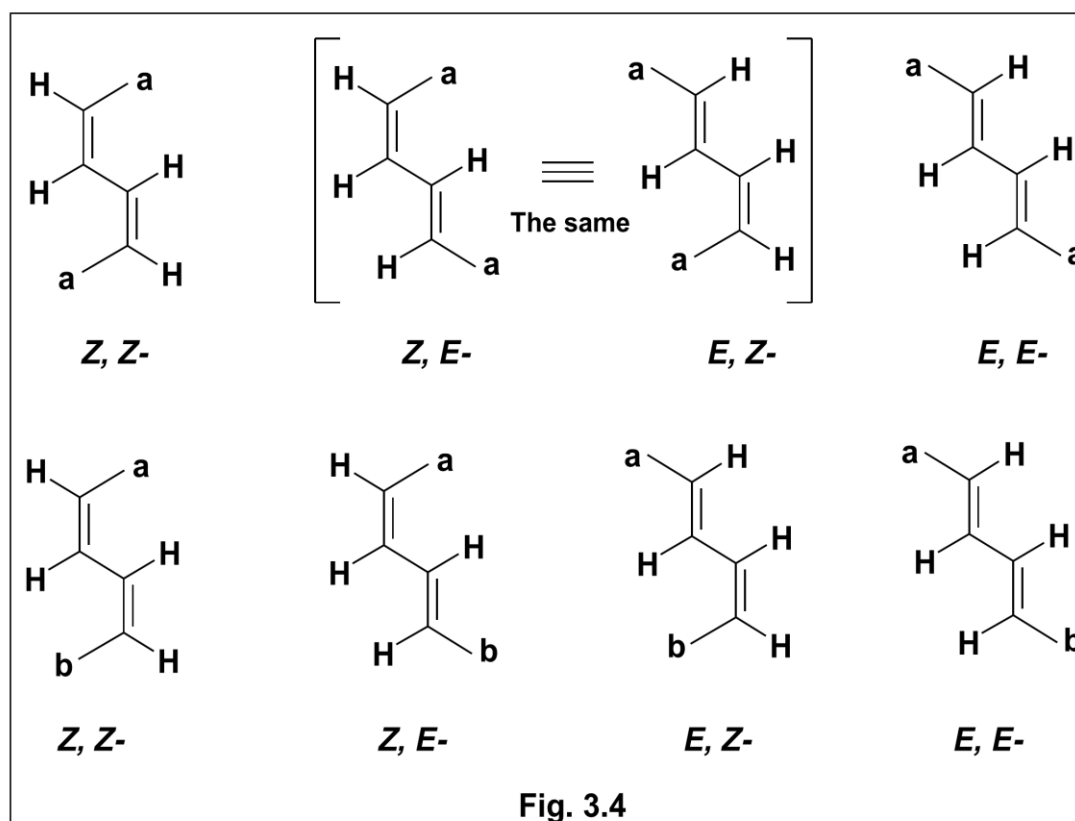
Example (1):-



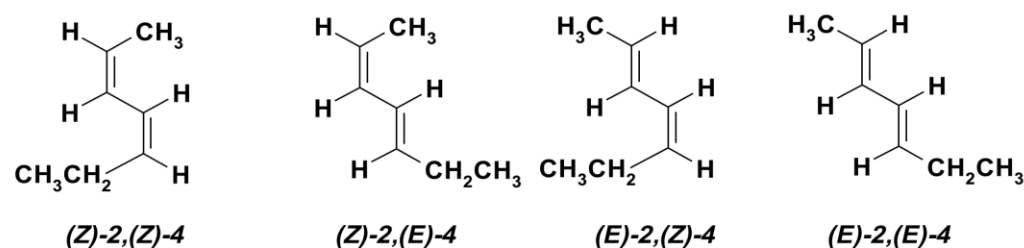
3.4 Stereoisomerism in compounds with more than C=C group

The number of geometrical isomers increase when a molecule contains more than one C=C group. If the terminal double bonds are not identical, e.g., aHC=CH-CH=CHb, a≠b. The number of geometrical isomers = 2^n , where (n) is the No. of double bonds (Fig. 3.4).

If the terminal double bonds are identical, e.g., aHC=CH-CH=CHa, the No. of isomers = 3 (Fig. 3.4).

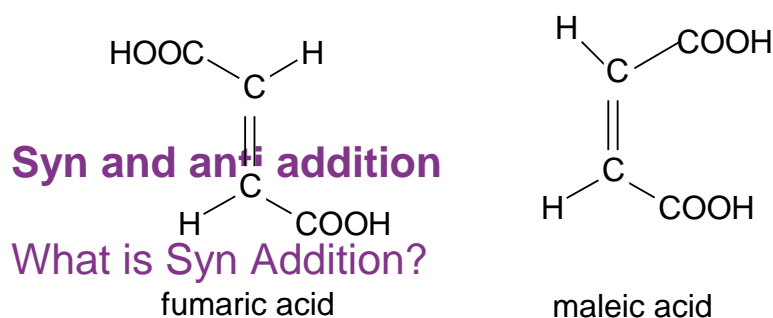


EX: *hepta-2,4-diene* is has a terminal double bonds exists as 4 geometrical isomers (Fig. 3.5).



Geometric isomers in carboxylic acid

- There are some compounds that have the same molecular formula and exist in two isomeric form . Among these compounds are malic acid and fumaric acid, and their molecular formula is C₄H₄O₄ One of them is in the form of cis and it is called malic acid and the other in the form is called trans and it is called fumaric acid.



The addition of two substituents to the same side (or face) of a double or triple bond reduces the bond order but increases the number of substituents.

The addition of two substituents to the same side of an unsaturated molecule is known as syn addition. The addition of two substituents in opposite directions is known as anti-addition. This is the major distinction between syn addition and anti addition. These addition reactions change the bond order and the number of substituents in the reactant molecule.

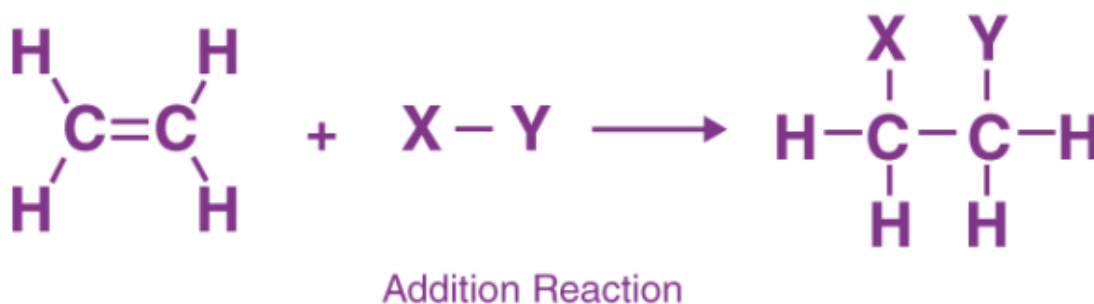
Syn and anti Addition Reaction

A syn addition is an addition reaction of an alkene or alkyne in which the net reaction is the addition of two ligands to the multiple-bonded carbon atoms from the same face of the multiple bond ,

Stereochemistry

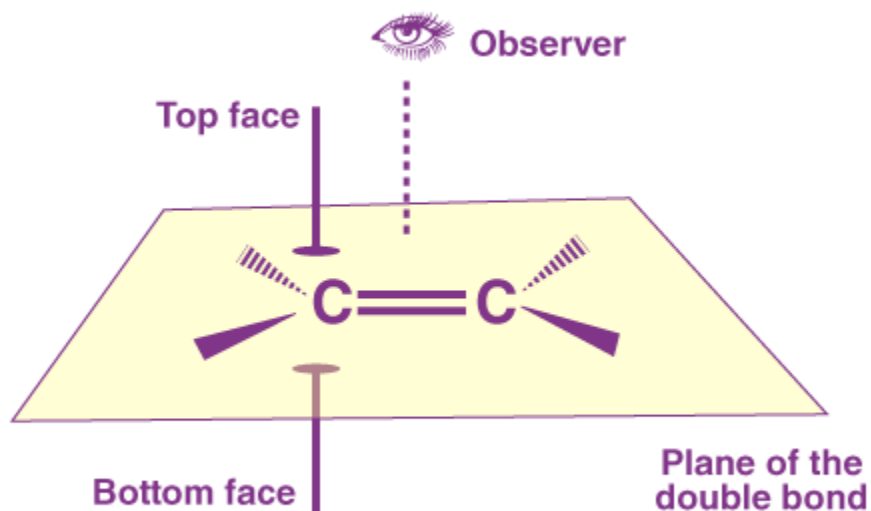
an anti addition is an addition reaction in which the net reaction is the addition of two ligands from the opposite faces of the multiple bond.

However, because a double or triple bond is frequently broken to generate the requisite single bonds, only chemical compounds with multiple bond characters can conduct an addition reaction. An addition reaction is essentially a reverse decomposition reaction, whereas a decomposition reaction is one in which one or more elements or compounds are compounded. Consider the following reaction (hydrochlorination) of propane (an alkene) as an example of an addition reaction.

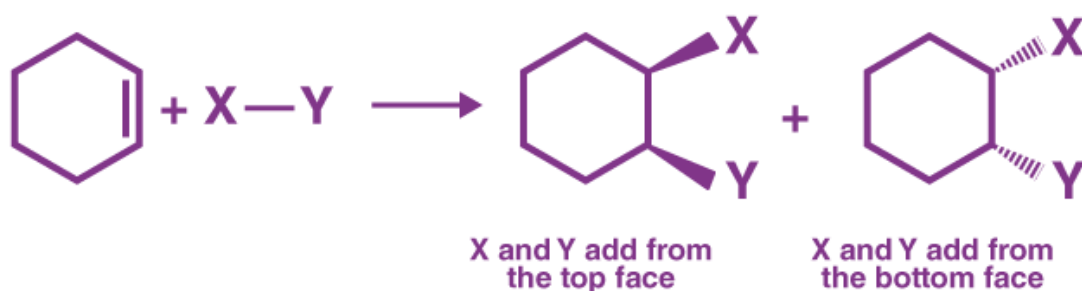


Stereochemistry of Alkene Addition Reactions

The stereochemistry of addition to a double bond is explained in terms of the plane in which the double bond and its four associated groups are located. This plane's sides are referred to as faces. The top face is the side of the plane closest to the observer, while the bottom face is the opposite side.



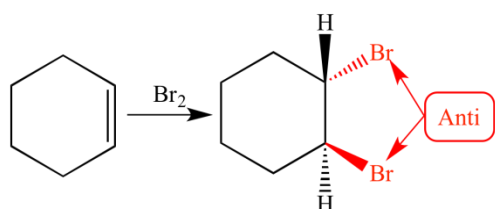
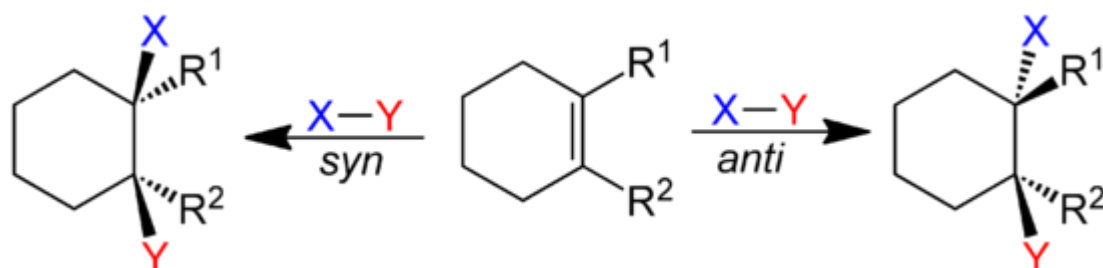
Two groups add to a double bond from the same face in a syn-addition:



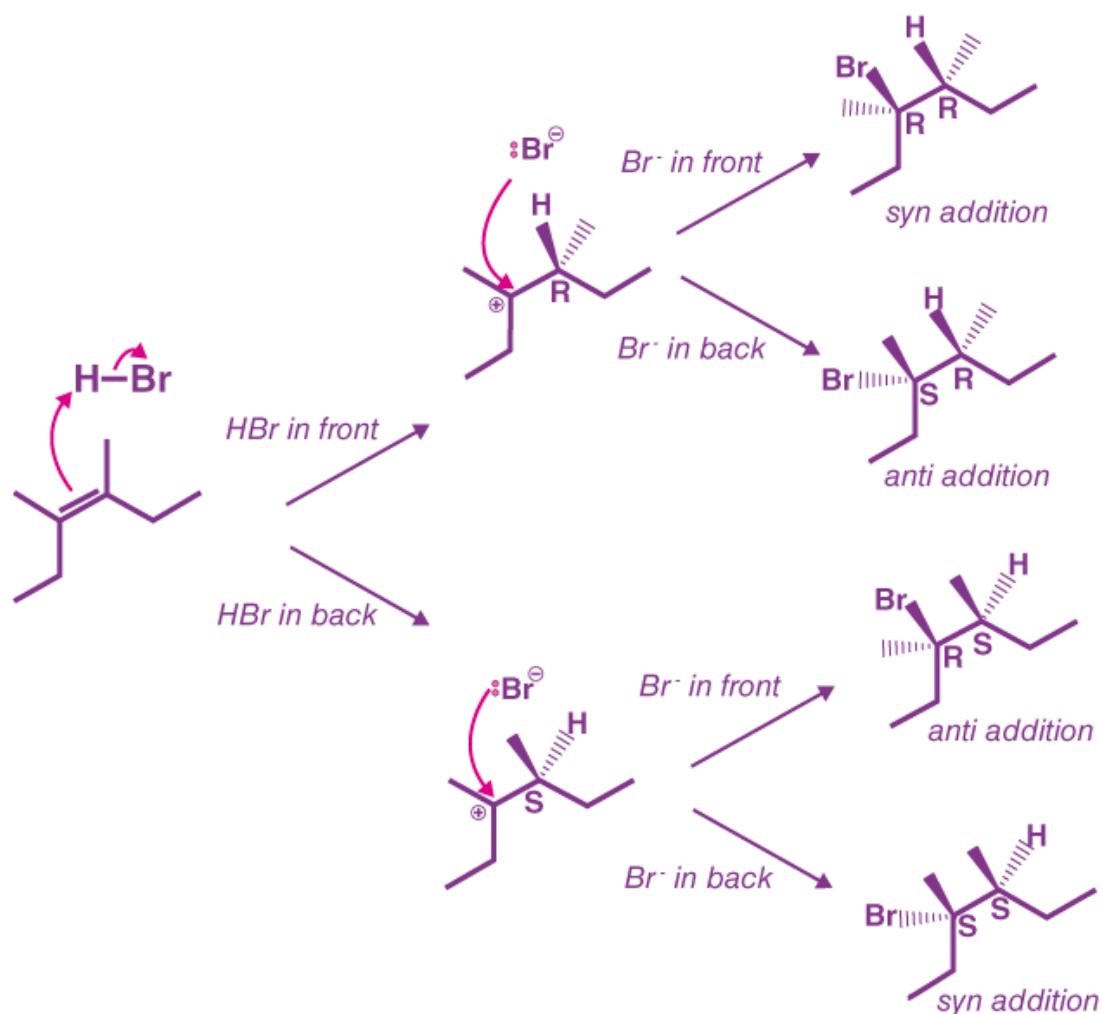
Electrophilic addition has the ability to create two additional chiral centres, depending on the structure of the initial alkene. The reaction between HBr and an alkene is not stereoselective; racemization occurs at both alkene carbons. Consider cis-3,4-

Stereochemistry

dimethyl-3-hexene with HBr added to it. Because the acidic proton might be transferred to either side of the planar alkene carbon with equal chance during the initial proton abstraction stage, the centre could have either syn and anti addition.



Addition of Br₂ to an alkene is an anti addition because the two new carbon-bromine bonds are formed on opposite faces of the alkene.



Difference between Syn and Anti Addition

The difference between syn and anti addition is tabulated below.

Syn Addition	Anti Addition
The addition of two substituents to the same side (or face) of a double or triple bond reduces the bond order but increases the number of substituents. The substrate is usually an alkene or alkyne.	Anti addition is the polar opposite of syn addition. Anti addition involves adding two substituents to opposite sides (or faces) of a double or triple bond, resulting in a drop in bond order and an increase in the number of substituents. Bromination (any halogenation) of alkenes is a classic example of this.

Stereochemistry

The addition of substituents to the same side of a double or triple bond is known as syn addition.

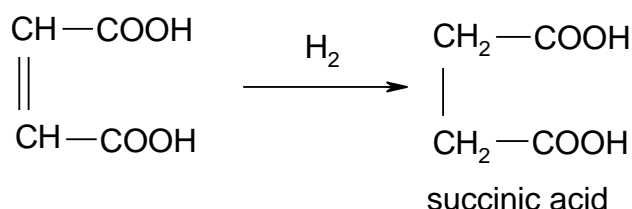
The addition of substituents to the opposite sides of a double or triple bond is known as anti addition.

Ex: Oxidation of alkenes to diols in the presence of OsO₄

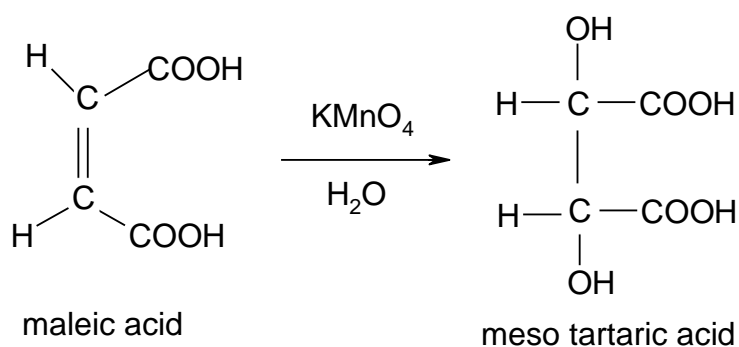
Ex: Halogenation of alkenes

Characteristics of these compounds by experimental :-

1- Reduction :-



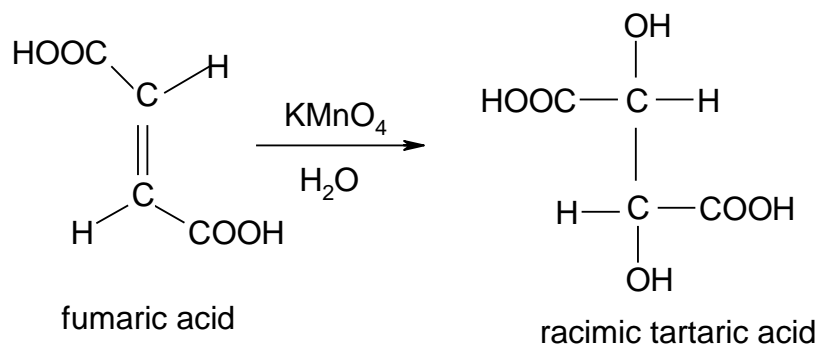
2- Oxidation :-



Oxidation of maleic acid form meso tartaric acid (acid have no optical activity) due to present of plane of symmetry divided the molecule into two identical part .

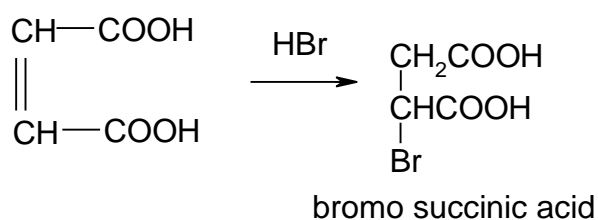
*** (which will explain by details in optical isomers)

Stereochemistry

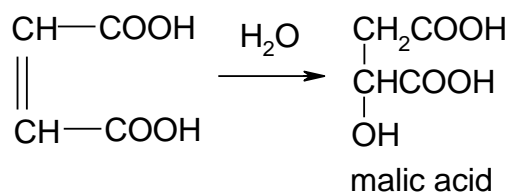


While oxidation of fumaric acid form racemic tartaric acid which have optical activity .

3- Reaction with HBr :-



4- Reaction with water :-



Carboxylic acids containing a double bond: -

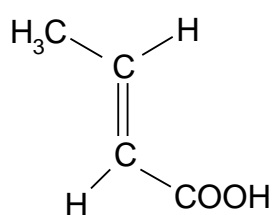
- If the shape of acids that are similar in molecular formula but different in geometrical form, it is possible to distinguish them by names specific to each geometric shape (i.e. without

Stereochemistry

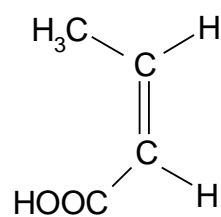
placing any syllable in front of the name of the acid), for

example: - malic and fumaric acid

- If the syllable (ISO) is placed in front of the name of **aliphatic acid**, it has an advantage in terms of stability, as the syllable (ISO) indicates the less stable form.



cotonic acid
(trans)
most stable

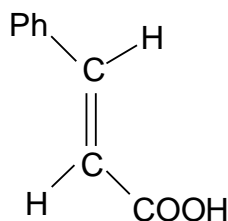


isocrotonic acid
(cis)
less stable

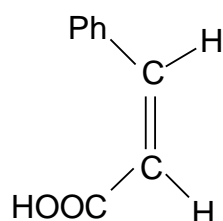
. If the syllable (allo) is placed in front of the name of the acid in

aromatic acids, it has an advantage in terms of stability and

indicates the less stable form .



cinnamic acid
(trans)
most stable

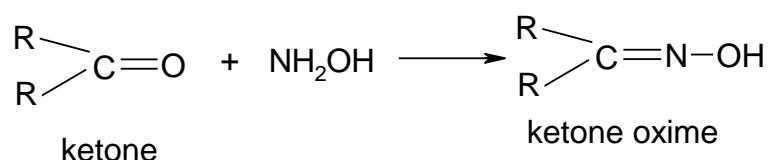
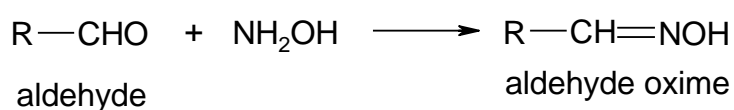


allo cinnamic acid
(cis)
less stable

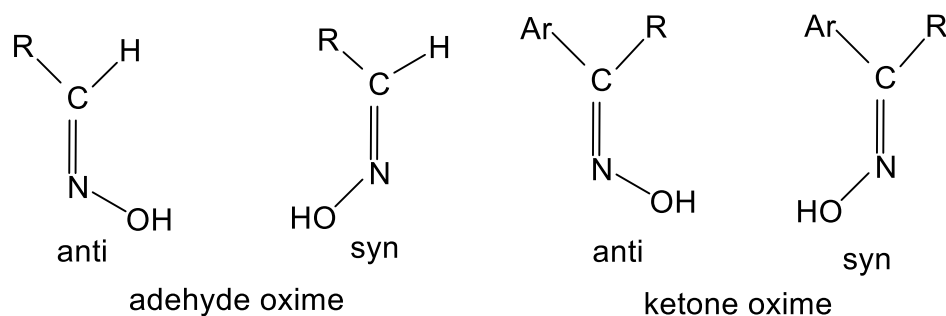
Stereochemistry

Geometric isomers in oxime

- An oxime is a **chemical compound** belonging to the **imines**, with the general formula $RR'C=NOH$, where R is an **organic side-chain** and R' may be hydrogen, forming an aldoxime, or another organic group, forming a ketoxime.



Stereochemistry of oxime

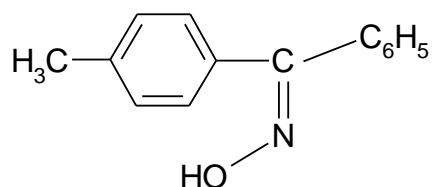


For aldehyde oxime, if the OH is found in the same direction as the big group, the compound is called (Syn), but if they are oppositely found, the compound is called (Anti).

While the ketone oxime can named by the two way

Stereochemistry

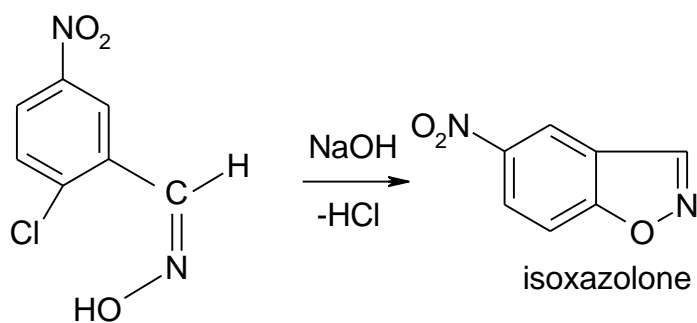
Example:-



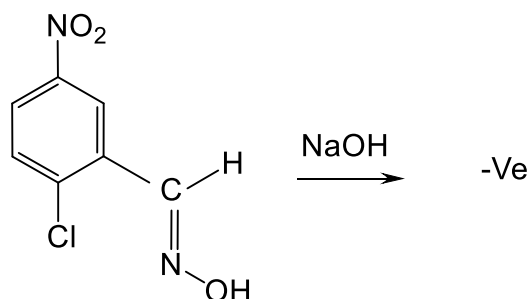
Syn p-tolyl phenyl ketoxime

Anti phenyl p-tolyl ketoxime

syn oxime more active in reaction than anti and the following reaction show that.

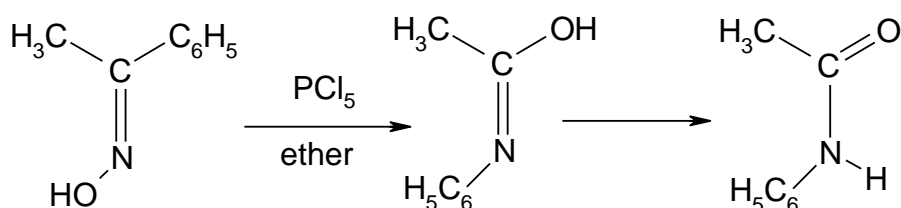


While the anti form for the same compound don't give the reaction



Beckmann rearrangement

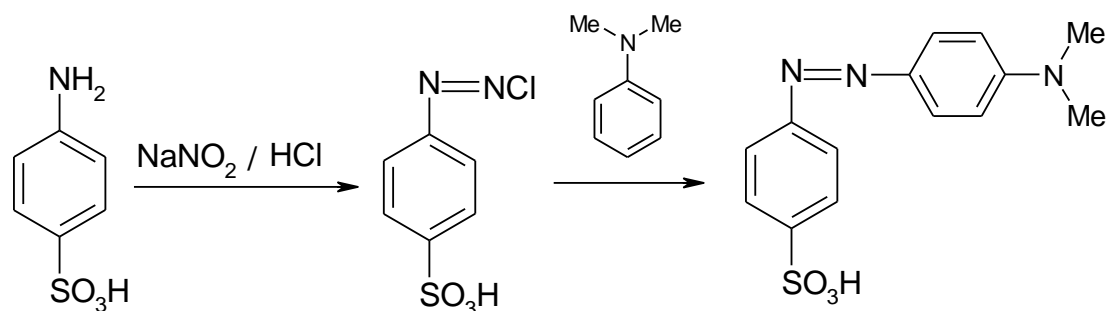
is a [rearrangement](#) of an [oxime](#) functional group to substituted [amides](#). By treatment the oxime with phosphoresce [phosphorus pentachloride](#) PCl_5 in ether .



The most common [reaction mechanism](#) of the Beckmann rearrangement consists generally of an [alkyl](#) migration anti-periplanar to the expulsion of a leaving group to form a [nitrilium ion](#). This is followed by [solvolysis](#) to an [imidate](#) and then [tautomerization](#) to the amide.

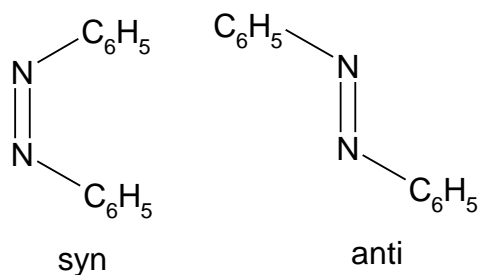
Geometrical isomerism in azo compound :-

Azo compounds are organic dyes prepared from the reaction of aromatic amines with hydrochloride and sodium nitrite salt and then combined with phenol or any compound containing an active methylene group.



Example (1):-

Azo benzol found in two form (syn) and (anti)



Geometrical isomerism in azoxy compound

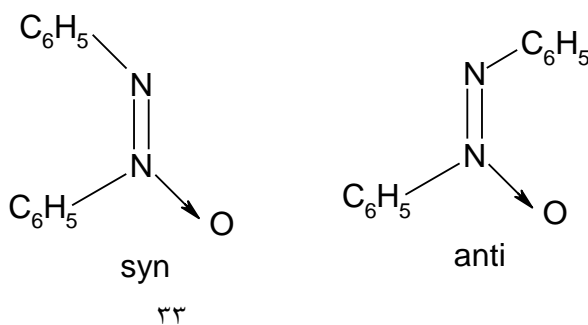
Azoxy compounds are a group of [chemical compounds](#) sharing a common [functional group](#) with the general structure

$\text{RN}=\text{N}^+(\text{O}^-)\text{R}$ They are considered [N-oxides](#) of [azo compounds](#).

Azoxy compounds are [1,3-dipoles](#).

Example (2) :-

Azoxy benzol found also in two form syn and anti

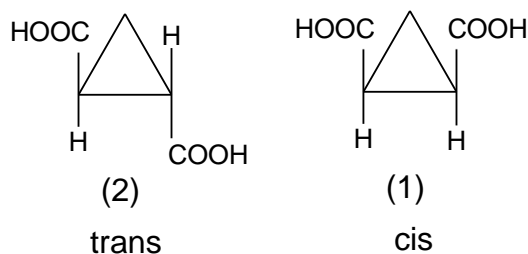


Geometrical isomer in cyclic compound

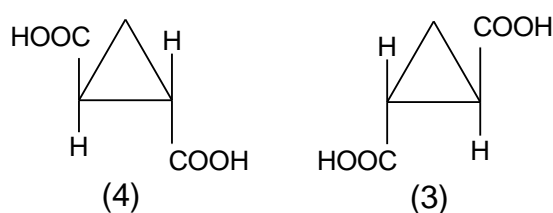
The cyclic compounds that begin with cyclo-propane (cyclo-propane) are in a state of geometric symmetry, and it is possible that these geometric images in these compounds also have optical activity.

Example (1):-

The simplest cyclic compounds cyclopropane from which we take a derivative such as cyclopropane-1,2-dicarboxylic acid (compounds 1,2) There are two forms, one is called (cis) and the other is (Trans).



Cis (also called meso) is optically inactive. (Trans) is optically active and there are two forms of it (3, 4), which rotate the left (L) and right (D).

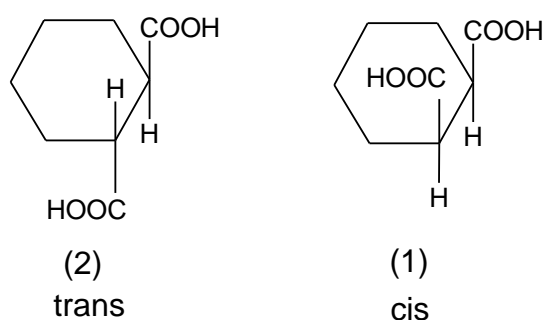


Stereochemistry

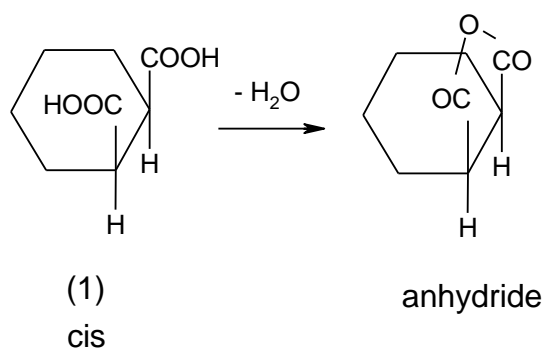
Example (2) Cyclohexane If two carboxylate groups enter it to become a dicarboxylic acid.

The two carboxyl groups on two neighboring atoms, in this case we get the two forms (1 and 2).

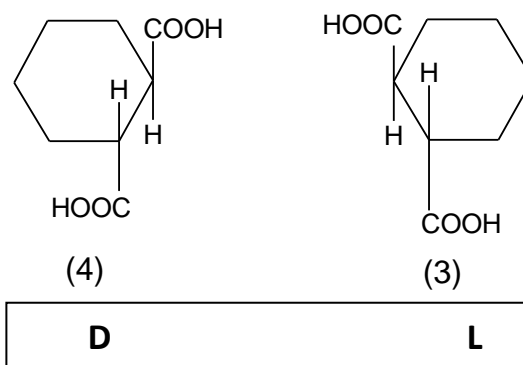
1,2-hexahydrophthalic acid (cis and trans)



Compound (1) is called (cis) and it optically inactive and gives the anhydride easily.



Compound (2) is called(trans), and it is optically active and has two forms (D, L)



Stereochemistry

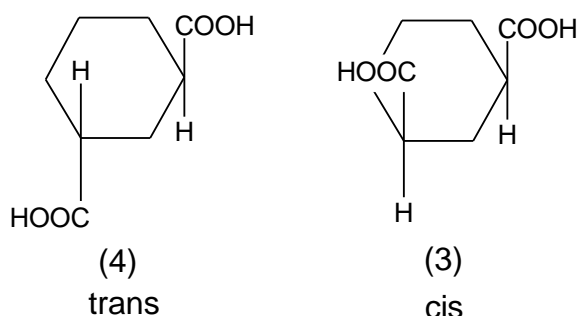
2- The two carboxyl groups on the two carbon atoms (1, 3).

The compound is called hexahydroisophthalic acid and there are two forms of it (3, 4).

Compound (3) is called (cis) and it is optically inactive,

compound (4) is called (trans) and it is optically active

Compound (3) give anhydride rapidly, in contrast to (4) which give with difficulty.

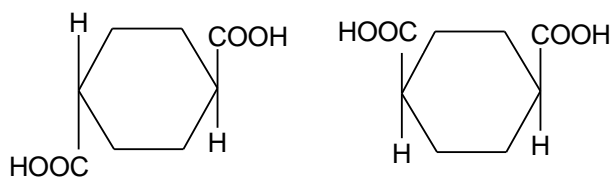


3-The two carboxyl groups on the two carbon atoms (1, 4).

The compound is called hexahydro-terphthalic acid and there are two forms of it (5, 6). Compound (5) is called (cis) and it is optically inactive. Compound (6) is called (trans) and it is also optically inactive.

Stereochemistry

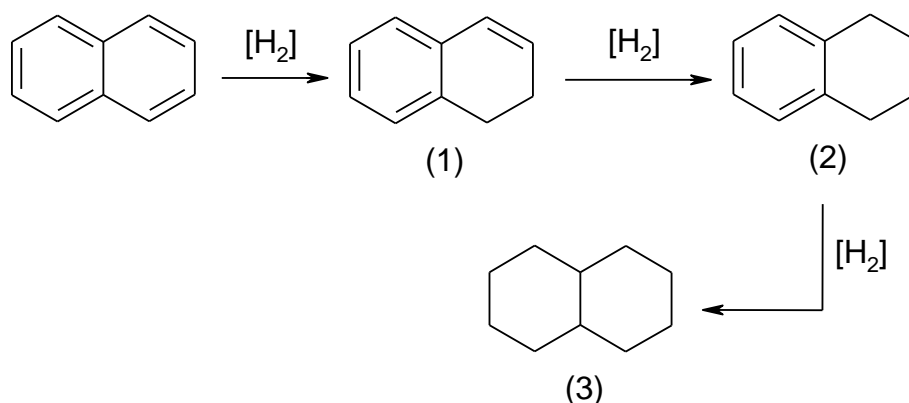
Compound (5) gives anhydride quickly but (6) does not give anhydride at all.



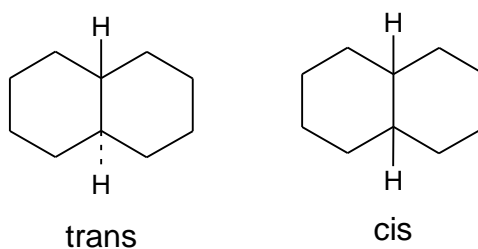
Geometrical isomer in bicyclic compound
trans (6) cis (5)

Naphthalene

Which convert to Decalene by repeat hydration (addition of hydrogen).

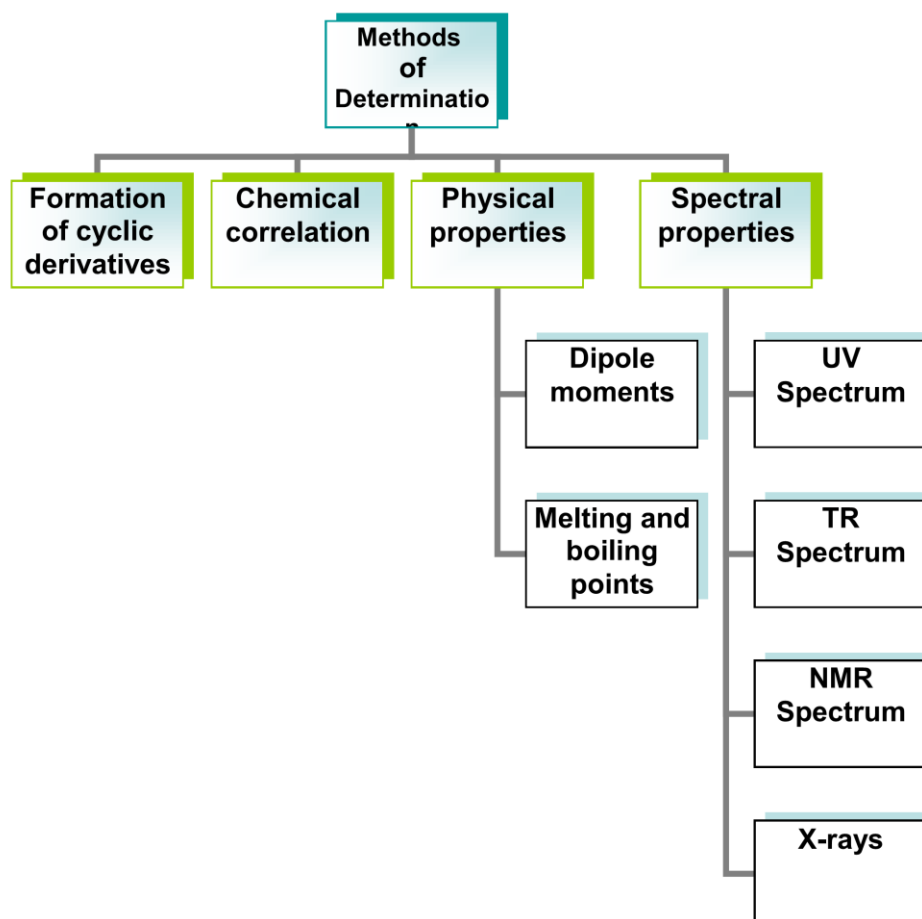


Compound (3) is called decalene, and it has geometrical isomerism as it is found in two forms (CIS) and (Trans). We note that hydrogen in both compounds is responsible for the emergence of this activity.



Determination of the configuration of geometrical isomers

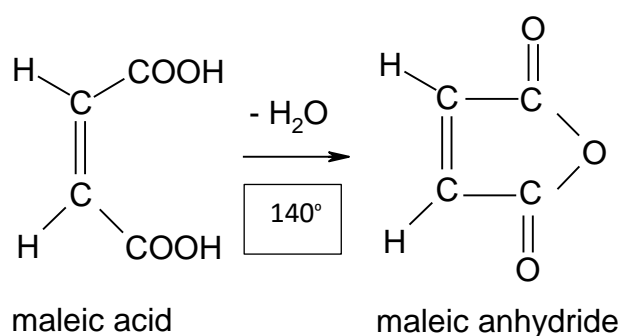
There are many methods used for the determination of the configuration of geometrical isomers.



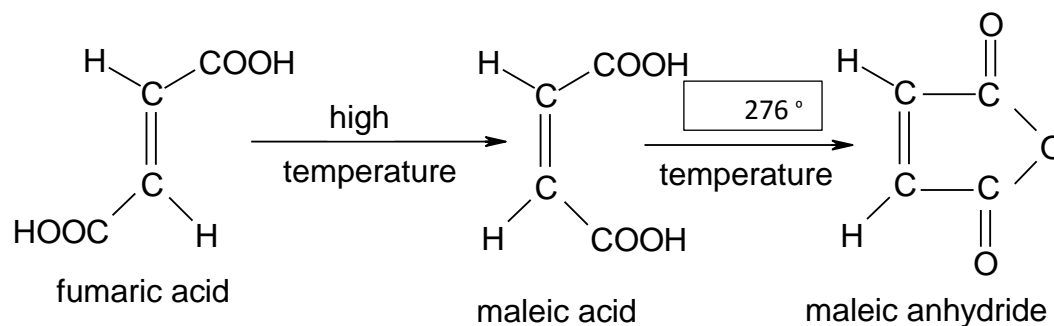
1- formation of cyclic derivatives :-

this behavior can be illustrated in maleic and fumaric acid

the melting point of maleic acid = 130° and easily form maleic anhydride on heating to 140° , while fumaric acid doesn't give anything at the same temperature.



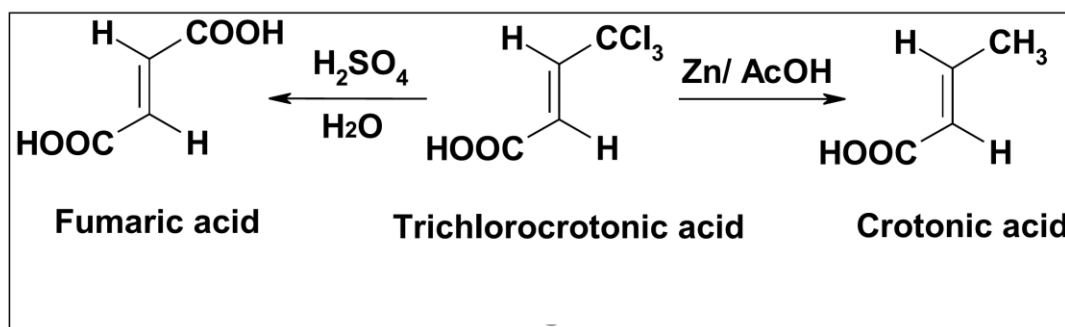
the melting point of fumaric acid = 270° and hardly form maleic anhydride on heating to 276° , so we can conclude that the two carboxylic groups must be in the same direction in maleic acid, and in opposite directions in fumaric acid.



2- chemical correlation :-

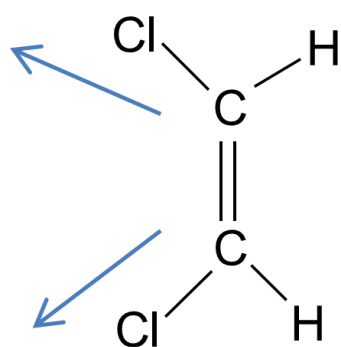
This method depends on conversion of unknown configurationally isomer into known isomer.

An example of chemical correlation is the transformation of trichlorocrotonic acid (m.p.=114) into fumaric acid by hydrolysis in acid water with H_2SO_4 , and by reduction into crotonic acid (m.p.=72).

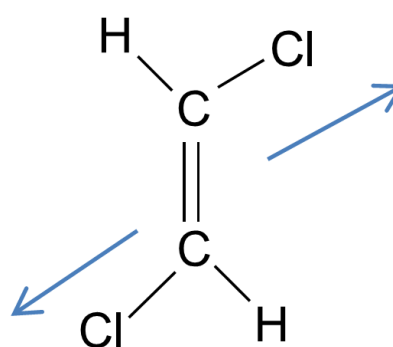


3- physical properties :-

a- dipole moments:- occur when there is a separation of charge. They can occur between two ions in an ionic bond or between atoms in a covalent bond; **dipole moments** arise from differences in electronegativity.



1.9 D



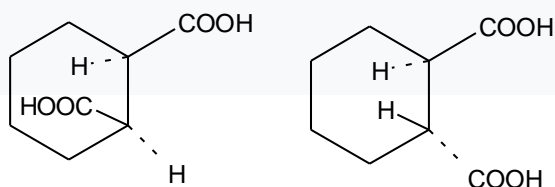
ZERO D

b- optical activity

optical activity is **the ability of a chiral molecule to rotate the plane of plane-polarised light**, measured using a polarimeter.

... When light passes through a sample that can rotate plane polarised light.

The geometrically symmetrical compounds (with the shape of **cis**) are not optically active, while the compounds (with the shape of **trans**) are optically active because they are not asymmetric (not identical).



Stereochemistry

c- melting and boiling points

- Melting point in cis form less than trans (in acid) form
- Boiling point in cis form more than trans form (in acid)

Stereomutation

Is a conversion of cis to trans-isomer or the reverse process

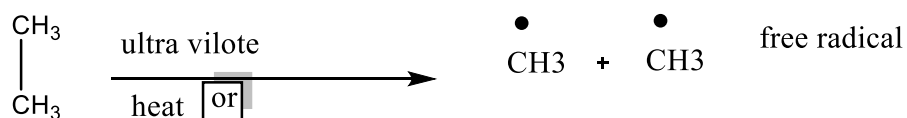
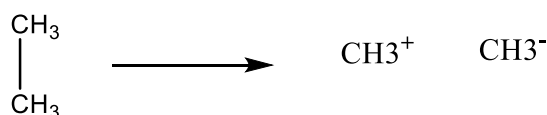
The transformation of (cis) into (trans) is easy under the appropriate conditions such as exposure of the compounds (cis) to halogens or nitroso acid ((HNO₂) or by heating.

As for the transformation of (trans) into (cis), it is difficult.

Free radical

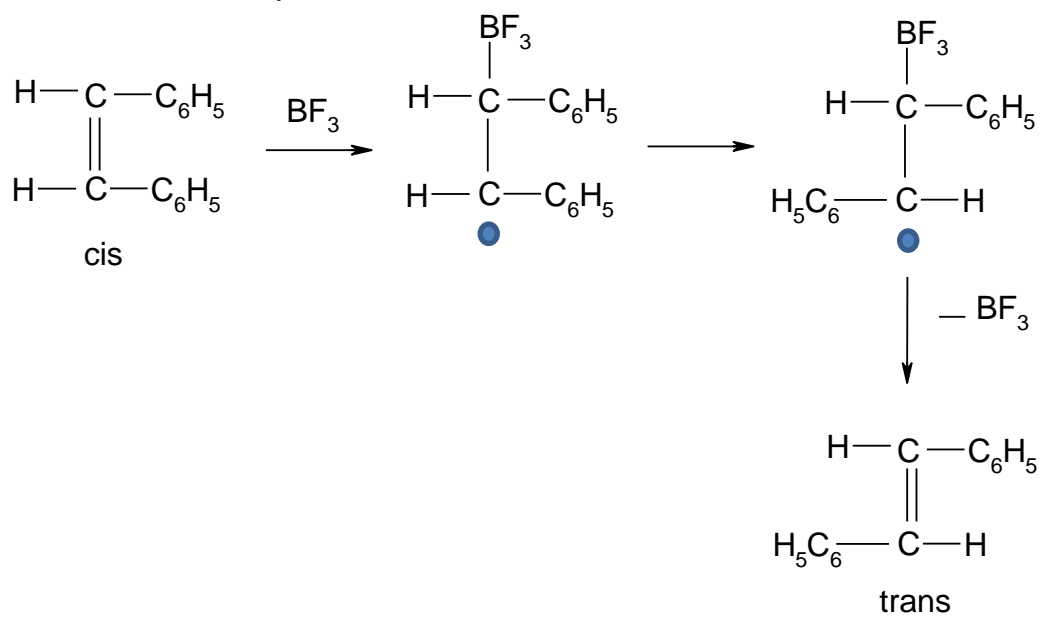
It was developed to explain the transformation of the compounds (Cis) into (trans). It states that the compound (Cis) is transformed into (trans) by forming free radicals using cofactors such as (BF₃).

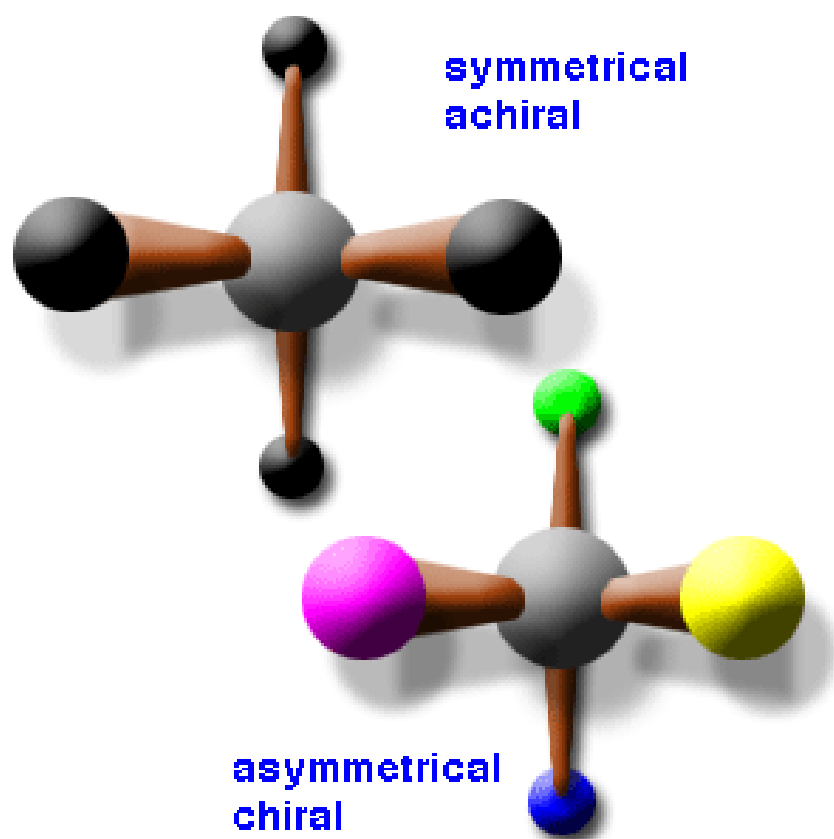
Initiation step :-



Stereochemistry

transformation step :-





Optical isomerism

Optical isomerism is a case where the isomers display identical characteristics in terms of molecular weight as well as chemical and physical properties. However, they differ in their effect on the rotation of polarized light.

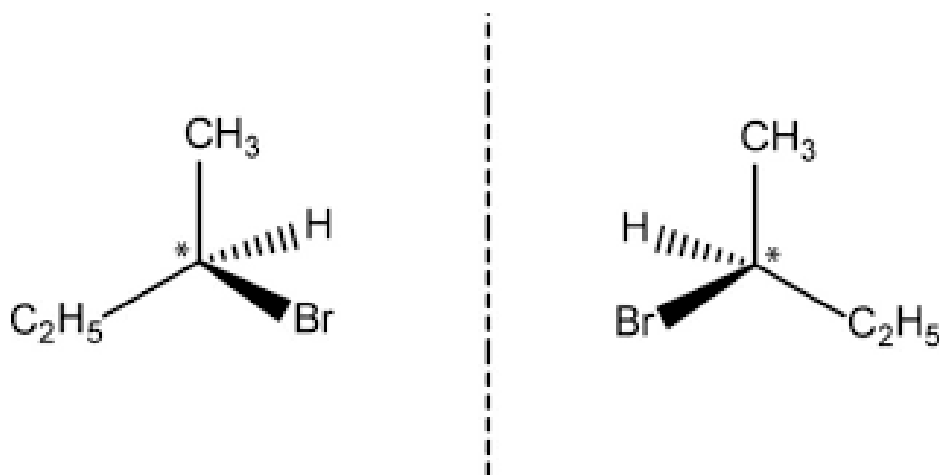
Optical isomerism occurs mainly in substances that have the same molecular and structural formula, but they cannot be superimposed on each other.

Stereochemistry

In simple words, we can say that they are mirror images of each other. Alternatively, it can also be found in *substances that have an asymmetric carbon atom*.

asymmetric carbon atom (chiral carbon) :-

- The molecule that cannot be superimposed on its mirror image is chiral
- **Chiral carbon atoms :-**
- Carbon atom are connected to four different group called chiral carbon
- Such molecule is chiral and exist as pair of enantiomers



Optical activity

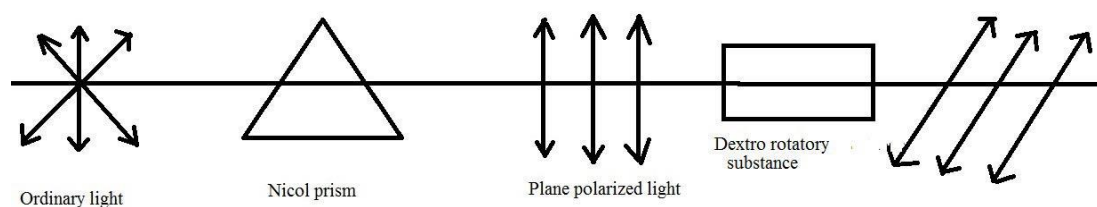
An optical activity substance is one that rotate the plane of polarized light ,if the rotation of plane to right the substance is

Stereochemistry

dextrorotatory , while ,if the rotation of plane to left the substance is levorotatory

The direction of rotation and its degree can be determined by polarimeter.

polarimeter is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically active substance



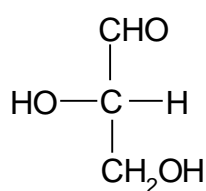
The observed angle of rotation in the case of an optically active substance depend in :-

- 1- Concentration of the substance in the solution
- 2- Length of the tube
- 3- Wave length of polarized light
- 4- Temperature
- 5- Nature of solvent used

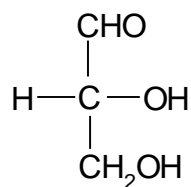
Stereochemistry



Example :-

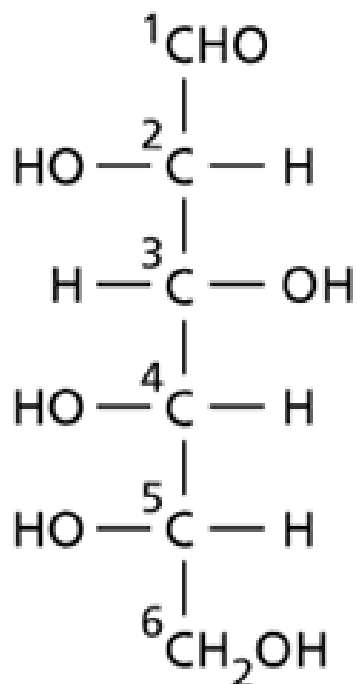


L (-) glyceraldehyde

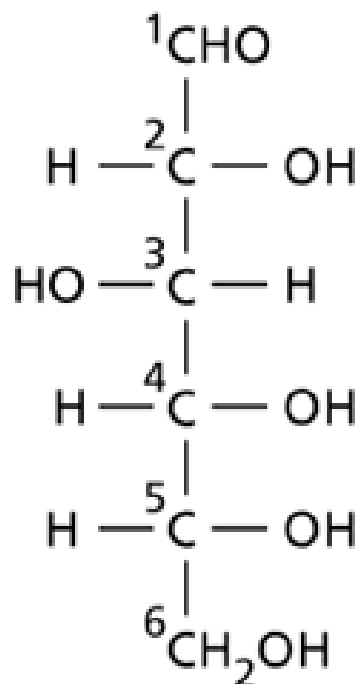


D (+) glyceraldehyde

- If the OH- group right it become (D)
- If the OH- group left it become (L)
- If the compound have more than one chiral carbon we take the last one .



L-Glucose



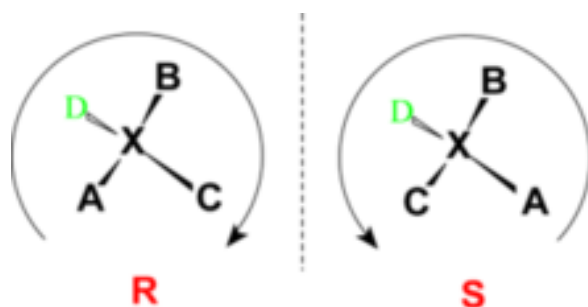
D-Glucose

The chiral carbon atoms are (C2-C3-C4-C5) because they are attached to dissimilar atoms or groups, while C1-C6 are non-chiral because they are attached to similar atoms.

As for the nomenclature, the last chiral carbon atom is looked at, which is C5. If the OH is to the right, the name becomes D-glucose, but if it is vice versa, it is called L-glycose.

no. of optical Isomer in Glycose = $2^n = 2^4 = 16$

Rectus (R) and sinister (S)

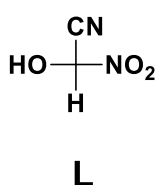
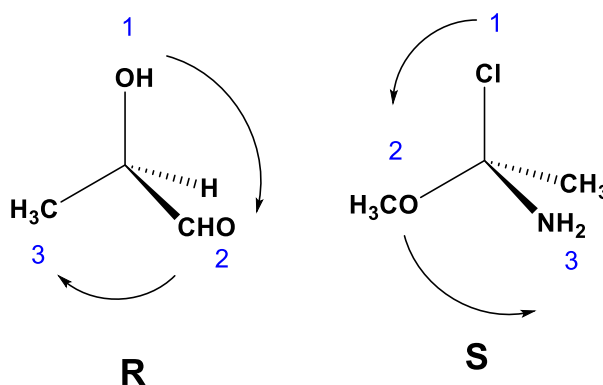


The "right hand" and "left hand" nomenclature is used to name the enantiomers of a chiral compound. The stereo centers are labeled as R or S.

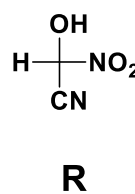
Consider the first picture: a curved arrow is drawn from the highest priority to the lowest priority. If the arrow points in a counterclockwise direction configuration at stereo center is considered S ("Sinister" → Latin= "left").

If, the arrow points clockwise then the stereo center is labeled R ("Rectus" → Latin= "right").

Example :-



٤٩



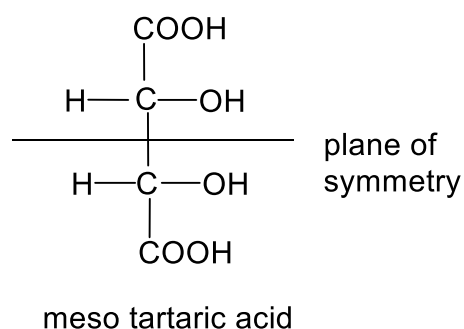
Element of symmetry

symmetry elements. A symmetry element is a line, a plane or a point in or through an object, about which a rotation or reflection leaves the object in an orientation indistinguishable from the original.

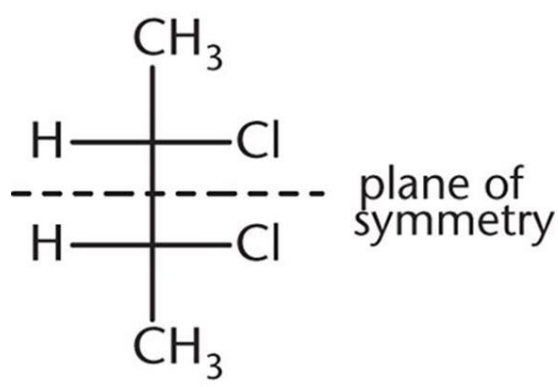
The compound have symmetry element become optically inactive .

1- **plane of symmetry** :- which dividing the molecule into two identical part and become optically inactive.

Example (1):-



Example (2):-

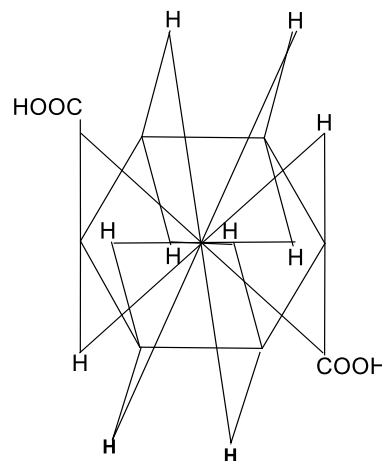


Stereochemistry

2- center of symmetry :- is any point in space such that any group on the molecule can be reflected back through that point an equal distance but opposite direction and an equivalent group are found.

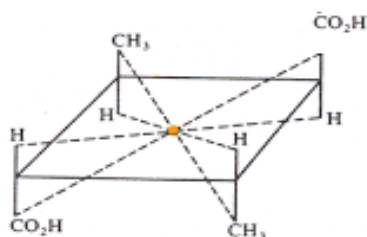
Example (1):-

Hexahydro-terphthalic acid



Example (2):-

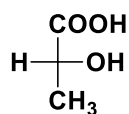
Trans-2,4-dimethylcyclobutane-1,3-dicarboxylic acid



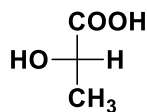
Enantiomer:-

In enantiomer (also named optical isomer) the two **stereoisomers** that are **mirror images** of each other that are non-superposable (not identical), much as one's left and right **hands** are mirror images of each other that cannot appear identical simply by reorientation.

Stereochemistry



D- lactic acid



L-lactic acid

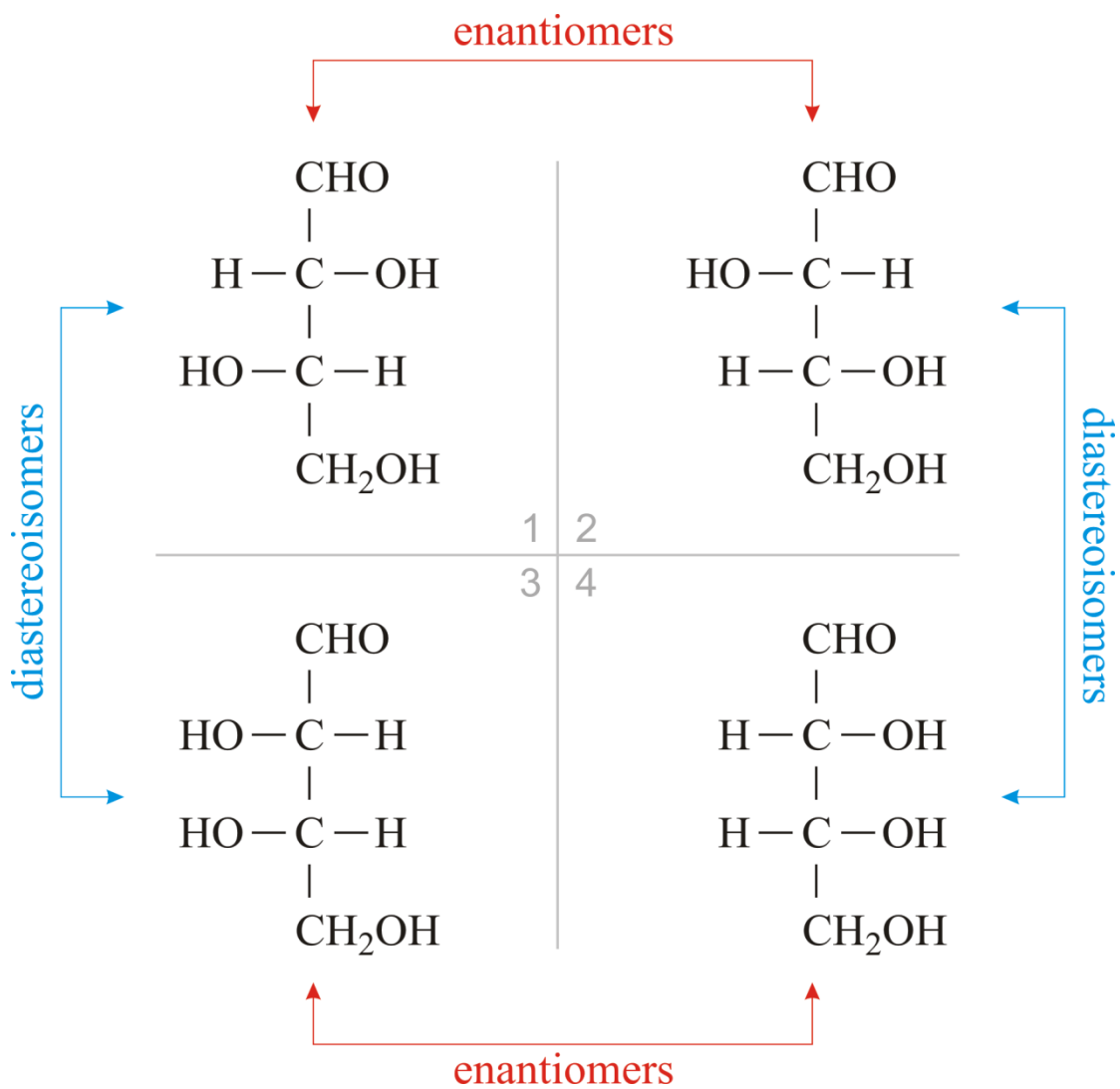
Diastereoisomers

Diastereoisomers are defined as non-mirror image non-identical stereoisomers. They occur when two or more stereoisomers of a compound have different configurations at one or more (but not all) of the equivalent ([stereocenters](#)) and are not mirror images of each other.

** in the structure below, **1** and **2** are enantiomers and so are **3** and **4** while **1** and **3** are diastereoisomers, as are **2** and **4**.

**Unlike enantiomers, diastereoisomers need not have closely similar physical and chemical properties.

Stereochemistry

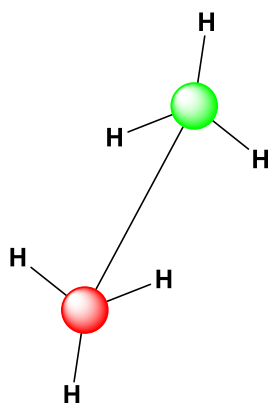


conformational isomers

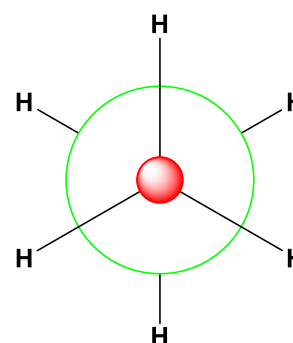
They are stereoisomers that describe the phenomenon of molecules that have the same structural formula but have a different chemical conformation due to the rotation of the atoms around the single sigma bond. As a result of this rotation the compound exists in more than one form, these forms are called isomers of the (formal) shape.

Conformational of Ethan CH₃CH₃

Some forms of the ethane molecule were expressed by the method (the projection of the scientist Sowers and the Newman world) as a result of free rotation around the carbon-carbon single bond.



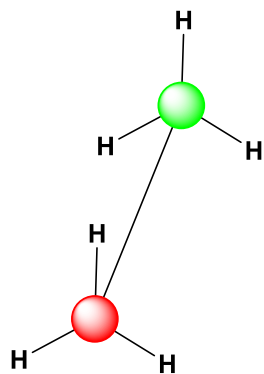
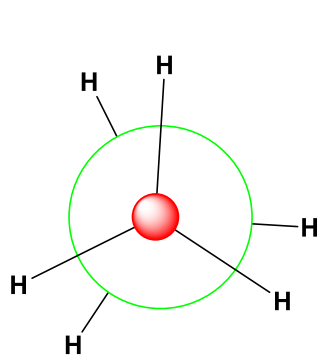
Sawhorse projection



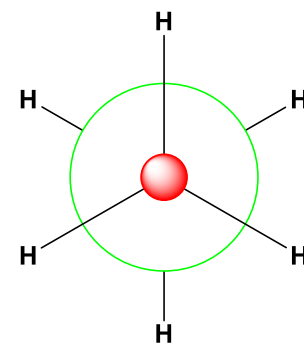
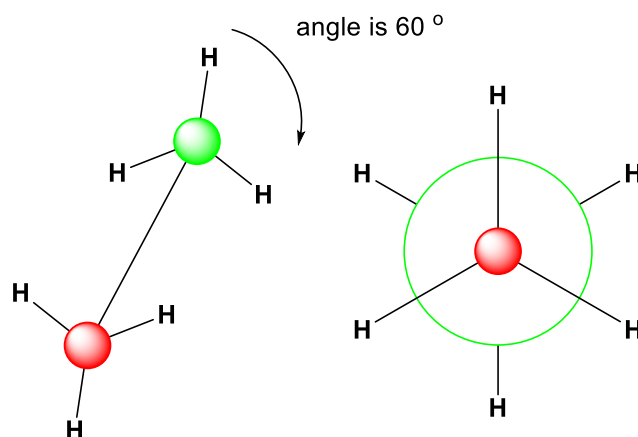
Newman projection

Ethane have 6 form (3 eclipsed form and 3 staggered form)

(eclipsed form)



(staggered form)



We note that the staggered form is the most stable form, as the angle between groups or atoms is 60 degrees, but in the eclipsed form, the angle is zero.

The conformation of cyclohexane:

All cyclohexane bonds are single, and therefore there are four free forms:

1- Chair form

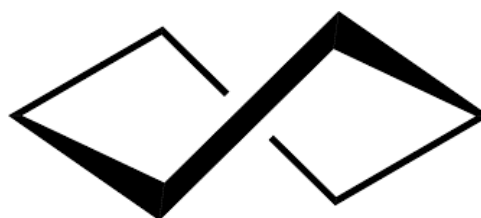


Chair conformation is a term used for the most stable chemical conformation of hexagonal carbon rings such as cyclohexane.

When atoms are bonded together, the electrons tend to scatter as far from each other as possible.

Due to the natural need for the sp^3 hybrid orbital (i.e carbon-hydrogen bonds) in the tetravalent carbon atoms to reach 109.5° , cyclohexane is not a planar molecule. Cyclohexane exists in chair and twisted form, the chair form being the most stable form, and stress in this form makes the angle C-C-C 111.5° .

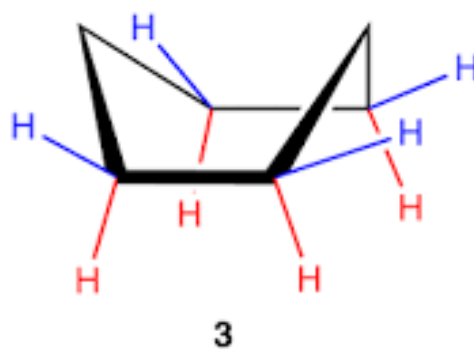
2- Twisted boat form :-



Cyclohexane is also present in conformers in the form of a twisted boat. The twisted boat is the only one that can be isolated like the chair form, because it represents a low energy, although its energy is higher than the seat structure (chair), due to the presence of torsion stress that is not present in the chair form.

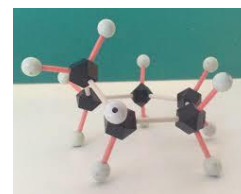
3- Boat form

The boat structure and the chair form represent a transitional state between the twisted boat structure and the chair structure, respectively, and they cannot be separated.

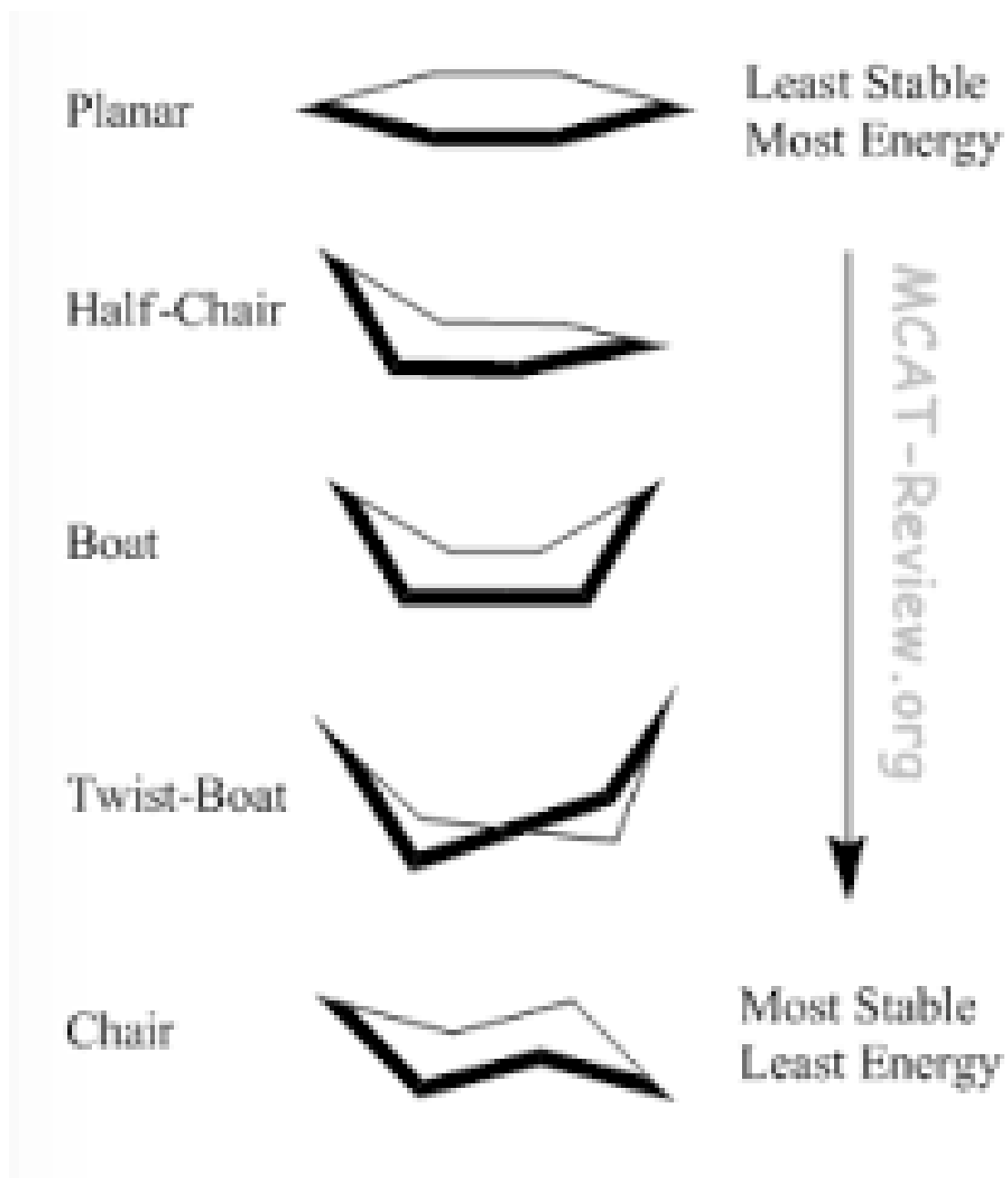


4- Half chair form

It is the highest form of energy



Energy level of four form

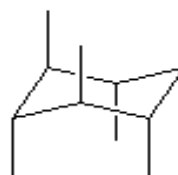


Stereochemistry

As for the distribution of groups, it is equatorial and axial as in the pictures .



equatorial bonds



axial bonds

Reference :-

1- Stereochemistry of organic compound

المراجع :-

- ١ - كتاب الكيمياء العضوية الفراغية
- ٢ - كتاب اسس الكيمياء العضوية