

# Stereochemistry

*Chemistry in three dimensions*



*Basics of Stereochemistry for Undergraduate and Postgraduate Studies*

With QR Codes of Video Lectures

**ISBN : 978-93-5426-742-0**

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Department of Chemistry

Shri R.L.T. College of Science, Akola



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## Preface ...

I am extremely cheerful to introduce the book “Stereochemistry-Chemistry in Three Dimensions” to the students and teachers offering subject chemistry. Stereochemistry is the study of three dimensional structures of molecules. To determine the cause of chemical reaction, it is essential to have the complete understanding of stereochemistry.

This book is incorporated with QR codes of videos prepared by the author related to the topics given in this book. By scanning these QR codes using ‘Google Lens’ application readers may watch these videos.

In this book, three dimensional illustrations, figures, representations and numbers of examples are incorporated to make the reading quite interesting and understandable. I sincerely hope that the method of presentation in the book will be helpful to the students and teachers learning the subject independently. The emphasis is on simplicity and clarity but not at the cost of logical scientific discussion.

Almost all the basic aspects and concepts related to stereochemistry required for the undergraduate and postgraduate study are incorporated in this book. While preparing the book, I have referred numbers of standard books. I wish to put on record my indebtedness to authors of these books.

I would like to place on record my deep sense of gratitude towards Hon'ble Adv. Motisingh G. Mohta, President, Hon'ble Shri Pavan N. Maheshwari, Honorary Secretary, The Berar General Education Society, Akola and Respected Dr. Vijay D. Nanoty, Principal, Shri R.L.T. College of Science, Akola for encouraging me to write the book. I would like to acknowledge the support received from Prakash Printers, Akola in preparation of manuscript of this book.

It gives me a great pleasure to acknowledge the love and support of my family members, my wife Harsha and sons Smit and Sparsh to finish this herculean task.

I believe that a man would do nothing if he waited until he could do it so well that no one would find fault with what he has done. Despite of my sincere efforts, there may have some errors in the book which might be escaped from my notice. Constructive suggestions regarding the improvement of contents of the book are most welcome.

**Dr. Pradip P. Deohate**

# Stereochemistry

Chemistry in three dimensions .....

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# Stereochemistry

Chemistry in three dimensions .....

## QR Codes ...

Scan the QR codes with **Google Lens** and watch the related videos.

### 1. Isomerism



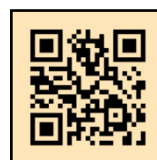
### 2. Elements of Symmetry or Symmetry Elements



### 3. Chirality, Enantiomers, Diastereomers, Relative Configuration



### 4. Absolute Configuration



### 5. Racemisation and Resolution of Racemic Mixture



### 6. Cis-Trans and E-Z Isomerism or Configuration or Nomenclature





## 7. Conformations and Conformational Analysis



## 8. Conformational Analysis of Ethane



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## 10. Conformational Analysis of Cyclohexane



## 11. Projection Formulae



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## 13. Examples - Baeyer's Strain Theory





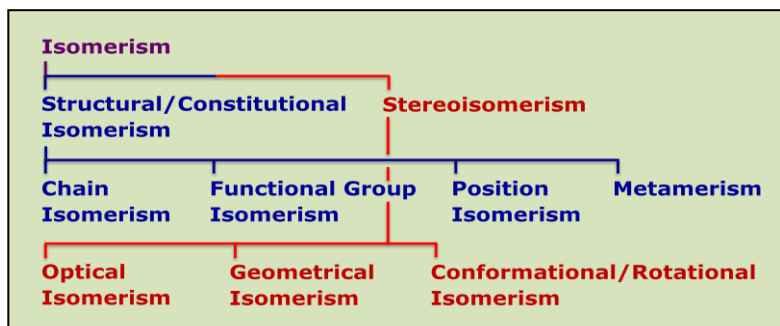
# Stereochemistry

Stereochemistry is the study of three dimensional structures of molecules. To determine the cause of chemical reaction, it is essential to have the complete understanding of stereochemistry.

## 1. Isomerism

The compounds which have same molecular formula but differ in their physical and chemical properties are called as isomers and the phenomenon is known as isomerism.

Isomerism is classified as given below.



### A. Structural or Constitutional Isomerism

The compounds which have same molecular formula but differ in the structure are called as structural or constitutional isomers and the phenomenon is structural or constitutional isomerism.

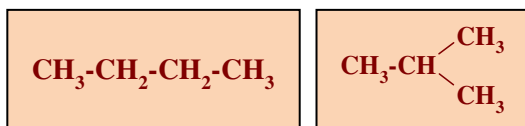
It is sub-divided into following four types.

#### I. Chain Isomerism

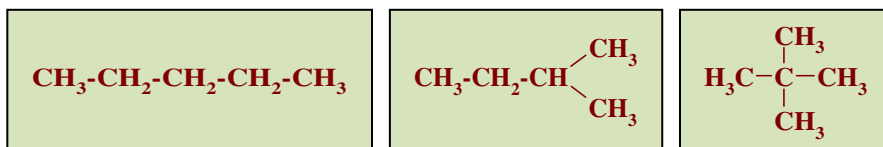
The compounds which have same molecular formula but differ in the carbon chain or carbon skeleton of the molecule are called as chain isomers and the phenomenon is chain isomerism.

Examples ...

#### *n*-Butane and *iso*-Butane (C<sub>4</sub>H<sub>10</sub>)



#### *n*-Pentane, *iso*-Pentane and *neo*-Pentane (C<sub>5</sub>H<sub>12</sub>)

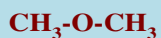


## II. Functional Group Isomerism

The compounds which have same molecular formula but differ in the type of functional group present in the molecule are called as functional group isomers and the phenomenon is functional group isomerism.

Examples ...

Ethanol and Dimethyl ether ( $C_2H_6O$ )



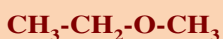
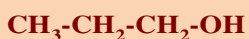
Propionic acid and Methyl acetate ( $C_3H_6O_2$ )



*n*-Butyric acid and Methyl propionate ( $C_4H_8O_2$ )



*n*-Propanol and Ethyl methyl ether ( $C_3H_8O$ )

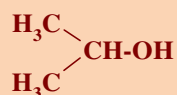
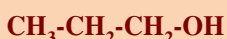


## III. Position Isomerism

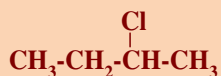
The compounds which have same molecular formula but differ in the position of same functional group or substituent or unsaturation in the chain of the molecule are called as position isomers and the phenomenon is position isomerism.

Examples ...

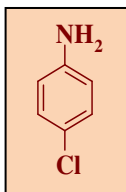
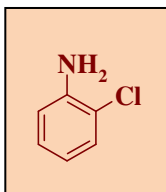
*n*-Propanol and *iso*-Propanol ( $C_3H_8O$ )



1-Chlorobutane and 2-Chlorobutane ( $C_4H_9Cl$ )



*o*-Chloroaniline and *p*-Chloroaniline ( $C_6H_6NCl$ )



## 2-Pentanone and 3-Pentanone (C<sub>5</sub>H<sub>10</sub>O)

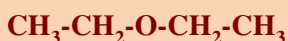


### IV. Metamerism

The compounds which have same molecular formula but differ in the carbon chain or carbon skeleton on either side of polyvalent functional group present in the molecule are called as metamers and the phenomenon is metamerism.

Examples ...

#### Diethyl ether and Methyl *n*-propyl ether (C<sub>4</sub>H<sub>10</sub>O)



## 2-Pentanone and 3-Pentanone (C<sub>5</sub>H<sub>10</sub>O)



Metamers may also be position isomers.

### B. Stereoisomerism

The compounds which have same molecular formula and same structure but differ in configuration or conformation (i.e. the arrangement of atoms or groups in space) are called as stereoisomers and the phenomenon is stereoisomerism.

Stereoisomers are not structural or constitutional isomers; they have their constituent atoms connected in same sequence.

It is sub-divided into following three types -

#### I. Optical Isomerism

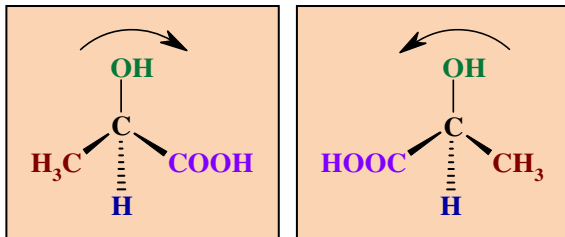
The stereoisomers which have different arrangement of atoms or groups about chiral or asymmetric centre and hence differ in optical properties are called as optical isomers and the phenomenon is optical isomerism.

It may also defined as the stereoisomers which rotate the plane polarized light to some extent in opposite direction about chiral or asymmetric centre are called as optical isomers and the phenomenon is optical isomerism.

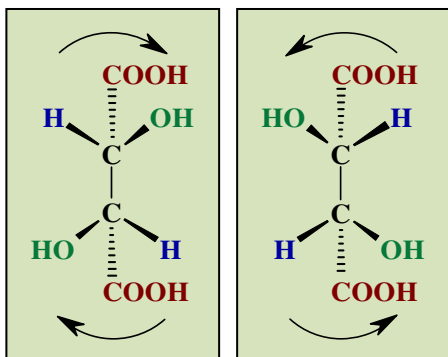
Optical isomerism arises due to the chirality or asymmetry of molecule. It is generally observed in compounds which have at least one chiral or asymmetric carbon atom. The carbon with four different atoms or groups attached to it is called as chiral or asymmetric carbon.

Examples ...

### *d*-Lactic acid and *l*-Lactic acid



### *d*-Tartaric acid and *l*-Tartaric acid



## II. Geometrical Isomerism

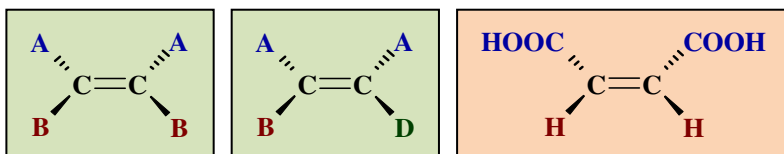
The stereoisomers which have different geometrical arrangement of atoms or groups about restricted bond (C=C) are called as geometrical isomers and the phenomenon is geometrical isomerism.

There are two types of geometrical isomers.

**Cis Isomer** - The geometrical isomer in which similar atoms or groups are at the same side of restricted bond (C=C) is called as cis geometrical isomer or cis isomer.

Example ...

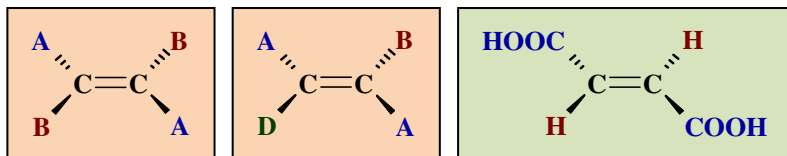
### Maleic acid



**Trans Isomer** - The geometrical isomer in which similar atoms or groups are at the diagonally opposite side of restricted bond (C=C) is called as trans geometrical isomer or trans isomer.

Example ...

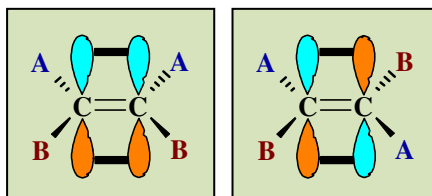
### Fumaric acid



### Cause of Geometrical Isomerism

The pi-bond in C=C is formed by sidewise or lateral overlapping of two parallel *p*-orbitals. When one of the double bonded carbon atoms is rotated about double bond; the pi-bond breaks and the parallel *p*-orbitals does not remain parallel. But when rotation is completed by 180°, two *p*-orbitals again becomes parallel to each other and hence again pi-bond is formed. Thus due to breaking and reforming of pi-bond, due to restricted rotation about C=C, a new configurational isomer is formed.

Breaking and reforming of pi-bond by 180° rotation of one of the two double bonded carbons



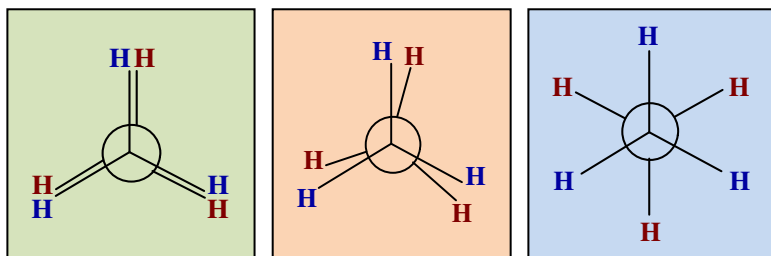
**Configurations** - The optical and geometrical isomers are the configurations. These are isolable and not easily inter-convertible from one form to other.

### III. Conformational or Rotational Isomerism

The stereoisomers which have different spatial arrangement of atoms or groups about C-C single bond and can be obtained by rotation of half of the molecule about C-C single bond are called as conformational isomers or rotational isomers or conformations and the phenomenon is conformational or rotational isomerism.

The stable conformations having minimum potential energy are called as conformers or rotamers.

Three important types of conformations of ethane i.e. eclipsed, skew and staggered conformations represented by Newman projection formula are as shown below.



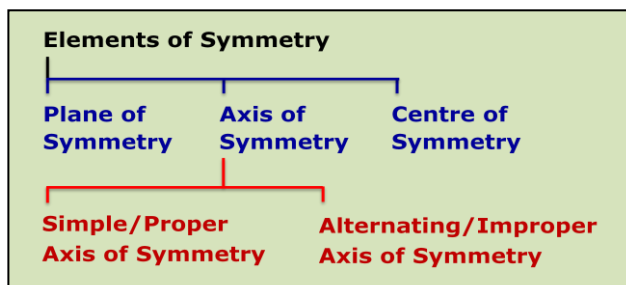
**Conformations** - The conformational or rotational isomers are the conformations. These are non-isolable and easily inter-convertible from one form to other.

## 2. Elements of Symmetry or Symmetry Elements

The numbers of planes, lines (axes) and points (centres) which gives relationship between equal parts of molecules are called as elements of symmetry or symmetry elements.

The symmetry elements of a given molecule give the information about the molecule, whether it superimposes on its mirror image or not.

Elements of symmetry are classified as given below.

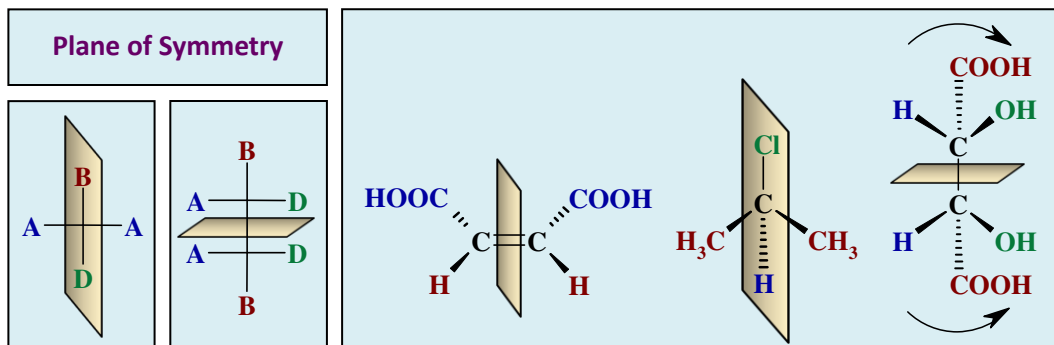


### I. Plane of Symmetry ( $\sigma$ )

It is an imaginary plane which passes through the centre of molecule and divides the molecule into two equal mirror image parts.

Examples ...

**Maleic acid, 2-Chloropropane and *meso*-Tartaric acid**

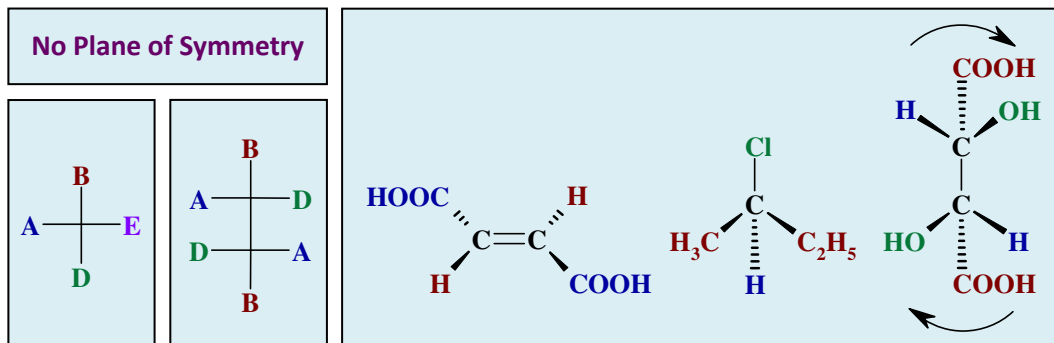


Plane of symmetry is commonly found in achiral (symmetric) molecule.

The *meso*-tartaric acid has two asymmetric carbon atoms, even though it is optically inactive. It is because of the presence of a plane of symmetry. Due to plane of symmetry the molecule as a whole becomes symmetrical and it superimposes on its mirror image.



## Fumaric acid, 2-Chlorobutane and *d*-Tartaric acid

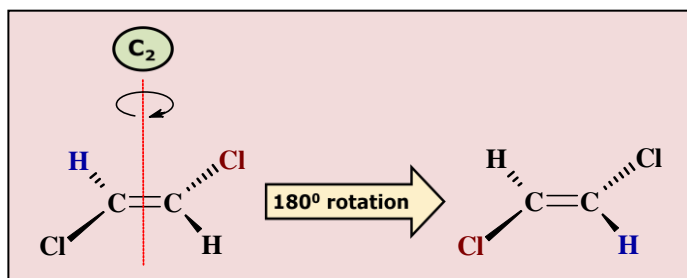


## II. Simple or Proper Axis of Symmetry ( $C_n$ )

It is an imaginary line which passes through the centre of molecule and one complete rotation of molecule about it by  $360^\circ$  shows identical structures more than one time.

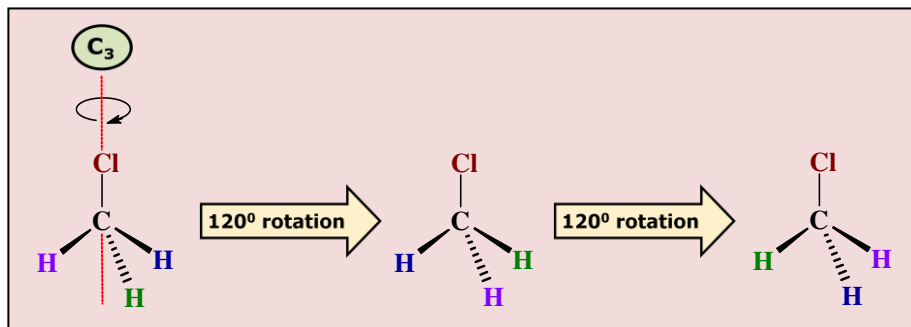
Examples ...

### *trans*-1,2-Dichloroethene



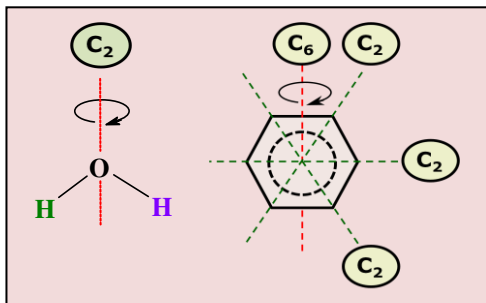
The *trans*-1,2-dichloroethene has a simple axis of symmetry that passes through the midpoint (centre) of molecule and it is perpendicular to the plane of molecule. Rotation of *trans*-1,2-dichloroethene about this vertical axis shows identical structures (arrangement of groups) for two times in one complete rotation by  $360^\circ$ . So it is called as two fold axis of symmetry ( $C_2$ ).

### Methyl chloride



Methyl chloride has an axis passing through the midpoint of molecule and chlorine atom. Rotation of methyl chloride about this vertical axis shows identical structures for three times in one complete rotation by  $360^\circ$ . So it is called as three fold axis of symmetry ( $C_3$ ).

### Water, Benzene



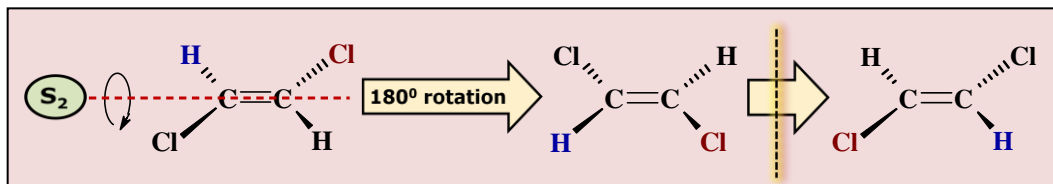
Water molecule has two fold axis of symmetry ( $C_2$ ). Benzene has two fold axes of symmetry ( $C_2$ ) as well as six fold axis of symmetry ( $C_6$ ).

### III. Alternating or Improper Axis of Symmetry ( $S_n$ )

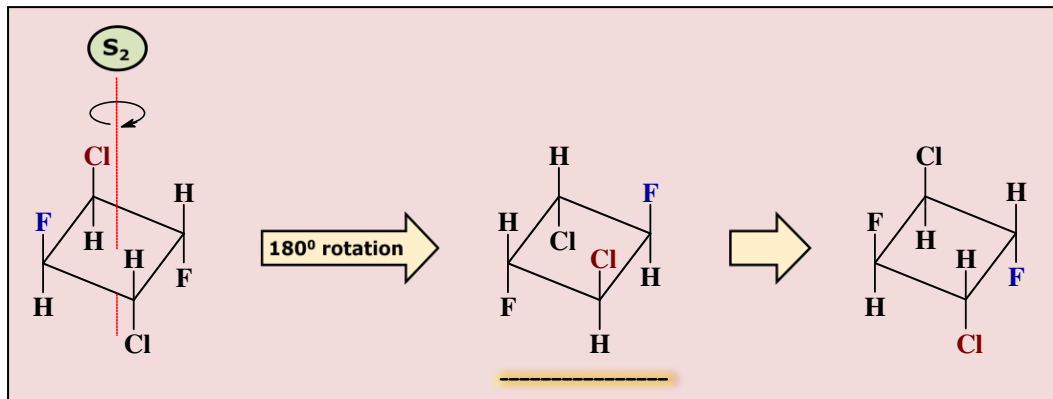
It is an imaginary line which passes through the centre of molecule and on rotation of molecule about it by particular angle followed by reflection perpendicular to the axis of rotation shows identical structures more than one time in one complete rotation of molecule about it by  $360^\circ$ .

Examples ...

#### *trans*-1,2-Dichloroethene



#### *trans*-1,3-Dichloro-2,4-difluoro cyclobutane



In both the above molecules, simple rotation by  $180^\circ$  on the molecular axis does not give identical structure, but rotation followed by reflection perpendicular to the axis of rotation shows identical structure. So this molecular axis is called as alternating axis of symmetry. In one complete rotation of these molecules by  $360^\circ$  followed by reflection perpendicular to the axis of rotation shows identical structures for two times. So it is called as two fold alternating axis of symmetry ( $S_2$ ).

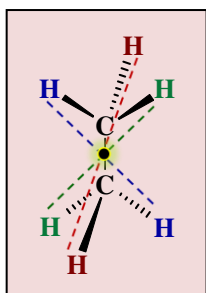
#### IV. Centre of Symmetry (i)

It is an imaginary point which lie at the centre of molecule and it is equidistant from the diagonally opposite identical atoms or groups.

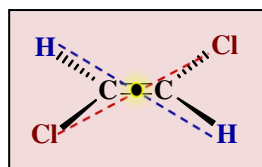
It may also defined as it is an imaginary point which lie at the centre of molecule and any straight line drawn through it encounters equivalent parts of the molecule on either side of the centre.

Examples ...

##### Ethane (Staggered)

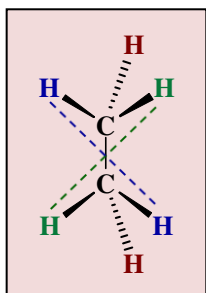


##### *trans*-1,2-Dichloroethene

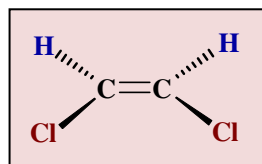


Centre of Symmetry

##### Ethane (Eclipsed)



##### *cis*-1,2-Dichloroethene



No Centre of Symmetry

### 3. Chirality

The molecules containing asymmetric centre or carbon, not having any element of symmetry and does not superimposes on its mirror image are called as chiral or asymmetric molecules and this property is the chirality of molecule.

For the chirality of molecule -

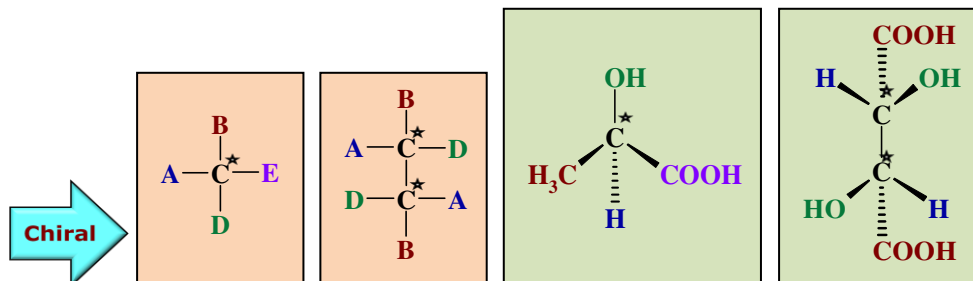
1. The molecule must contain asymmetric carbon atom or chiral centre i.e. carbon attached to four different groups or atoms.

- The molecule should not have any element of symmetry i.e. plane of symmetry, simple and alternating axis of symmetry or centre of symmetry).
- The molecule should not superimpose on its mirror image.

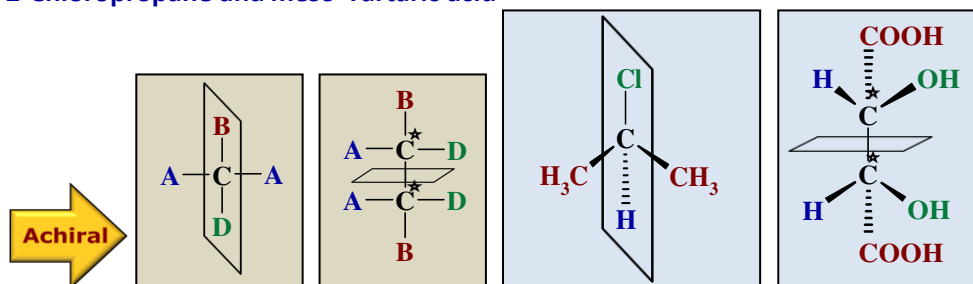
The molecules containing one asymmetric carbon are chiral, the molecules containing two asymmetric carbons and no element of symmetry are again chiral but the molecules containing two asymmetric carbons and have the element of symmetry are achiral. Chiral molecules are optically active.

**Examples ...**

***d* or *l*-Lactic acid and *d* or *l*-Tartaric acid**



**2-Chloropropane and *meso*-Tartaric acid**

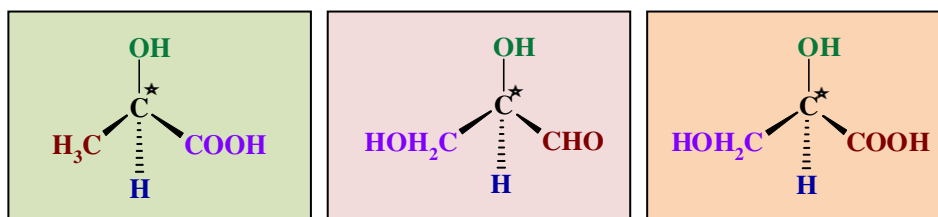


**Asymmetric Carbon (C\*)** - The carbon to which four different atoms or groups are attached is called as asymmetric carbon. It is denoted by asterisk or stars trick (C\*).

All organic compounds containing one asymmetric carbon atom are optically active.

**Examples ...**

***d* or *l*-Lactic acid, Glyceraldehyde and Glyceric acid**



## 4. Enantiomers

The stereoisomers which are non-superimposable mirror images of each other are called as enantiomers.

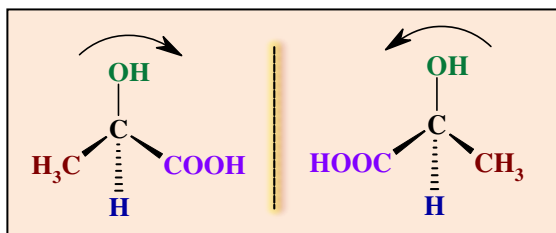
Enantiomers have identical chemical and physical properties like melting point, boiling point, density, refractive index etc. but differ from each other in their action on plane polarized light. One of the enantiomers rotates the plane polarized light in clockwise direction and other in anticlockwise direction. Direction of optical rotation of one enantiomeric form is always opposite to that of other; however the extent of rotation remains the same.

The stereoisomers or enantiomers which rotate the plane polarized light in clockwise direction are called as dextro rotatory or *d* or (+) isomers, whereas the stereoisomers or enantiomers which rotate the plane polarized light in anticlockwise direction are called as laevo rotatory or *l* or (-) isomers.

The equimolecular mixtures of *d* and *l* isomers are called as racemic mixtures or racemates or R or *dl* or ( $\pm$ ) isomers. The racemic mixtures are optically inactive because of the cancellation of optical rotation of *d* and *l* isomers by each other. It is called as external compensation.

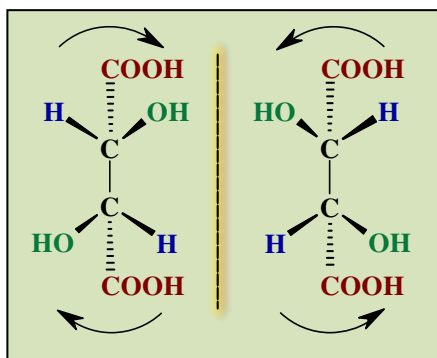
**Examples ...**

### *d*-Lactic acid and *l*-Lactic acid



*d*-Lactic acid (+2.2°, mp:299K/26°C) and *l*-Lactic acid (-2.2°, mp:299K/26°C)

### *d*-Tartaric acid and *l*-Tartaric acid



*d*-Tartaric acid (+12°, mp:443K/170°C) and *l*-Tartaric acid (-12°, mp:443K/170°C)

## 5. Diastereomers

The stereoisomers which are not mirror images of each other and hence non-superimposable are called as diastereomers.

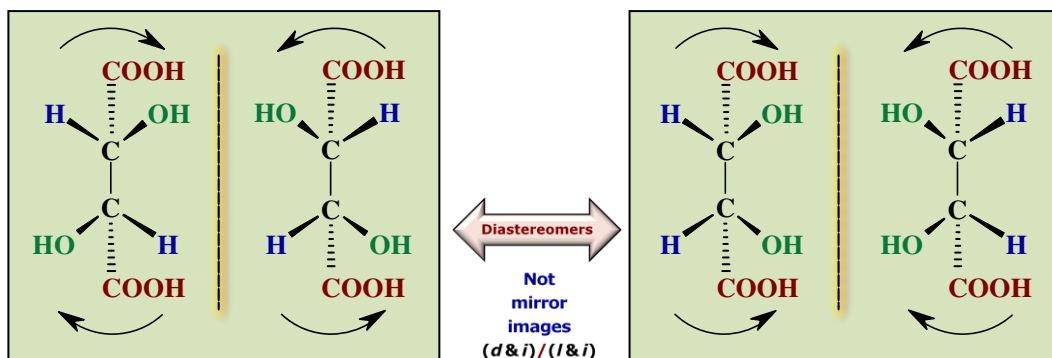
Diastereomers have different chemical and physical properties like melting point, boiling point, density, refractive index etc.

The stereoisomers which rotate the plane polarized light in clockwise direction are called as dextro rotatory or *d* or (+) isomers, whereas the stereoisomers which rotate the plane polarized light in anticlockwise direction are called as laevo rotatory or *l* or (-) isomers. The stereoisomers in which half of the molecules having one asymmetric carbon atom rotates the plane polarized light in clockwise direction and remaining half of the molecules having second asymmetric carbon atom rotates the plane polarized light in anticlockwise direction are called as meso or *i* isomers.

Meso isomers (*i*) are optically inactive because of the cancellation of optical rotation of half of the molecule by other half of the molecule. It is called as internal compensation.

Examples ...

### *d/l*-Tartaric acid and *i*-Tartaric acid



*d/l*-Tartaric acid (optically active)  
Non-superimposable mirror images  
Enantiomers

*i*-Tartaric acid (optically inactive)  
Superimposable mirror images  
(Turn by 180°)  
Meso isomers (Not enantiomers)

The pairs of *d*-Tartaric acid and *i*-Tartaric acid as well as *l*-Tartaric acid and *i*-Tartaric acid are diastereomers. These are not mirror images of each other.

## 6. Relative Configuration

The configuration of enantiomers or asymmetric carbon atom of compounds correlated with the configuration of a known or standard compound is called as relative configuration.

To specify the relative configuration at asymmetric carbon atom, the most common method used is D and L configuration.

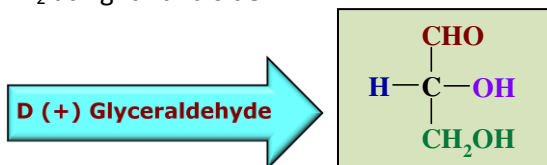
## I. D and L Configuration

This system of configuration is given by the scientists Dee and Ell. The terminologies D and L are mainly used in carbohydrate chemistry to show the position of bottom secondary OH group using Fischer projection formula.

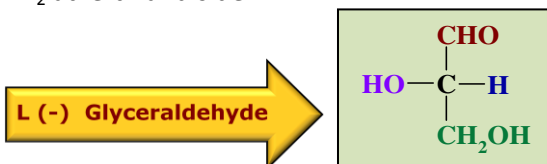
The configuration in which OH group to the right hand side in Fischer projection formula is called as D-isomer whereas the configuration in which OH group to the left hand side in Fischer projection formula is called as L-isomer.

In this system, the configuration of enantiomers is correlated to known standard glyceraldehydes. The arbitrary standards or accepted conventions for representing the D (+) glyceraldehyde and L (-) glyceraldehyde are as given below.

The D (+) glyceraldehyde is represented by the Fischer projection formula with vertical carbon chain, having CHO group at the top, H at left hand side and OH at right hand side. In general, lowest number carbon ( $sp^2$ ) at the top, H at left hand side and OH or  $NH_2$  at right hand side.



The D (-) glyceraldehyde is represented by the Fischer projection formula with vertical carbon chain, having CHO group at the top, H at right hand side and OH at left hand side. In general, lowest number carbon ( $sp^2$ ) at the top, H at right hand side and OH or  $NH_2$  at left hand side.

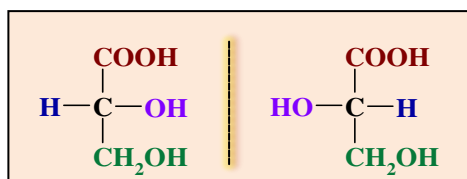


If the configuration of an enantiomer or asymmetric carbon atom of a compound is correlated to D-glyceraldehyde it belongs to D-series and if it is correlated to L-glyceraldehyde then it belongs to L-series.

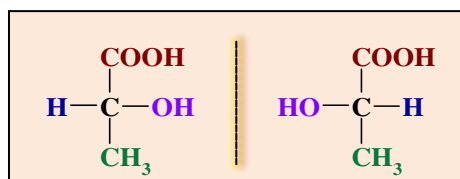
So any compound that can be prepared from or converted to D (+) glyceraldehyde belongs to the D-series whereas the compound that can be prepared from or converted to L (-) glyceraldehyde belongs to L-series.

**Examples ...**

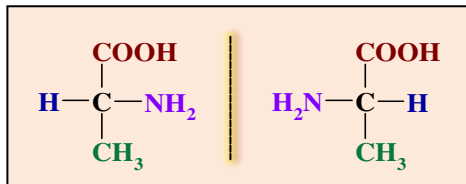
### D-Glyceric acid and L-Glyceric acid



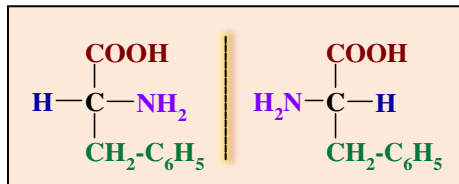
### D-Lactic acid and L-Lactic acid



### D-Alanine and L-Alanine



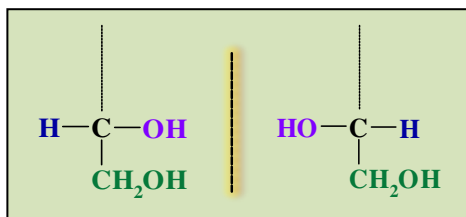
### D-Phenyl alanine and L-Phenyl alanine



In case of compounds having more than one asymmetric carbon atom, the configuration of lowest asymmetric carbon atom relative to glyceraldehyde unit should be considered. For this the asymmetric carbon atom of glyceraldehyde unit is always drawn at the bottom and the rest of the part is drawn above this unit.

**Example ...**

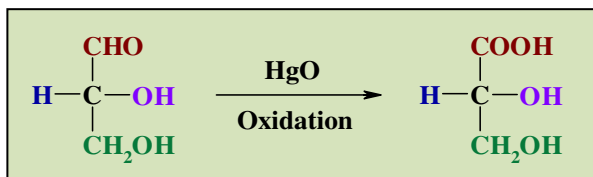
### D-Series and L-Series



There is no relationship between configuration and the sign (+/-) of rotation. The configuration D or L may be (+/-). Configurations D and L shows the arrangement of atoms or groups whereas (+/-) and (d/l) gives information about rotation of plane polarized light.

**Example ...**

**D (+) glyceraldehyde on oxidation using HgO gives D (-) glyceric acid.**



## 7. Absolute Configuration

The self consistent configuration of enantiomers or asymmetric carbon atom of compounds without any reference or correlation to the known or standard compound is called as absolute configuration.

It may also defined as the exact spatial arrangement of four different atoms or groups about asymmetric carbon atom.

To specify the absolute configuration at asymmetric carbon atom, the most common method used is R and S configuration.



## I. R and S Configuration

This system of configuration is given by the scientists Cahn, Ingold and Prelog. The letter R stands for rectus i.e. right handed or clockwise and S stands for sinister i.e. left handed or anticlockwise.

In this system, the configuration of enantiomers is decided on the basis of following rules.

1. Identify the asymmetric carbon atom ( $C^*$ ) in molecule and four different atoms or groups attached to it.
2. Assign priority to the four different atoms or groups (1,2,3,4) as per the priority or sequence rules given below.
3. Arrange the four different atoms or groups about asymmetric carbon atom keeping lowest priority atom or group at the bottom (or top).
4. View the molecule from side opposite to the lowest priority atom or group (4).

### • Priority or sequence rules

- a. The groups with key atom (atom directly attached to  $C^*$ ) of higher atomic number have higher priority.

Example ...



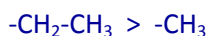
- b. The Isotopes with higher atomic mass number have higher priority.

Example ...



- c. If key atoms have same atomic number then the key atoms with more attachments of higher atomic number atoms have higher priority.

Example ...



Here for both ethyl and methyl groups, key atoms are same i.e. carbon and their attachments are C,H,H and H,H,H with atomic numbers 12,1,1 and 1,1,1 respectively.

If key atoms have same atomic number and their attachments are also same then the key atoms with next or second attachments of higher atomic number atoms have higher priority.

Example ...



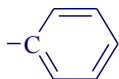
Here for both bromo-ethyl and chloro-ethyl groups, key atoms are same i.e. carbon and their attachments are also same i.e. C,H,H. Their next attachments are H,H,Br and H,H,Cl with atomic numbers 1,1,35 and 1,1,17 respectively.

- d. The multiple bonded atoms are equivalent to multiple numbers of attachments of atoms by single bond.

Examples ...



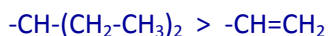
Here attachments of carbon are C,C,H / C,C,C / O,O,H / N,N,N respectively.



Here attachments of carbon are C,C,C.

But the two or three atoms attached actually to another atoms, have higher priority than that of doubly or triply bonded atoms.

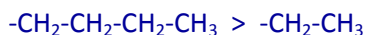
Example ...



Here attachments of carbon are C,C,H.

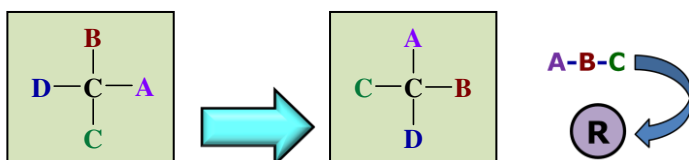
- e. The groups with maximum numbers of carbon atoms have higher priority.

Example ...



On the basis of above rules, the configuration in which priority of atoms or groups (1,2,3) decreases in clockwise direction is called as R-isomer or configuration whereas the configuration in which priority of atoms or groups (1,2,3) decreases in anticlockwise direction is called as S-isomer or configuration.

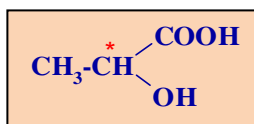
In R and S configuration, while using Fischer projection formula it is necessary to carry out even number of exchanges of pair of atoms or groups, so as to bring the lowest priority atom or group (4) at the bottom (or top).



In first Fischer projection formula, the group of lowest priority (D) is at the left hand side. So as to bring this group (D) at the bottom (or top), carry out the even number of exchanges i.e. exchange the position of group (D) with (C) and then (A) with (B). Now the second Fischer projection formula obtained has the group of lowest priority (D) is at the bottom. View the molecule from the side opposite to the group (D). Since the arrangement of remaining three groups (A,B,C) is in clockwise direction, the above molecule is R-isomer.

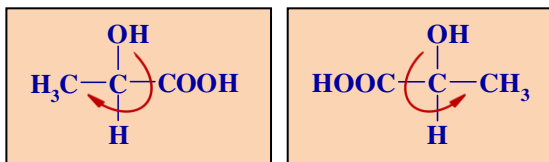
Examples ...

Lactic acid

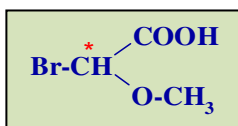


Groups	:	CH <sub>3</sub>	H	OH	COOH
Atomic no. of key atoms	:	6	1	8	6
Attachments of key atoms	:	H,H,H	--	--	O,O,O
Order of priority	:	3	4	1	2

Configurations: R-Lactic acid and S-Lactic acid

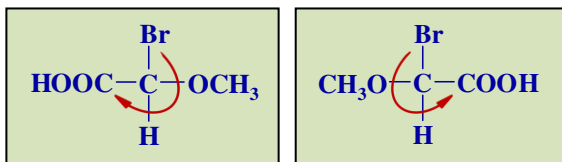


**Bromo methoxy acetic acid**

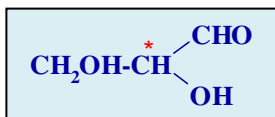


Groups	:	Br	H	OCH <sub>3</sub>	COOH
Atomic no. of key atoms	:	35	1	8	6
Attachments of key atoms	:	--	--	--	--
Order of priority	:	1	4	2	3

Configurations: R-Bromo methoxy acetic acid and S-Bromo methoxy acetic acid

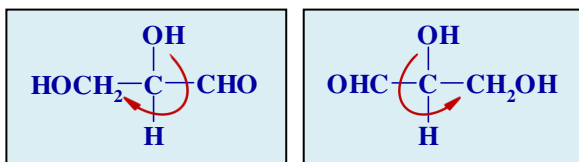


**Glyceraldehyde**

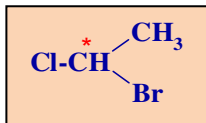


Groups	:	CH <sub>2</sub> OH	H	OH	CHO
Atomic no. of key atoms	:	6	1	8	6
Attachments of key atoms	:	H,H,O	--	--	H,O,O
Order of priority	:	3	4	1	2

Configurations: R-Glyceraldehyde and S-Glyceraldehyde

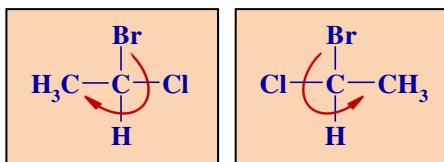


### 1-Chloro-1-bromo ethane

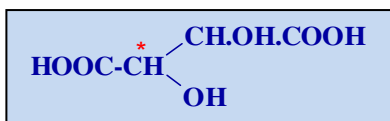


Groups	:	Cl	H	Br	CH <sub>3</sub>
Atomic no. of key atoms	:	17	1	35	6
Attachments of key atoms	:	--	--	--	--
Order of priority	:	2	4	1	3

Configurations: R-1-Chloro-1-bromo ethane and S-1-Chloro-1-bromo ethane

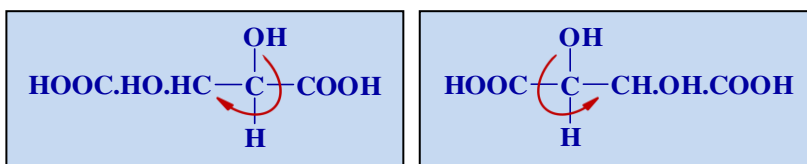


### Tartaric acid

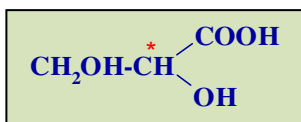


Groups	:	COOH	H	OH	CH.OH.COOH
Atomic no. of key atoms	:	6	1	8	6
Attachments of key atoms	:	O,O,O	--	--	H,O,C
Order of priority	:	2	4	1	3

Configurations: R-Tartaric acid and S-Tartaric acid

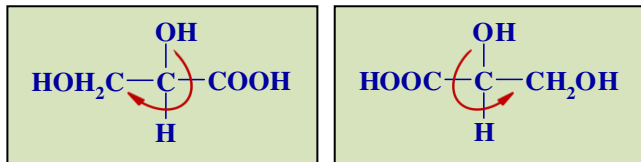


### Glyceric acid

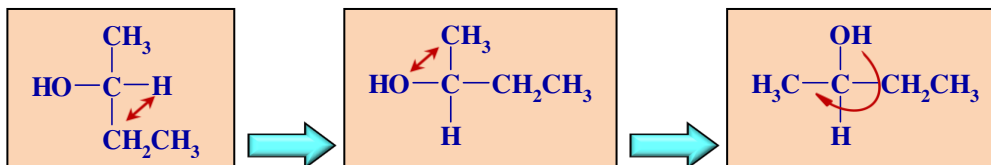


Groups	:	CH <sub>2</sub> OH	H	OH	COOH
Atomic no. of key atoms	:	6	1	8	6
Attachments of key atoms	:	H,H,O	--	--	O,O,O
Order of priority	:	3	4	1	2

Configurations: R-Glyceric acid and S-Glyceric acid



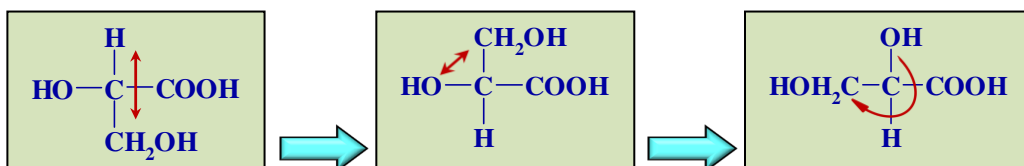
**Problems** - To assign R and S configuration to the compounds whose Fischer projection formula is given.



Fischer projection formula      After 1<sup>st</sup> exchange of groups      After 2<sup>nd</sup> exchange of groups

Order of priority: OH > CH<sub>2</sub>CH<sub>3</sub> > CH<sub>3</sub> > H

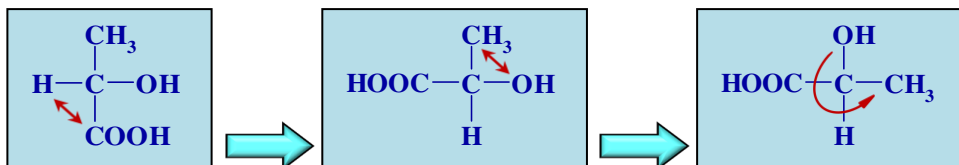
Configuration : R



Fischer projection formula      After 1<sup>st</sup> exchange of groups      After 2<sup>nd</sup> exchange of groups

Order of priority: OH > COOH > CH<sub>2</sub>OH > H

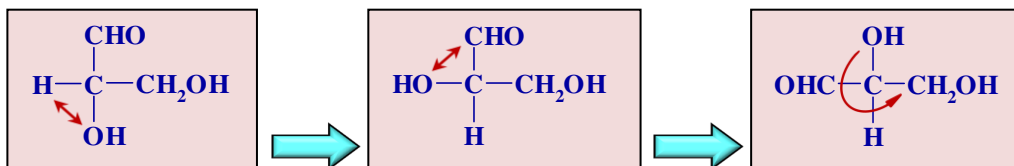
Configuration : R



Fischer projection formula      After 1<sup>st</sup> exchange of groups      After 2<sup>nd</sup> exchange of groups

Order of priority: OH > COOH > CH<sub>3</sub> > H

Configuration : S



Fischer projection formula      After 1<sup>st</sup> exchange of groups      After 2<sup>nd</sup> exchange of groups

Order of priority: OH > CHO > CH<sub>2</sub>OH > H

Configuration : S

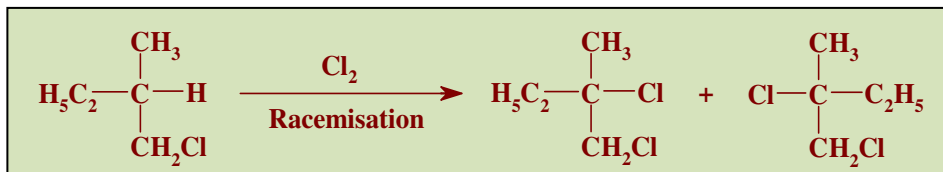
## 8. Racemisation and Resolution of Racemic Mixture

### A. Racemisation

The conversion of optically active pure enantiomer (+) or (-) into racemic mixture ( $\pm$ ) is called as racemisation.

The (+) and (-) forms of most of the compounds are capable of racemisation under the influence of heat, light or chemical reagents.

**Example ...**



The (-) 1-chloro-2-methyl butane, which is a pure enantiomer on chlorination undergoes the process of racemisation to form the mixture of (+) 1,2-dichloro-2-methyl butane and (-) 1,2-dichloro-2-methyl butane. This mixture is called as the racemic mixture and it is optically inactive.

### B. Resolution of Racemic Mixture

The separation of racemic mixture ( $\pm$ ) into its optically active pure enantiomeric constituents (+) or (-) is called as resolution of racemic mixture.

Resolution racemic mixture can be carried out by the following different methods.

#### I. Mechanical Separation

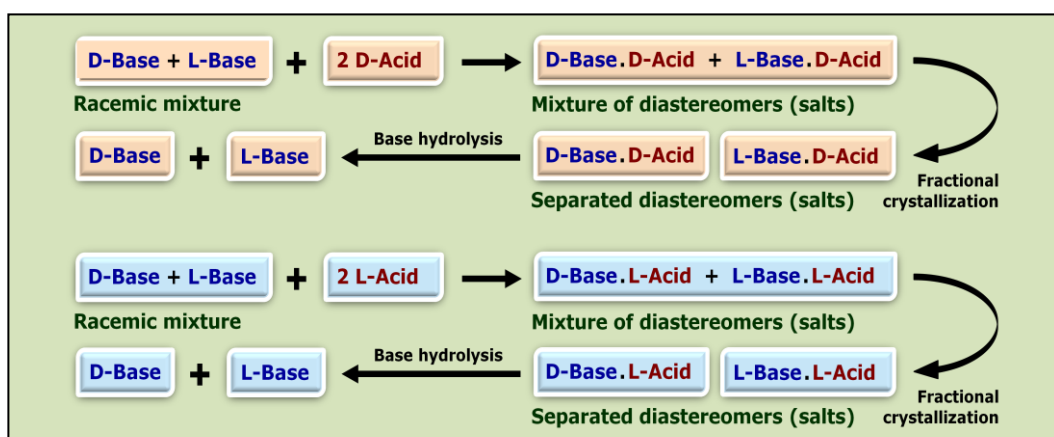
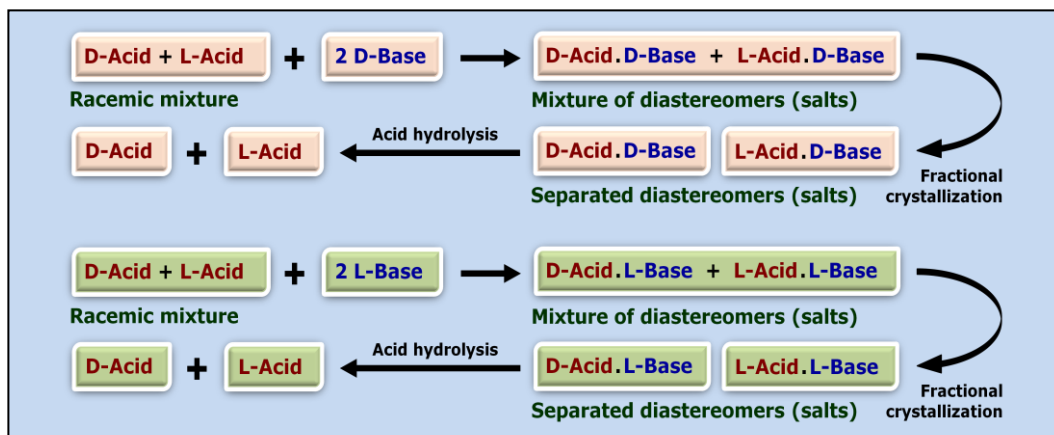
In mechanical separation, enantiomeric compounds which form the left handed and right handed (R and S) crystals can be separated manually using magnifying glass/lens. It is somewhat time consuming method and not applicable to all enantiomers.

#### II. Biochemical Separation (Bacterial or Biological) (Asymmetric Destruction)

Certain bacteria tend to destroy selectively only one of the enantiomeric forms and so these bacteria are useful in isolation of the other. The bacteria *penicillium glaucum* can be used to remove the *d*-ammonium tartarate from racemic mixture to leave back only the *l*-ammonium tartarate, after a suitable time interval.

#### III. Chemical Separation

This is the best method of separation or resolution of racemic mixture. It involves the conversion of active constituents of racemic mixture into diastereomers i.e. salts by reacting with another active acid or base. The two diastereomers or salts are differ in their solubility and can be separated by fractional crystallization followed by the hydrolysis with inorganic acid or alkali to get the original active compounds.



The racemic mixture of ( $\pm$ ) tartaric acid on treatment with (+) cinchonine gives (+) cinchonine (+) tartarate and (+) cinchonine (-) tartarate, which are separated by the fractional crystallization. During crystallization saturated solution is formed. The (+) cinchonine (-) tartarate is less soluble and hence it crystallizes out first. The (+) tartaric acid and (-) tartaric acid can be formed by hydrolysis of these salts. The commonly used bases in the chemical separation are quinine, brucine, cinchonine, morphine etc. whereas the commonly used acids are tartaric acid, camphoric acid, malic acid, lactic acid etc.

#### IV. Selective or Chromatographic Adsorption

It can be done by using certain optically active adsorbents by column chromatography. Constituents of racemic ( $\pm$ ) camphor can be separated using *d*-lactose as an adsorbent.

### 9. Cis-Trans and E-Z Isomerism or Configuration or Nomenclature

#### I. Cis-Trans Isomerism or Configuration

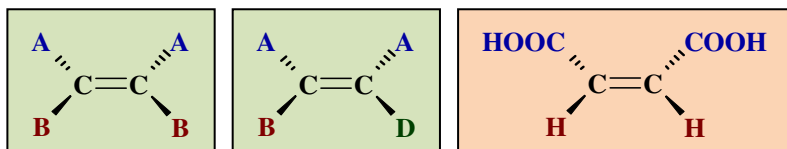
The cis-trans isomerism is geometrical isomerism. In cis-trans isomerism stereoisomers have different geometrical arrangement of atoms or groups about restricted bond (C=C).

In this isomerism each double bonded carbon atom must contain at least one similar atom or group.

**Cis Isomer** - The geometrical isomer in which similar atoms or groups are at the same side of restricted bond (C=C) is called as cis geometrical isomer or cis isomer.

Example ...

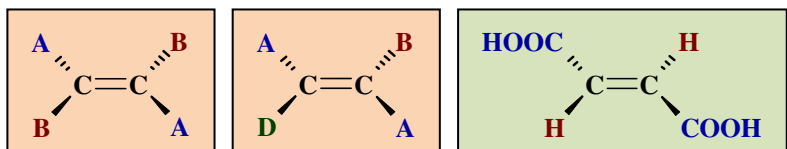
**Maleic acid**



**Trans Isomer** - The geometrical isomer in which similar atoms or groups are at the diagonally opposite side of restricted bond (C=C) is called as trans geometrical isomer or trans isomer.

Example ...

**Fumaric acid**



Trans isomers are more stable as compared to the cis isomers, because in trans isomers larger size similar groups are far away from each other and hence there is no Vander Waal's steric repulsion or strain, but in cis isomers the larger size similar groups are close to each other so there is Vander Waal's steric repulsion and hence less stable. The cis and trans isomers differ in most of their physical and chemical properties, maleic acid has melting point 403K/130<sup>0</sup>C whereas fumaric acid has 560K/287<sup>0</sup>C.

## II. E-Z Isomerism or Configuration

The E-Z isomerism is geometrical isomerism. In E-Z isomerism stereoisomers have different geometrical arrangement of atoms or groups about restricted bond (C=C). In this isomerism no need of each double bonded carbon atom must contain at least one similar atom or group.

As in many cases it is not possible to designate the geometrical isomers by cis-trans nomenclature; Cahn, Ingold and Prelog have suggested this system of nomenclature in terms of priority of groups at each double bonded carbon atom.

In this system, the configuration of geometrical isomers is decided on the basis of following rules.

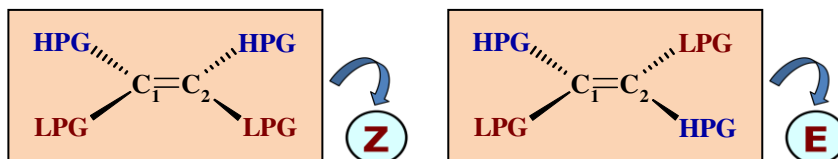
1. Locate the double bonded carbon atoms in molecule (geometrical isomer).
2. Assign priority separately to the different atoms or groups attached to each double bonded carbon atom as per the priority rules given below.



3. If molecule contains more number of double bonds then configuration at each double bond is to be specified independently.

**Z-Configuration** - The configuration in which higher priority atoms or groups attached to each double bonded carbon atom are at same side of double bond (C=C) is called as Z-configuration (Z : Zusammen i.e. together / same side).

**E-Configuration** - The configuration in which higher priority atoms or groups attached to each double bonded carbon atom are at diagonally opposite side of double bond (C=C) is called as E-configuration (E : Entgegen i.e. opposite side).



- **Priority rules**

- The groups with key atom (directly attached to double bonded carbon atom) of higher atomic number have higher priority and another have lower priority.

Example ...



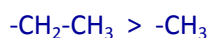
- The Isotopes with higher atomic mass number have higher priority.

Example ...



- If key atoms have same atomic number then the key atoms with more attachments of higher atomic number atoms have higher priority.

Example ...



Here for both ethyl and methyl groups, key atoms are same i.e. carbon and their attachments are C,H,H and H,H,H with atomic numbers 12,1,1 and 1,1,1 respectively.

If key atoms have same atomic number and their attachments are also same then the key atoms with next or second attachments of higher atomic number atoms have higher priority.

Example ...



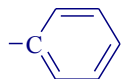
Here for both bromo-ethyl and chloro-ethyl groups, key atoms are same i.e. carbon and their attachments are also same i.e. C,H,H. Their next attachments are H,H,Br and H,H,Cl with atomic numbers 1,1,35 and 1,1,17 respectively.

- The multiple bonded atoms are equivalent to multiple numbers of attachments of atoms by single bond.

Examples ...



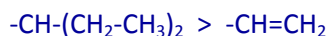
Here attachments of carbon are C,C,H / C,C,C / O,O,H / N,N,N respectively.



Here attachments of carbon are C,C,C.

But the two or three atoms attached actually to another atoms, have higher priority than that of doubly or triply bonded atoms.

Example ...



Here attachments of carbon are C,C,H.

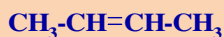
- e. The groups with maximum numbers of carbon atoms have higher priority.

Example ...



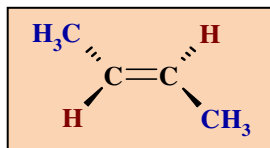
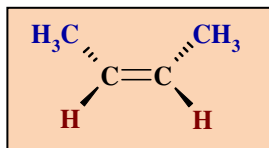
Examples ...

### 2-Butene

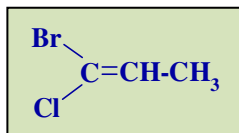


Groups at C <sub>1</sub> and C <sub>2</sub>	:	CH <sub>3</sub>	H	:	CH <sub>3</sub>	H
Atomic no. of key atoms	:	6	1	:	6	1
Attachments of key atoms	:	--	--	:	--	--
Order of priority	:	HPG	LPG	:	HPG	LPG

Configurations: Z-2-Butene and E-2-Butene

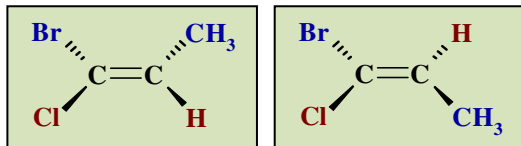


### 1-Bromo-1-chloro propene



Groups at C <sub>1</sub> and C <sub>2</sub>	:	Br	Cl	:	CH <sub>3</sub>	H
Atomic no. of key atoms	:	35	17	:	6	1
Attachments of key atoms	:	--	--	:	--	--
Order of priority	:	HPG	LPG	:	HPG	LPG

Configurations: Z-1-Bromo-1-chloro propene and E-1-Bromo-1-chloro propene

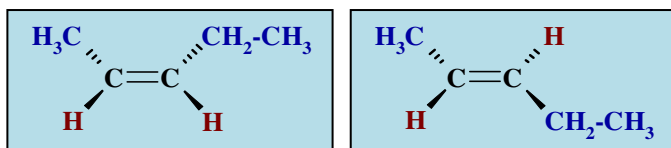


## 2-Pentene

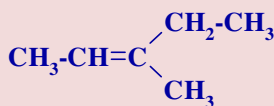


Groups at C <sub>1</sub> and C <sub>2</sub>	:	CH <sub>3</sub>	H	:	CH <sub>2</sub> -CH <sub>3</sub>	H
Atomic no. of key atoms	:	6	1	:	6	1
Attachments of key atoms	:	--	--	:	--	--
Order of priority	:	HPG	LPG	:	HPG	LPG

Configurations: Z-2-Pentene and E-2-Pentene



## 3-Methyl-2-pentene



Groups at C <sub>1</sub> and C <sub>2</sub>	:	CH <sub>3</sub>	H	:	CH <sub>2</sub> -CH <sub>3</sub>	CH <sub>3</sub>
Atomic no. of key atoms	:	6	1	:	6	6
Attachments of key atoms	:	--	--	:	H,H,C	H,H,H
Order of priority	:	HPG	LPG	:	HPG	LPG

Configurations: Z-3-Methyl-2-pentene and E-3-Methyl-2-pentene



## 10. Conformations and Conformational Analysis

### A. Conformations (Conformational or Rotational Isomers)

The stereoisomers which have different spatial arrangement of atoms or groups about C-C single bond and can be obtained by rotation of half of the molecule about C-C single bond are called as conformations or conformational isomers or rotational isomers.

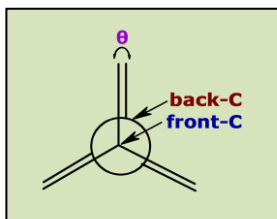
The stable conformations having minimum potential energy are called as conformers or rotamers. Conformations are non-isolable and easily inter-convertible from one form to other. Various types of conformations of molecules can be represented by Newman, Sawhorse or Flying Wedge projection formulae.

Three important types of conformations are as given below.

## I. Eclipsed Conformations

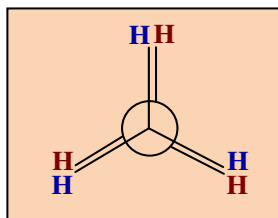
The conformations in which bonds of back carbon atom lie exactly behind the bonds of front carbon atom are called as eclipsed conformations.

In eclipsed conformations the bonds of back and front carbon atoms are seen closer to each other. The dihedral angle ( $\theta$ ) is equal to  $0^\circ$ ,  $120^\circ$  or  $240^\circ$ . General eclipsed conformation can be represented by Newman projection formula as shown below.



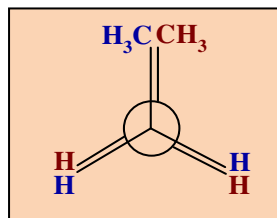
Examples ...

### Ethane (Eclipsed)



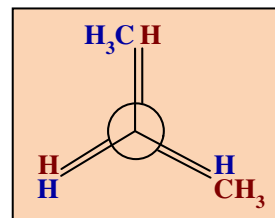
$\theta = 0^\circ, 120^\circ$  or  $240^\circ$

### *n*-Butane (Fully Eclipsed)



$\theta = 0^\circ$

### *n*-Butane (Eclipsed)

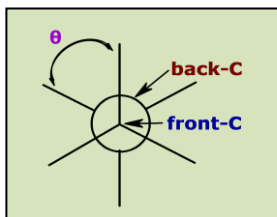


$\theta = 120^\circ$  or  $240^\circ$

## II. Staggered Conformations

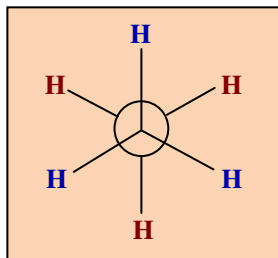
The conformations in which bonds of back carbon atom lie exactly between the bonds of front carbon atom are called as staggered conformations.

In staggered conformations the bonds of back and front carbon atoms are seen far apart from each other. The dihedral angle ( $\theta$ ) is equal to  $60^\circ$ ,  $180^\circ$  or  $300^\circ$ . General staggered conformation can be represented by Newman projection formula as shown below.



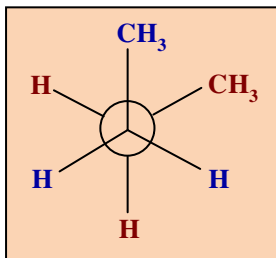
Examples ...

Ethane (Staggered)



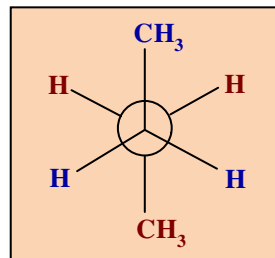
$$\theta = 60^\circ, 180^\circ \text{ or } 300^\circ$$

*n*-Butane (Gauche/Staggered)



$$\theta = 60^\circ \text{ or } 300^\circ$$

*n*-Butane (Anti / Staggered)

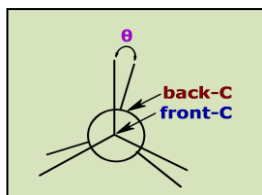


$$\theta = 180^\circ$$

### III. Skew Conformations

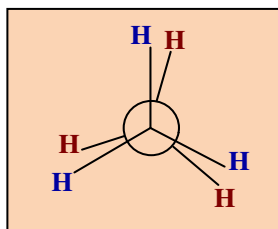
Any intermediate conformation lies between the eclipsed and staggered conformations are called as skew conformations.

The dihedral angle ( $\theta$ ) is equal to any value other than  $0^\circ$ ,  $60^\circ$ ,  $120^\circ$ ,  $180^\circ$ ,  $240^\circ$  and  $300^\circ$ . General skew conformation can be represented by Newman projection formula as shown below.



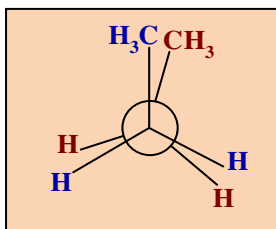
Examples ...

Ethane (Skew)

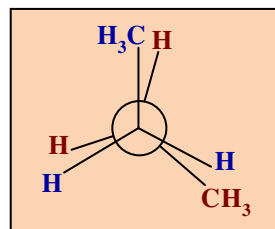


$$\theta \neq 0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ \text{ and } 300^\circ$$

*n*-Butane (Skew)



*n*-Butane (Skew)



### B. Conformational Analysis

The study of existence, relative physical and chemical properties, stability and stabilization energy of conformations is called as conformational analysis.

In general, staggered conformations have -

1. Less potential energy
2. Less eclipsing strain
3. Less Vander-Waal's steric strain

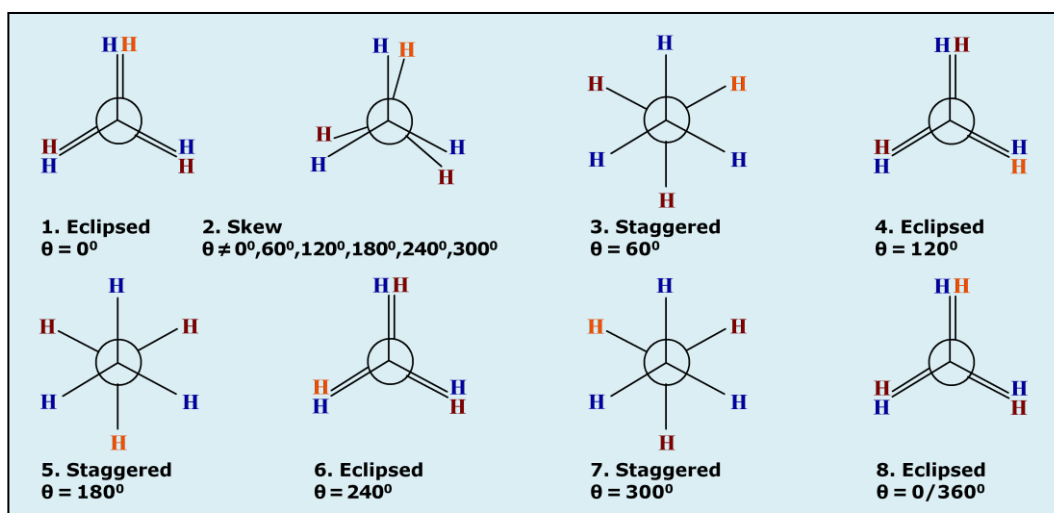
Hence, staggered conformations are more stable than eclipsed or skew conformations.

## I. Conformational Analysis of Ethane (Acyclic System)

The study of existence, relative stability and stabilization energy of conformations is called as conformational analysis.

The stereoisomers which have different spatial arrangement of atoms or groups about C-C single bond and can be obtained by rotation of half of the molecule about C-C single bond are called as conformations or conformational isomers or rotational isomers and the phenomenon is conformational or rotational isomerism.

The various types of conformations of ethane having different spatial arrangement of H about C-C single bond are represented by Newman projection formula as shown below.

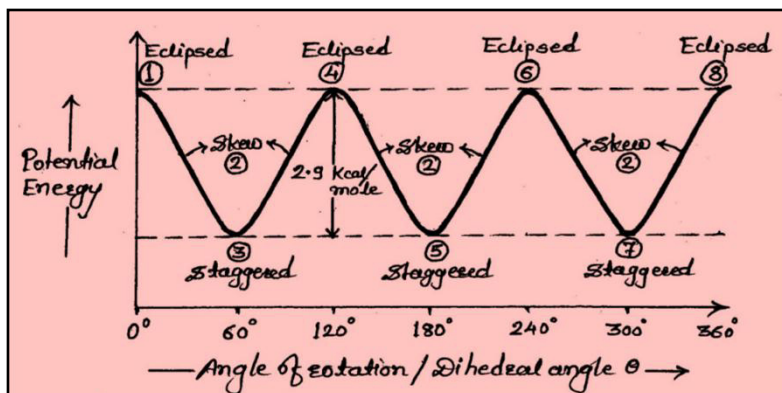


**Eclipsed Conformation** - In eclipsed conformation, bonds of back carbon atom lie exactly behind the bonds of front carbon atom. The bonds of back and front carbon atoms are seen closer to each other. The dihedral angle ( $\theta$ ) is equal to  $0^\circ$ ,  $120^\circ$  or  $240^\circ$ . The conformations 1, 4, 6 and 8 are eclipsed conformations.

**Staggered Conformation** - In staggered conformation, bonds of back carbon atom lie exactly between the bonds of front carbon atom. The bonds of back and front carbon atoms are seen far apart from each other. The dihedral angle ( $\theta$ ) is equal to  $60^\circ$ ,  $180^\circ$  or  $300^\circ$ . The conformations 3, 5 and 7 are staggered conformations.

**Skew Conformation** - The skew conformation is any intermediate conformation lies between the eclipsed and staggered conformations. The dihedral angle ( $\theta$ ) is equal to any value other than  $0^\circ$ ,  $60^\circ$ ,  $120^\circ$ ,  $180^\circ$ ,  $240^\circ$  and  $300^\circ$ . The conformation 2 is one of the skew conformations.

**Potential Energy Curve** - The potential energy curve of conformations and the energy changes during rotation of half of the molecule about C-C single bond is as given below.



Potential energy curve shows that -

1. All eclipsed conformations have same potential energy, so they have same stability.
2. All staggered conformations have same potential energy, so they have same stability.
3. The conformations having least potential energy are specially called as conformers, so staggered conformations are conformers.

All staggered conformations have -

- a. Least eclipsing or torsional strain between the bonds.
- b. Least Vander-Waal's steric strain or repulsion between non-bonded hydrogen atoms.
- c. Least potential energy than eclipsed conformations by 2.9 Kcal/mole.

Hence all staggered conformations of ethane are more stable than eclipsed conformations and these are more preferred. At equilibrium, most of the ethane molecules exist in staggered conformations and their percentage is higher.

The energy difference of 2.9 Kcal/mole between eclipsed and staggered conformations of ethane is easily overcome by their kinetic energy at room temperature. Hence eclipsed and staggered conformations of ethane can not be isolated from each other.

The increasing order of relative stabilities of conformations of ethane is as below.

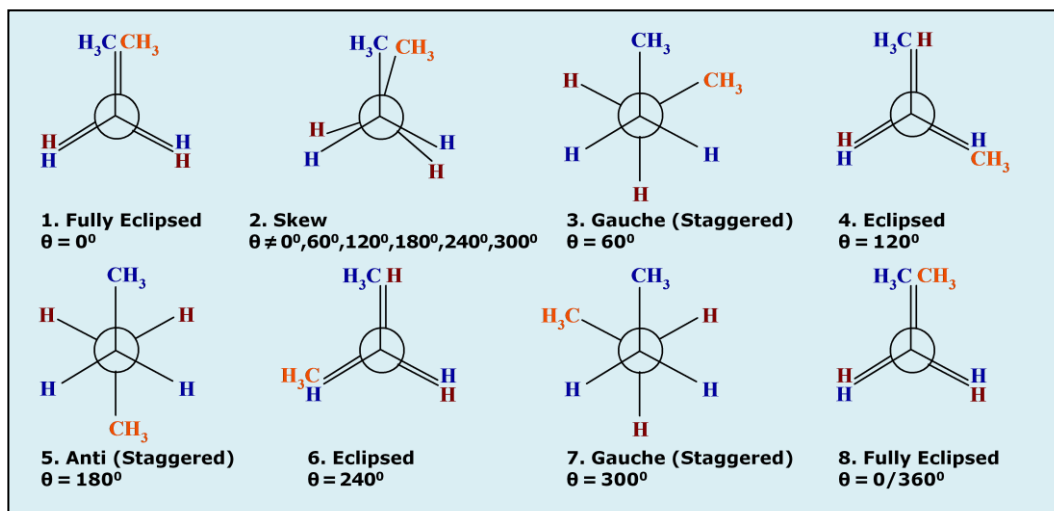
Eclipsed < Skew < Staggered  
 (Least stable) (Stable) (Most stable)

## II. Conformational Analysis of *n*-Butane (Acyclic System)

The study of existence, relative stability and stabilization energy of conformations is called as conformational analysis.

The stereoisomers which have different spatial arrangement of atoms or groups about C-C single bond and can be obtained by rotation of half of the molecule about C-C single bond are called as conformations or conformational isomers or rotational isomers and the phenomenon is conformational or rotational isomerism.

The various types of conformations of *n*-butane having different spatial arrangement of H and CH<sub>3</sub> about C-C single bond are represented by Newman projection formula as shown below.



**Eclipsed Conformation** - In eclipsed conformation, bonds of back carbon atom lie exactly behind the bonds of front carbon atom. The bonds of back and front carbon atoms are seen closer to each other. The dihedral angle ( $\theta$ ) is equal to  $0^\circ$ ,  $120^\circ$  or  $240^\circ$ . The conformations 1, 4, 6 and 8 are eclipsed conformations.

**Fully Eclipsed Conformation** - The eclipsed conformation in which identical groups ( $\text{CH}_3$ ) of back and front carbon atoms are seen closer to each other is specially called as fully eclipsed conformation. The dihedral angle ( $\theta$ ) is equal to  $0^\circ$ . The conformations 1 and 8 are fully eclipsed conformations.

**Staggered Conformation** - In staggered conformation, bonds of back carbon atom lie exactly between the bonds of front carbon atom. The bonds of back and front carbon atoms are seen far apart from each other. The dihedral angle ( $\theta$ ) is equal to  $60^\circ$ ,  $180^\circ$  or  $300^\circ$ . The conformations 3, 5 and 7 are staggered conformations.

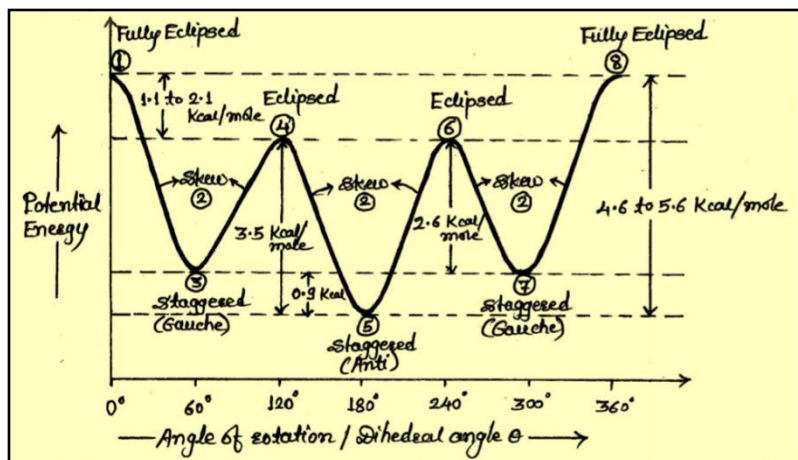
**Gauche (Staggered) Conformation** - The staggered conformation in which identical groups ( $\text{CH}_3$ ) of back and front carbon atoms are seen adjacent in position is specially called as gauche conformation. The dihedral angle ( $\theta$ ) is equal to  $60^\circ$  or  $300^\circ$ . The conformations 3 and 7 are gauche conformations.

**Anti (Staggered) Conformation** - The staggered conformation in which identical groups ( $\text{CH}_3$ ) of back and front carbon atoms are seen far apart (trans or opposite) in position is specially called as anti conformation. The dihedral angle ( $\theta$ ) is equal to  $180^\circ$ . The conformation 5 is anti conformation.

**Skew Conformation** - The skew conformation is any intermediate conformation lies between the eclipsed and staggered conformations. The dihedral angle ( $\theta$ ) is equal to any value other than  $0^\circ$ ,  $60^\circ$ ,  $120^\circ$ ,  $180^\circ$ ,  $240^\circ$  and  $300^\circ$ . The conformation 2 is one of the skew conformations.

**Potential Energy Curve** - The potential energy curve of conformations and the energy changes during rotation of half of the molecule about C-C single bond is as given below.





Potential energy curve shows that -

1. Eclipsed and fully eclipsed conformations have different potential energy, so they have different stability. Eclipsed conformations are more stable than fully eclipsed conformations.
2. Staggered conformations have different potential energy, so they have different stability. Anti conformation is more stable than gauche conformations.
3. The conformations having least potential energy are specially called as conformers, so anti conformation is conformer.

All staggered conformations have -

- a. Less eclipsing or torsional strain between the bonds.
- b. Less Vander-Waal's steric strain or repulsion between non-bonded hydrogen atoms or  $\text{CH}_3$  groups.
- c. Less potential energy than eclipsed conformations.

Hence all staggered conformations of *n*-butane are more stable than eclipsed conformations.

Anti staggered conformation has -

- a. Least eclipsing or torsional strain between the bonds.
- b. Least Vander-Waal's steric strain or repulsion between non-bonded hydrogen atoms or  $\text{CH}_3$  groups.
- c. Least potential energy than any other conformations.

Hence anti conformation of *n*-butane is most stable than any other conformations and it is most preferred. At equilibrium, most of the *n*-butane molecules exist in anti conformation and its percentage is higher.

Fully eclipsed conformations have -

- a. Highest eclipsing or torsional strain between the bonds.
- b. Highest Vander-Waal's steric strain or repulsion between non-bonded hydrogen atoms or  $\text{CH}_3$  groups.
- c. Highest potential energy than any other conformations.

Hence fully eclipsed conformations of *n*-butane are least stable than any other conformations. The remaining eclipsed conformations are slightly stable than fully eclipsed conformations.

The energy difference of 4.6 to 5.6 Kcal/mole between fully eclipsed and anti conformations of *n*-butane is easily overcome by their kinetic energy at room temperature. Hence conformations of *n*-butane can not be isolated from each other.

The increasing order of relative stabilities of conformations of *n*-butane is as below.

Fully Eclipsed < Eclipsed < Skew < Gauche < Anti  
 (Least stable) (Less Stable) (Stable) (More stable) (Most stable)

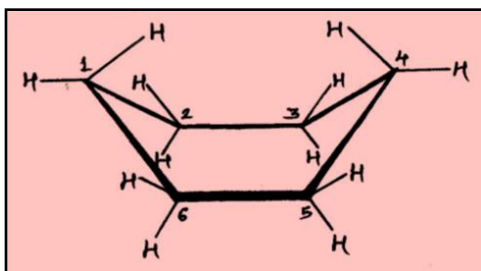
### III. Conformational Analysis of Cyclohexane (Cyclic System)

The study of existence, relative stability and stabilization energy of conformations is called as conformational analysis.

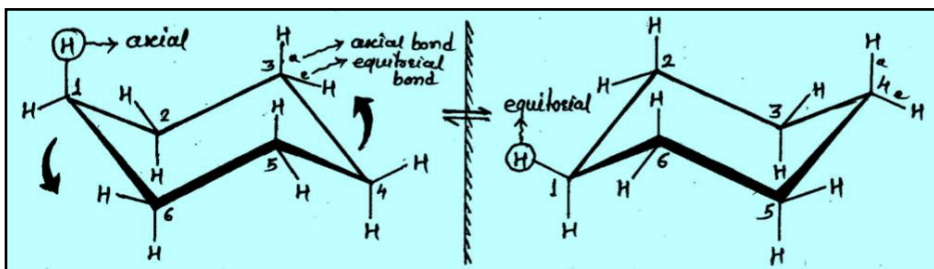
The stereoisomers which have different spatial arrangement of atoms or groups about C-C single bond and can be obtained by rotation of the molecule about C-C single bond are called as conformations or conformational isomers or rotational isomers and the phenomenon is conformational or rotational isomerism.

The various types of conformations of cyclohexane having different spatial arrangement of H about C-C single bond are represented as shown below.

**Boat Conformation** - In boat conformation, carbon atoms 2, 3, 5 and 6 lie in a same plane while carbon atoms 1 and 4 lie above the plane.



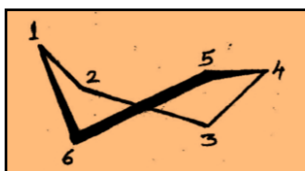
**Chair Conformation** - In chair conformation, carbon atoms 2, 3, 5 and 6 lie in a same plane while carbon atom 1 lie above the plane and carbon atom 4 lie below the plane.



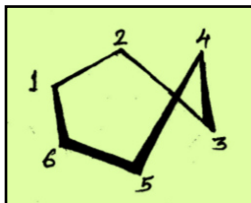
There are two types of C-H bonds in chair conformation i.e. axial and equatorial C-H bonds. The vertical C-H bonds parallel to vertical axis of symmetry is called as axial C-H bond and it is denoted by letter 'a'. The C-H bonds which makes an angle of  $109^{\circ}.28'$  with vertical axis of symmetry or an angle of  $19^{\circ}.28'$  with horizontal plane is called as equatorial C-H bond and it is denoted by letter 'e'. There are six axial and six equatorial C-H bonds in chair conformation of cyclohexane. The hydrogen atom attached to carbon atom by axial bond is called as axial hydrogen atom whereas hydrogen atom attached to carbon atom by equatorial bond is called as equatorial hydrogen atom.

One chair conformation can be converted into another chair conformation and during this conversion the axial bonds become equatorial while equatorial bonds become axial.

**Twist Boat or Twist Conformation** - In twist boat or twist conformation, no one carbon atoms lie in a same plane. It can be obtained by twisting or folding the boat form.

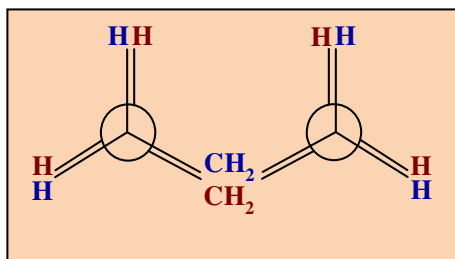


**Half Chair Conformation** - In half chair conformation, carbon atoms of one end of the ring lie in a same plane.



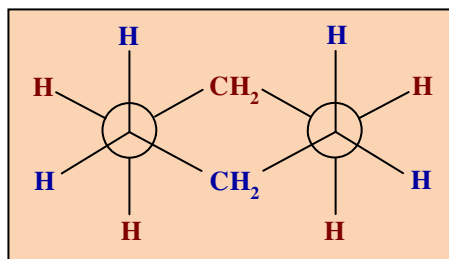
The boat and chair conformations of cyclohexane are represented by Newman projection formula as shown below.

**Cyclohexane (Eclipsed)**



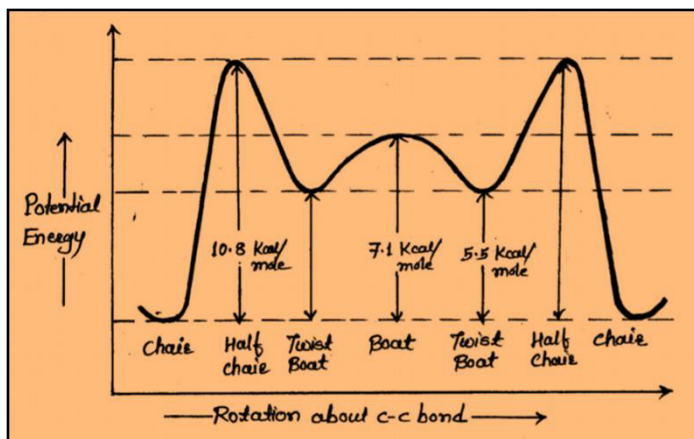
Boat conformation (Less stable)

**Cyclohexane (Staggered)**



Chair conformation (More stable)

**Potential Energy Curve** - The potential energy curve of conformations and the energy changes during rotation of the molecule about C-C single bond is as given below.



Potential energy curve shows that -

1. Boat, chair, twist boat and half chair conformations have different potential energy, so they have different stability. Chair conformation is most stable than any other.
2. The conformations having least potential energy are specially called as conformers, so chair conformation is conformer.

The both boat and chair conformations of cyclohexane are stable conformations because they have -

1. Normal tetrahedral angle  $109^{\circ}.28'$ .
2. Zero angle strain (strainless rings).
3. No dipole-dipole repulsive strain, because no polar bonds.

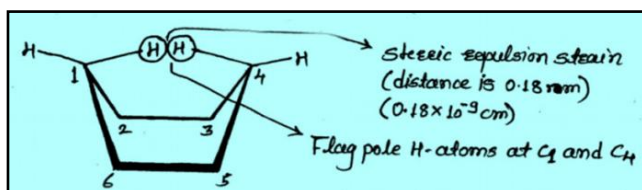
Chair conformation has -

- a. Least eclipsing or torsional strain between the bonds.
- b. Least Vander-Waal's steric strain or repulsion between non-bonded hydrogen atoms.
- c. No non-bonded steric strain or repulsion between flagpole hydrogen atoms at  $C_1$  and  $C_4$  position.
- d. Least potential energy than any other conformations.

**Note** - See the Newman projection formula of chair conformation

Boat conformation has -

- a. High eclipsing or torsional strain between the bonds.
- b. High Vander-Waal's steric strain or repulsion between non-bonded hydrogen atoms.
- c. High non-bonded steric strain or repulsion between flagpole hydrogen atoms at  $C_1$  and  $C_4$  position.



- d. High potential energy than chair conformation.

**Note** - See the Newman projection formula of boat conformation

Hence chair conformation of cyclohexane is most stable than any other conformations and it is most preferred whereas boat conformation is less stable. At equilibrium, most of the cyclohexane molecules exist in chair conformation and its percentage is higher.

Twist boat conformation is more stable than boat conformation whereas half chair conformation is least stable than any other conformations.

The energy difference of 10.8 Kcal/mole between half chair and chair conformations of cyclohexane is easily overcome by their kinetic energy at room temperature. Hence conformations of cyclohexane can not be isolated from each other.

The increasing order of relative stabilities of conformations of cyclohexane is as below.

Half Chair < Boat < Twist Boat < Chair  
 (Least stable) (Less Stable) (More Stable) (Most stable)

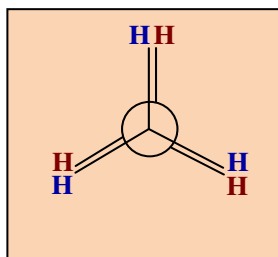
## 11. Projection Formulae

### I. Newman Projection Formula

To write a Newman projection formula, the molecule is to be viewed from the one end of carbon-carbon bond axis. The front carbon atom is represented by a point and the back by a circle. The bond between two carbon atoms is not seen. The atoms or groups attached to the front carbon atom are shown by three lines or bonds which meet together at point. The atoms or groups that attached to the back carbon atom are shown by three lines or bonds pointing out from the circle. The atoms or groups are then written in the same clockwise order on each carbon atom.

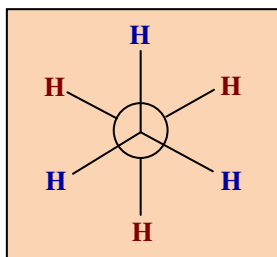
Examples ...

#### Ethane (Eclipsed)



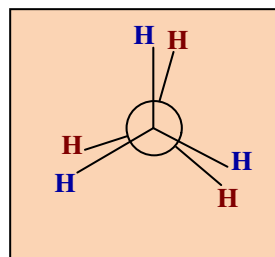
$\theta = 0^\circ, 120^\circ$  or  $240^\circ$

#### Ethane (Staggered)



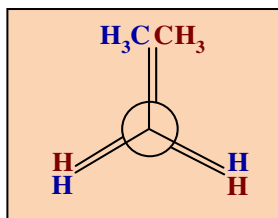
$\theta = 60^\circ, 180^\circ$  or  $300^\circ$

#### Ethane (Skew)



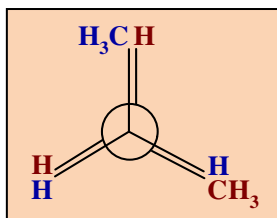
$\theta \neq 0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ, 300^\circ$

#### *n*-Butane (Fully Eclipsed)



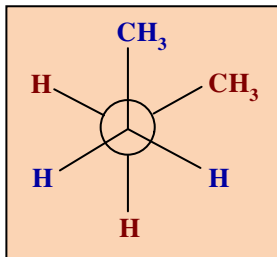
$\theta = 0^\circ$

#### *n*-Butane (Eclipsed)

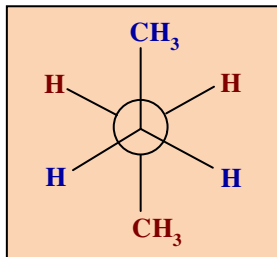


$\theta = 120^\circ$  or  $240^\circ$

***n*-Butane(Gauche/Staggered)    *n*-Butane (Anti / Staggered)**

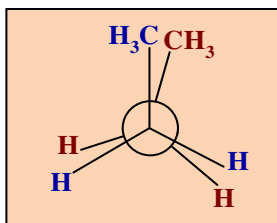


$$\theta = 60^\circ \text{ or } 300^\circ$$



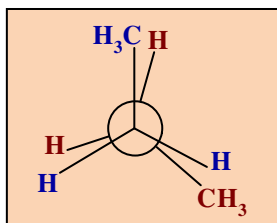
$$\theta = 180^\circ$$

***n*-Butane (Skew)**



$$\theta \neq 0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ \text{ and } 300^\circ$$

***n*-Butane (Skew)**

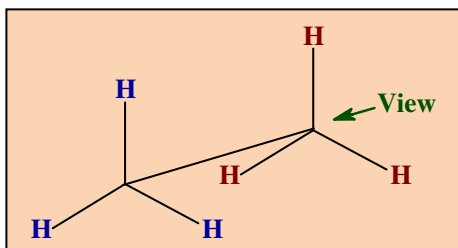


**II. Sawhorse Projection Formula**

To write a Sawhorse projection formula, the molecule is to be viewed slightly from above and the right hand side. The bond between two carbons is drawn diagonally and slightly elongated. The lower left hand carbon atom is always taken to be towards the front.

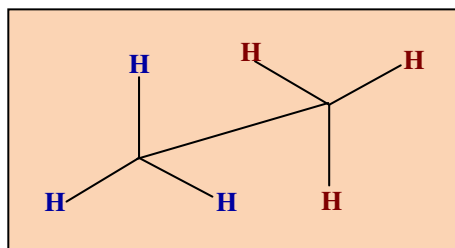
Examples ...

**Ethane (Eclipsed)**



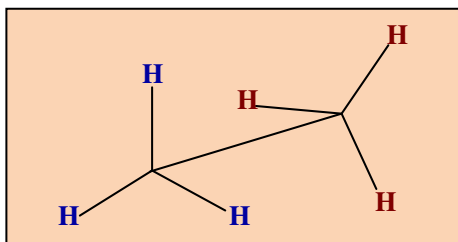
$$\theta = 0^\circ, 120^\circ \text{ or } 240^\circ$$

**Ethane (Staggered)**



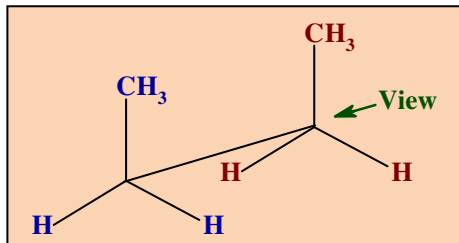
$$\theta = 60^\circ, 180^\circ \text{ or } 300^\circ$$

**Ethane (Skew)**



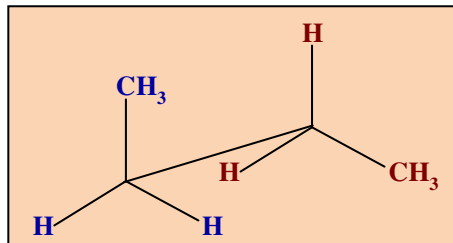
$$\theta \neq 0^\circ, 60^\circ, 120^\circ, 180^\circ, 240^\circ \text{ and } 300^\circ$$

### *n*-Butane (Fully Eclipsed)



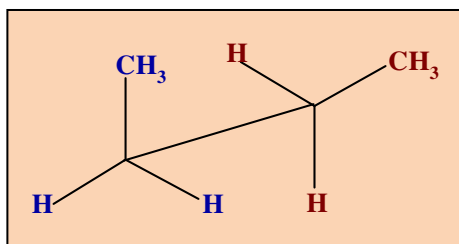
$$\theta = 0^{\circ}$$

### *n*-Butane (Eclipsed)



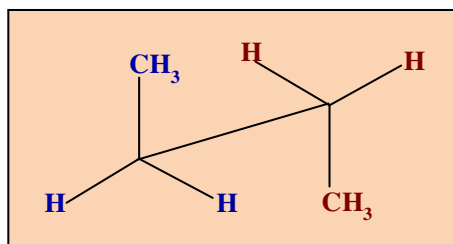
$$\theta = 120^{\circ} \text{ or } 240^{\circ}$$

### *n*-Butane (Gauche / Staggered)



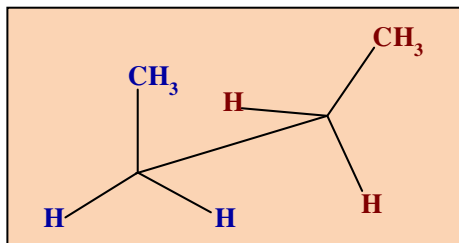
$$\theta = 60^{\circ} \text{ or } 300^{\circ}$$

### *n*-Butane (Anti / Staggered)



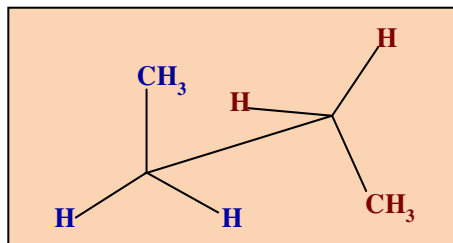
$$\theta = 180^{\circ}$$

### *n*-Butane (Skew)



$$\theta \neq 0^{\circ}, 60^{\circ}, 120^{\circ}, 180^{\circ}, 240^{\circ} \text{ and } 300^{\circ}$$

### *n*-Butane (Skew)

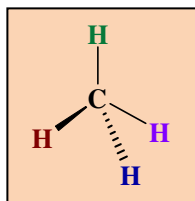


## III. Flying Wedge Projection Formula

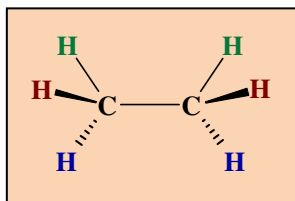
To write a flying wedge projection formula, three types of lines are to be used i.e. heavy line (solid wedge), dashed line (broken wedge) and solid line. A solid wedge represents a bond above the plane of paper i.e. pointing towards the observer, a broken wedge represents a bond below the plane of paper i.e. pointing away from the observer and a solid line is a bond in the plane of paper.

### Examples ...

#### Methane



#### Ethane

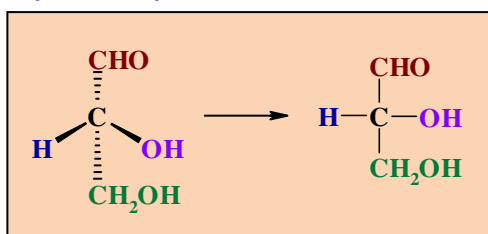


#### IV. Fischer Projection Formula

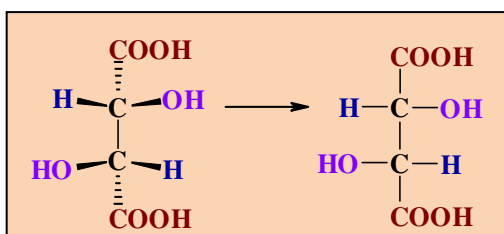
To write a Fischer projection formula, is the method of representing three dimensional tetrahedral structures in two dimensional forms on paper. These projection formulas are particularly used in carbohydrates, amino acids and other chiral molecules. For writing Fischer projection formula, the tetrahedral molecule is so oriented that the central atoms lies in the plane of paper and the bonds on the right and left side conventionally lie above the plane while the other two vertical bonds below the plane. The bonds above the plane are drawn as horizontal lines and below the plane as vertical lines in the shape of plus (+) sign. The atom that is the stereo-centre is often omitted; it is symbolized by the intersection point of the two lines of a cross. The carbon chain is drawn along the vertical line of the Fischer projection, usually with the most highly oxidized end carbon at the top.

Examples ...

##### Glyceraldehyde



##### Tartaric acid



#### 12. Baeyer's Strain Theory (BST)

Baeyer's strain theory explains the relative stability of cycloalkanes (alicyclic compounds) on the basis of angle strain. Angle strain is also called as Baeyer's strain.

##### I. Postulates or Assumptions or Characteristics of BST

1. All alicyclic compounds are planer.
2. Four valencies of carbon atom are directed towards the four corners of regular tetrahedron. The normal tetrahedral angle between two adjacent carbon-carbon bonds is  $109^{\circ}.28'$ .
3. The alicyclic compounds having actual valence bond angle equal to the normal tetrahedral angle  $109^{\circ}.28'$  have no strain, so they are stable.
4. The deviation of actual valence bond angle from the normal tetrahedral angle  $109^{\circ}.28'$  is called as angle strain or distortion or deviation. The angle strain is calculated from the equation -  
Angle strain per C-C bond =  $\frac{1}{2} [109^{\circ}.28' - \text{actual valence bond angle}]$
5. With increase in magnitude of the angle strain, the stability decreases and reactivity increases.
6. The positive (+) sign of angle strain shows that the actual valence bond angle is lesser than  $109^{\circ}.28'$ , indicating that carbon-carbon bonds are compressed towards each other to satisfy the geometry of ring (inward angle strain).



- The negative (-) sign of angle strain shows that the actual valence bond angle is greater than  $109^{\circ}.28'$ , indicating that carbon-carbon bonds are forced apart from each other to satisfy the geometry of ring (outward angle strain).

## II. Applications of BST

- It explains relative stability of cycloalkanes and alkanes.
- It explains stability or instability of alkenes.

## III. Limitations or defects or demerits of BST

- It does not explain greater stability of cyclohexane than cyclopentane.
- It does not explain easy preparations of alkenes.
- According to BST, seven and higher membered ring compounds (higher cycloalkanes) are unstable and difficult to prepare but actually they are quite stable and easy to prepare. e.g. stable 34 membered ring compounds can be prepared.
- It can not be applied to non-planer compounds.

## IV. Stability of cycloalkanes

Cyclopropane ( $\delta$ ) =  $+ 24^{\circ}.44'$

Cyclobutane ( $\delta$ ) =  $+ 9^{\circ}.44'$

Cyclopentane ( $\delta$ ) =  $+ 0^{\circ}.44'$

Cyclohexane ( $\delta$ ) =  $- 5^{\circ}.16'$

Cycloheptane ( $\delta$ ) =  $- 9^{\circ}.33'$

Cyclooctane ( $\delta$ ) =  $- 12^{\circ}.46'$

From cyclopropane to cyclopentane the magnitude of angle strain decreases, so stability increases and reactivity decreases while from cyclopentane to cyclooctane the magnitude of angle strain increases, so stability decreases and reactivity increases.

In cyclopropane, angle strain is maximum ( $+ 24^{\circ}.44'$ ), so it is highly unstable and highly reactive, it easily undergoes addition reaction with  $\text{Br}_2$  by opening the cyclic ring. In cyclobutane, angle strain is  $+ 9^{\circ}.44'$ , so it is more stable and less reactive than cyclopropane, it undergoes addition reaction under vigorous conditions. In cyclopentane, angle strain is minimum ( $+ 0^{\circ}.44'$ ), so it is most stable and least reactive, it does not undergo addition reaction by opening the cyclic ring.

In cyclohexane, magnitude of angle strain ( $- 5^{\circ}.16'$ ) is higher than cyclopentane ( $+ 0^{\circ}.44'$ ). So according to BST, cyclohexane and other higher cycloalkanes are unstable and reactive than cyclopentane, but actually, cyclohexane and other higher cycloalkanes are quite stable and do not give ring opening reaction (addition reaction).

In alkanes, actual valence bond angle is approximately equal to  $+ 109^{\circ}.28'$ , so there is zero angle strain and hence alkanes have maximum stability and minimum reactivity.

In alkenes, two carbon-carbon bonds ( $\text{C}=\text{C}$ ) are in same direction, so actual valence bond angle is  $0^{\circ}$  and hence angle strain is  $\frac{1}{2} [109^{\circ}.28' - \text{actual VBA}] = \frac{1}{2} [109^{\circ}.28' - 0^{\circ}]$   
 $= \frac{1}{2} [109^{\circ}.28']$

$$= \frac{1}{2} [108^{\circ}.88']$$

$$= + 54^{\circ}.44'$$

Thus in alkenes, the angle strain is maximum, so alkenes have highest instability (lowest stability) and highest reactivity.

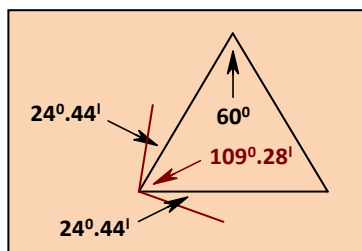
### Examples ...

#### Cyclopropane

$$\begin{aligned} \text{Actual VBA} &= (2n-4) \times 90^{\circ} / n && \text{Where, } n = 3 \text{ (no. of ring carbon atoms)} \\ &= (2 \times 3 - 4) \times 90^{\circ} / 3 \\ &= (6 - 4) \times 90^{\circ} / 3 \\ &= 60^{\circ} \end{aligned}$$

$$\begin{aligned} \text{Angle strain per C-C bond } (\delta) &= \frac{1}{2} [109^{\circ}.28' - \text{actual VBA}] \\ &= \frac{1}{2} [109^{\circ}.28' - 60^{\circ}] \\ &= \frac{1}{2} [49^{\circ}.28'] \\ &= \frac{1}{2} [48^{\circ}.88'] \\ &= + 24^{\circ}.44' \end{aligned}$$

This angle strain in cyclopropane is represented diagrammatically as shown below.

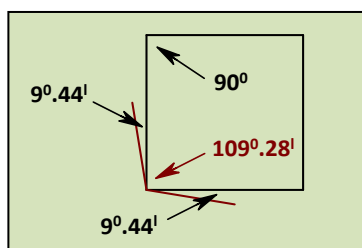


#### Cyclobutane

$$\begin{aligned} \text{Actual VBA} &= (2n-4) \times 90^{\circ} / n && \text{Where, } n = 4 \text{ (no. of ring carbon atoms)} \\ &= (2 \times 4 - 4) \times 90^{\circ} / 4 \\ &= (8 - 4) \times 90^{\circ} / 4 \\ &= 90^{\circ} \end{aligned}$$

$$\begin{aligned} \text{Angle strain per C-C bond } (\delta) &= \frac{1}{2} [109^{\circ}.28' - \text{actual VBA}] \\ &= \frac{1}{2} [109^{\circ}.28' - 90^{\circ}] \\ &= \frac{1}{2} [19^{\circ}.28'] \\ &= \frac{1}{2} [18^{\circ}.88'] \\ &= + 9^{\circ}.44' \end{aligned}$$

This angle strain in cyclobutane is represented diagrammatically as shown below.

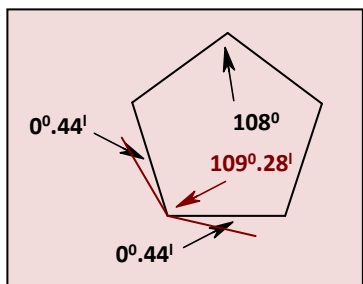


## Cyclopentane

$$\begin{aligned}\text{Actual VBA} &= (2n-4) \times 90^\circ / n && \text{Where, } n = 5 \text{ (no. of ring carbon atoms)} \\ &= (2 \times 5 - 4) \times 90^\circ / 5 \\ &= (10 - 4) \times 90^\circ / 5 \\ &= 108^\circ\end{aligned}$$

$$\begin{aligned}\text{Angle strain per C-C bond } (\delta) &= \frac{1}{2} [109^\circ.28' - \text{actual VBA}] \\ &= \frac{1}{2} [109^\circ.28' - 108^\circ] \\ &= \frac{1}{2} [1^\circ.28'] \\ &= \frac{1}{2} [0^\circ.88'] \\ &= +0^\circ.44'\end{aligned}$$

This angle strain in cyclopentane is represented diagrammatically as shown below.

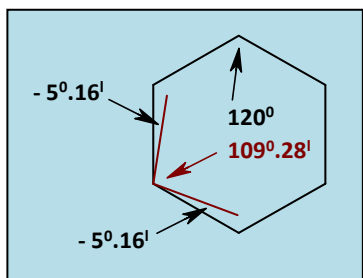


## Cyclohexane

$$\begin{aligned}\text{Actual VBA} &= (2n-4) \times 90^\circ / n && \text{Where, } n = 6 \text{ (no. of ring carbon atoms)} \\ &= (2 \times 6 - 4) \times 90^\circ / 6 \\ &= (12 - 4) \times 90^\circ / 6 \\ &= 120^\circ\end{aligned}$$

$$\begin{aligned}\text{Angle strain per C-C bond } (\delta) &= \frac{1}{2} [109^\circ.28' - \text{actual VBA}] \\ &= \frac{1}{2} [109^\circ.28' - 120^\circ] \\ &= \frac{1}{2} [-10^\circ.32'] \\ &= -5^\circ.16'\end{aligned}$$

This angle strain in cyclohexane is represented diagrammatically as shown below.



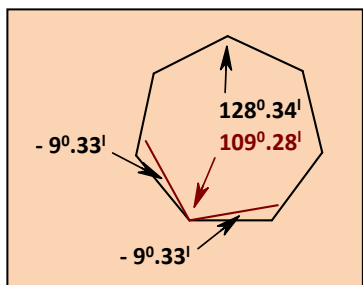
## Cycloheptane

$$\begin{aligned}\text{Actual VBA} &= (2n-4) \times 90^\circ / n \\ &= (2 \times 7 - 4) \times 90^\circ / 7 \\ &= (14 - 4) \times 90^\circ / 7 \\ &= 128^\circ.34'\end{aligned}$$

Where,  $n = 7$  (no. of ring carbon atoms)

$$\begin{aligned}\text{Angle strain per C-C bond } (\delta) &= \frac{1}{2} [109^\circ.28' - \text{actual VBA}] \\ &= \frac{1}{2} [109^\circ.28' - 128^\circ.34'] \\ &= \frac{1}{2} [-19^\circ.6'] \\ &= \frac{1}{2} [-18^\circ.66'] \\ &= -9^\circ.33'\end{aligned}$$

This angle strain in cycloheptane is represented diagrammatically as shown below.



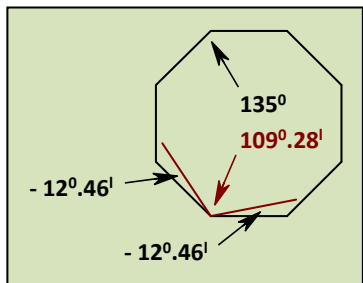
## Cyclooctane

$$\begin{aligned}\text{Actual VBA} &= (2n-4) \times 90^\circ / n \\ &= (2 \times 8 - 4) \times 90^\circ / 8 \\ &= (16 - 4) \times 90^\circ / 8 \\ &= 135^\circ\end{aligned}$$

Where,  $n = 8$  (no. of ring carbon atoms)

$$\begin{aligned}\text{Angle strain per C-C bond } (\delta) &= \frac{1}{2} [109^\circ.28' - \text{actual VBA}] \\ &= \frac{1}{2} [109^\circ.28' - 135^\circ] \\ &= \frac{1}{2} [-25^\circ.32'] \\ &= \frac{1}{2} [-24^\circ.92'] \\ &= -12^\circ.46'\end{aligned}$$

This angle strain in cyclooctane is represented diagrammatically as shown below.







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- 20 Years of teaching experience.
- 17 Years of research experience.
- 02 Students are awarded with Ph.D.
- 03 Students are awarded with M.Phil.
- 70 Research papers are published.
- 04 Books are published as author, co-author and editor.
- Received 'Young Scientist Award' in conference of Indian Council of Chemists, I.I.T., Roorkee.
- Received "Award for Excellence in Research" in 3<sup>rd</sup> South Asian Education Awards, Hyderabad.
- Received "State Level Ideal Teacher Award" from Congress Teachers Cell, Akola, Maharashtra.
- Recognized Ph.D. guide of S.G.B. Amravati University, Amravati and R.T.M. Nagpur University, Nagpur.

**Publisher ...**

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