

Ex.
$$CH_3 - CH_2 - CH_2 - CH_2 - OH$$

 1 -Butanol
 $CH_3 - CH_2 - CH_2 - CH_3 - CH_3 - CH_2 - CH_3 - CH_3$
 $CH_3 - CH_2 - CH_2 - CH_3 - CH_3 - CH_2 - CH_3 - CH_3$

$$\begin{array}{c} \textbf{Ex.} \qquad \textbf{CH}_3 & \textbf{-} \textbf{CH}_2 & \textbf{-} \textbf{CH}_2 & \textbf{-} \textbf{CH}_2 & \textbf{-} \textbf{CI} \\ 1 & \textbf{-} \textbf{Chlorobutane} \end{array}$$

Ex.
$$CH_3$$
— CH_2 — CH_2OH & CH_3 — CH_-CH_3
OH
 CH_3 — CH_2 — CH_2 — NH_2 & CH_3 — CH_-CH_3
 H_2





Ċl



(2)

CH₃

(3) RING CHAIN ISOMERISM (RCI): Ring chain Isomers possess same molecular formula but different mode of linking (open or closed chain) of carbon atoms.



They have same molecular formula so they are Ring chain isomers.

Ex. Relate a,b and c :-

$$C_{3}H_{6} \xrightarrow{(a)} H_{3}C \xrightarrow{-}C \equiv CH$$

$$(b) CH_{2} = C = CH_{2}$$

$$(c) \xrightarrow{CH} CH_{2} \xrightarrow{-}CH$$
Ex. CH₃-CH₂-CH=CH₂ &

$$CH_{3} \xrightarrow{-}CH = CH_{2}$$

(i) Minimum carbons required for chain isomerism & position isomerism in alkanes \rightarrow 4, 6 (ii) Minimum carbons required for chain isomerism & position isomerism in alkenes \rightarrow 4, 4

(iii) Minimum carbons required for chain isomerism & position isomerism in alkynes $\rightarrow 5, 4$

(4) FUNCTIONAL ISOMERISM : Compounds having same molecular formula but possess different functional groups, they are called functional isomers and the phenomeanon is termed functional isomerism.
Ex.

(i)	Alcohol and ether	\longrightarrow	CH ₃ CH ₂ OH	and	CH ₃ -O-CH ₃
(ii)	Aldehydes and ketones	\rightarrow	CH ₃ —CH ₂ —C—H	and	$CH_3 - C - CH_3$
(iii)	Acids and ester	\rightarrow	CH ₃ —C—OH	and	
(iv)	Cyanide and isocyanide	\rightarrow	CH ₃ -CH ₂ -CH ₂ -CN	and	$CH_3 - CH_2 - CH_2 - NC$
(v)	Nitro and Nitrite	\rightarrow	CH ₃ —CH ₂ —N	and	$CH_{3}-CH_{2}-O-N=O$
			O II		
(vi)	keto and enol	\longrightarrow	$CH_3 - CH_3$	and	$CH_2 = C - CH_3$
(vii)	Amide and Oxime	\longrightarrow	$CH_3 - C - NH_2$	and	СН ₃ -СН=NOH
(viii)	1°, 2°, 3° amines	\longrightarrow	0	CH ₂	
	(i) CH_3 - CH_2 - CH_2 - NH_2	(ii) CH ₃	–NH–CH ₂ –CH ₃ (iii) CH	I ₃ —N—(CH ₃



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(5) **METAMERISM** : Compounds having same molecular formula, same polyvalent functional group but unequal distribution of substituents on either side of the functional groups / polyvalent functional group members belong to the some homologous series (class).

 Ex. CH₃-O-CH₂-CH₂-CH₃; CH₃-CH₂-O-CH₂-CH₃ Both are metameres
 Ex. CH₃-CH₂-NH-CH₂-CH₃ CH₃-NH-CH₂-CH₂-CH₃ N-Ethyl ethanamine N-Methyl propanamine They are only metamers not Chain Isomers.
 Ex. CH₃-C-CH₃-CH₂-CH₃ CH₃-CH₂-CH₂-CH₃

Ex.
$$CH_3$$
 — CH_2 — CH_2

$$CH_{3} - CH_{2} - C - CH - CH_{3} - CH_{2} - CH_{3} - C$$

2-Methyl-3-pentanone

Both are Metamers, Chain and Position isomers

(6) **TAUTOMERISM**: Isomerism in which two functional isomers exist together in equilibrium. These two existing forms of equilibrium are called tautomerism.

$$CH_{3}-C-CH_{2}-COOC_{2}H_{5} = CH_{3}-C=CH-COOC_{2}H_{5}$$

$$OH$$

$$OH$$

$$CH_{3}-C-CH_{2}-COOC_{2}H_{5} = CH_{3}-C=CH-COOC_{2}H_{5}$$

$$OH$$

$$OH$$

$$enol form$$

- In the above tautomeric form one is more stable and exists in larger proportion.
 93% of keto form exist.
 7% of enol form exist.
- The tautomertism is also called kryptomerism or allotropism or desmotropsim or dynamic isomerism.

 α -H attached to carbonyl compound is active H

• Desmotropism means bond turning. [Desmos = Bond; Tropos = Turn]

α-Hydrogen or active H
Ex. H
$$-C - H$$

H $-C - H$
H $-H$
H $-C - H$
H $-H$
H $-C - H$
H $-H$



EDUBULL KEY POINTS

- (i) Number of electron and lone pairs in both tautomers always remain the same.
- (ii) It is a chemical phenomenon which takes place only in liquids and gaseous phase only. It never takes place in solid state.
- (iii) The process can be catalyzed by the acid as well a bases.
- (iv) Tautomers are also F.I. and exist in dynamic equilibrium is used to show tautomerism.

CONDITION FOR TAUTOMERISM

(a) For carbonyl compounds: Carbonyl compounds having atleast one α -H show tautomerism





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ISOMERISM

(i) Enol content ∝ number of >C=O group.
(ii) If number of >C = O groups are equal then proportional to number of α-H.
(iii) Group —OH attached to sp² carbon or double bond is less stable or unstable.
(iv) More active H, more take part in tautomerism.
(v) Stability of enol form depends on (i) Resonance and (ii) H – Bond.

Ex. Arrange the following in correct order of enol content.

(A)
$$CH_3 - C - H$$

O
(C) $CH_3 - C - CH_2 - C - H$
O
O
O
O

- (B) $CH_3 C CH_3$ (D) $CH_3 - C - CH_2 - C - CH_3$
- **Ex.** Which have maximum stable enol form





ETOOS KEY POINTS

Difference between Tautomerism & Resonance :

- (i) In tautomerism, an atom changes place but resonance involves a change of position of pi-electrons or unshared electrons.
- (ii) Tautomers are different compounds and they can be separated by suitable methods but resonating structures cannot be separated as they are imaginary structures of the same compound.
- (iii) Two tautomers have different functional groups but there is same functional group in all canonical structures of a resonance hybrid.
- (iv) Two tautomers are in dynamic equilibrium but in resonance only one compound exists.
- (v) Resonance in a molecule lowers the energy and thus stabilises a compound and decreases its reactivity. But no such effects occur in tautomerism.
- (vi) In resonance, bond length of single bond decreases and that of double bond increases e.g. all six C—C bonds in benzene are equal and length is in between the length of a single and a double bond.
- (vii) Resonance occurs in planar molecule but atoms of tautomers may remain in different planes as well.

$CH_3CH_2CH_2 - Cl \text{ and } CH_3 - CH_3 + CH_3$ shows which type isomerism 1. Cl (A) Chain isomers (B) Position isomers (C) Functional isomers (D) Metamers - CH—CH₃ shows which type of isomerism CH₂CH₂CH₂-OH and CH₃-2. ŌН (A) Chain isomers (B) Position isomers (C) Functional isomers (D) Metamers 3. CH, CH, OH and CH, -O-CH, express which type of isomerism (A) Functional isomers **(B)** Chain isomers (D) Position isomers (C) Metamers



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PROBLEMS

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4.	$CH_3 - CH_2 - CH_3$ and $CH_3 - CH - CH_3$ shows which type of isomerism				
	I CH ₃				
	(A) Chain isomer	(B) Position isomer	(C) Functional isomer	(D) Metamers	
5.	Alcohol and ether express	s which type of Isomerism			
	(A) Position isomers	(B) Chain isomers	(C) Metamers	(D) Functional isomers	
6.	How many position isome	ers are shown by CH ₃ -CH=0	CH–CH ₃		
	(A) 2	(B) 3	(C) 4	(D) 5	
7.	How many position isome	ers are shown by CH ₃ –CH ₂ –	-CH ₂ -NH ₂		
	(A) 5	(B) 3	(C)4	(D) 2	
	CH_3	CH,			
	CH ₃				
8.	and	shows which ty	pe of isomerism.		
	\checkmark				
	(A) Position isomers	(B) Chain isomers	(C) Functional isomers	(D) Metamers	
9.	How many Ring chain iso $(A)^2$	mers are possible for C_3H_6 .	(0)4	(D) 5	
	(A) 2	(B) 5	(C)4	(D) 5	
10.	CH ₃ -CH ₂ -CH=CH ₂ and	express which type ison	nerism.		
	(A) Ring chain isomers	(B) Metamers	(C) Position isomers	(D) Chain isomers	
11.	CH_3 - CH = CH_2 and \square	express which type of isome	erism		
	(A) Ring chain isomers	(B) Chain isomer	(C) Position isomers	(D) Metamers	
12.	CH ₃ CH ₂ CH ₂ NH ₂ , CH ₃ CH	NHCH ₃ and CH ₃ N—CH	I ₃ express which of Isomeris	sm	
		CH ₃			
	(A) Functional Isomers	(B) Chain Isomers	(C) Metamers	(D) Position isomers	
		0			
13.	CH CH COOH and CH-	C - C - C + express wh	ich of isomerism		
	(A) Position isomers	(B) Chain isomers	(C) Metamers	(D) Functional Isomers	
14	Allymas and Alkadianas	where which type of isome	ariem.		
14.	(A) Position isomers	(B) Chain isomers	(C) Metamers	(D) Functional isomers	
15	The type of isomerism ob	served in uses and $NH = CH$	=NOH		
15.	(A) Chain isomers	(B) Position isomers	(C) Geometrical isomers	(D) Functional isomers	
16.	CHCH-O-CH CH and	CH_OCH CH CH expres	s which type of Isomerism		
	(A) Metamers	(B) Functional isomers	(C) Tautomerism	(D) Functional isomers	



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ISOMERISM





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26.	The number of $(A) 6$	fstructura	l isomer sho (B) 5	wn by $C_6 H_{14}$	(C) 6		(D) 8	
27.	How many cha (A) 3	in isomer	s are shown (B) 2	by $C_4 H_{10}$.	(C) 4		(D) 5	
28.	How many cha (A) 2	iin isomer	s are shown (B) 3	by C ₄ H ₉ OH	(C) 4		(D) 5	
				ANSV	VERS		100	
1. 6. 11. 16. 21. 26.	(B) (A) (A) (A) (A) (B)	2. 7. 12. 17. 22. 27.	 (B) (D) (A) (A) (B) (B) 	3. 8. 13. 18. 23. 28.	 (A) (A) (D) (A) (C) (A) 	4. 9. 14. 19. 24.	(A) (A) (D) (C) (A)	5. (D) 10. (A) 15. (D) 20. (A),(C),(D) 25. (A),(B),(C),(D)

STEREO ISOMERISM



Two or more than two compound having same molecular formula, same structural formula but different arrangements of atoms or groups in space are known as **stereoisomers** and the phenomenon is called as **stereoisomerism**.

Stereo Isomerism : Stereo isomerism is actually permutation & combination of arrangement of atoms in different style (3-dimensionally) to form molecules by the nature.

Configuration Isomerism : Stereoisomers which are not interconvertible in each other at room temperature known as configurational isomerism.

Configurational isomers are further divided into two parts :-

- (A) Geometrical Isomerism : Stereoisomers which are not interconvertible in each other at room temperature due to restricted rotation known as Geometrical Isomerism.
- (B) **Optical Isomerism**: Stereoisomers which are not superimposable on each other due to chirality known as optical isomerism.



(1)

GEOMETRICAL ISOMERISM

- It is type of configurational isomerism which caused due to restricted rotation of atoms or groups around a double bonded systems or cyclic system.
- Compound having same molecular formula but differ in their properties due to the difference in the direction of attachment of same atoms or groups in their molecule.

GEOMETRICAL ISOMERISM IN ALKENE

• Generally alkene show Geometrical Isomerism because by the overlapping of p-orbital, formation of π bond takes place which produces restricted rotation.



Note : cis \longrightarrow trans is possible only when π bond is present.

Condition for Geometrical isomerism

Only alkenes show G.I. in which "Each sp² carbon have different atoms or groups" attached to the sp² carbon.

c = c < b

Geometrical isomers



a > C = C < y yNot Geometrical isomers

Not Geometrical isomers

- **Ex.** Which of the following show Geometrical isomerism :
 - (A) 1,2-diphenyl-1-butene
 - (B) 1, 1-diphenyl-2-butene
 - (C) 2,3-dimethyl-2-butene
 - (D) 3-phenyl-1-butene

Sol. (A), (B)



Nomenclature System of Geometrical Isomers

(a) Cis-Trans isomers (b) E and Z isomers

(a) Cis-Trans Isomers : When like atoms or groups attached at the **same side** of double bonded C-atom-called as **cis**. isomers. When like atoms or groups are on the opposite sides of doubly bonded carbon, are called trans isomers.

(c) Syn-anti isomers



Physical Properties of Cis-Trans Isomerism

S. No.	Physical Properties	Comparison	Remarks
1	Dipole moment	cis > trans	cis-isomer has resultant of dipole while in trans
		1	isomer dipole moments cancel out
2	Boiling point	cis > trans	Molecules having higher dipole moment have higher boiling point due to large intermolecular force of attraction
3	Solubility (in H2O)	cis > trans	More polar molecules are more soluble in H ₂ O
4	Melting point	trans > cis	More symmetric isomers have higher melting points due to better packing in crystalline lattice & trans isomers are more symmetric than cis.
5	Stability	trans > cis	The molecule having more vander waal strain are less stable. In cis isomer the bulky group are closer they have larger vander waal strain.

trans = 0

Dipole moment [µ]

н—С—С́Н₃ С́Н₃—С—Н ĊH₃ $CH_{3} - C - H$ $\vec{C}H_{3} - C - H$ $cis \mu \neq 0$ Ex. $\vec{C}H_{3}$ — C — HH — C — $\vec{C}H_{2}$ — CH_{3} С́н₃—С —Н ∥ С́і—С —Н Ex. trans $\mu \neq 0$ cis $\mu \neq 0$ $\vec{C}H_{3}$ —C—H \parallel trans $\mu \neq 0$ Ex. H-

E and Z isomers (CIP Rule) **(b)**

 $E \rightarrow Entgegen$

- $Z \rightarrow Zusamenn$
- The above system is used for derivatives of alkenes in which all the four substituents should be different (i)





- (ii) Following a set rules (Cahn - Ingold-Prelog rules) the substituents on a double bond are assigned priorities.
- (iii) The double bond is assigned the configuration E (From entgegen, the german word for opposite) if the two groups of higher priority are on the opposite sides of the double bond.



E form

(iv) On the other hand, the double bond is assigned the configuration Z (From zusamenn, the German word for together) if the two groups of higher priority are on the same side of the double bond.



Z form

Priority rule : Cahn, Ingold & Prelog proposed a sequence rule.

Rule 1: When atom or group of atoms which are directly attached to the stereogenic centre have higher atomic number will have higher priority. Example



Rule 2: When the atomic number will be same, priority assigned on basis of atomic weight.



Rule 3: When both atomic number and atomic weight are same then priority will be decided by the next joining atom.



Rule 4: If multiple bonded group attach to the double bonded carbon, then they are considered in following manner.





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E - form



In **unsymmetrical Ketoxime**, if–OH and the **alphabetically** alkyl present on the same side of double bond, then it is called as **syn form** and other isomer is **anti form**.



Geometrical Isomerism in Cyclo Alkane

- (1) In cyclic compound the rotation about C- C single bond is **not free** because of the rigidity caused by the presence of other carbon of the ring which keep them tightly held, thus a disubstituted cyclic compound (having the two substitution at the separate carbon) will also show Geometrical Isomerism. The substituents on the same side are cis-isomers while the substituents on opposite sides represent trans-isomers.
- (2) In simple words Cycloalkanes show Geometrical isomers due to **restricted rotation about single bond**. Only those cyclo alkanes show Geometrical isomers in which atleast two different carbons have two different groups.







Ex. Which of the following show Geometrical isomerism –



Sol. (A), (B)

Number of Geometrical Isomers in Polyenes

Case-1In case of unsymmetrical alkene. If
$$R_1 \neq R_2$$
 ($R_1 - CH = CH - CH = CH - R_2$)
no. of GI. = 2^n
n \rightarrow number of double bond showing geometrical isomerismEx. $CH_3 - CH = CH - CH = CH - CH_2 - CH_3$ Number of GI = $2^2 = 4$ Ans

Case - 2 In case of symmetric alkene. If
$$R_1 = R_2 (R_1 - CH = CH - CH = CH - R_2)$$

no. of G.I. = $2^{n-1} + 2^{p-1}$

if n is even no. then,
$$P = \frac{n}{2}$$

if n is odd no. then, $P = \frac{n+1}{2}$

Ex.

$$CH_3 - CH = CH - CH = CH - CH = CH - CH_3$$

 $|n = 3$

here
$$p = \frac{3+1}{2}$$

PROBLEMS

1. Which of the following compounds exhibits geometrical isomer			
	(A) CH ₃ CHO	(C) (CH ₂) ₂ (COOH) ₂	
	(B) C_2H_5Br	(D) $(CH)_2(COOH)_2$	
2.	The number of geometrical isomers of		
	$CH_3CH = CH - CH = CH - CH = CHCl is -$		
	(A) 4	(C) 2	
	(B) 6	(D) 8	
3.	Maleic and fumaric acids are :		
	(A) Geometrical isomers	(C) Tautomers	
	(B) Optical isomers	(D) Metamers	
4.	Which of the following can exhibit cis-trans ison	nerism -	
	$(\mathbf{A}) \mathbf{H} \mathbf{C} \equiv \mathbf{C} \mathbf{H}$	(C) ClCH = CHCl	
	(B) CH ₃ .CHCl.COOH	(D) ClCH ₂ – CH ₂ Cl	



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5.	Geometrical isomeri	ism is possible in case	e of:			
	(A) Pent-2-ene		(C) Buta	ane		
	(B) 2-Butene		(D) Ethe	ene		
6.	Give the E-Z design	ation of the following	g compound -			
		$C_{6}H_{3}$ C=	$=C <_{Br}^{1}$			
	(A)E		(C) Z			
	(B) E - Z		(D) E - E	1		
7.	Which of the followi	ing compounds will e	exhibit trans (geometri	ical) isomerism?		
	(A) 2-butene		(C) 2-Եւ	ıtyne		
	(B) 2-butanol		(D) buta	inal		
			ANSWERS		0	
1.	(D) 2. (D)	3. (A)	4. (B)	5. (A,C)	6. (A)	7. (A)

OPTICAL ISOMERISM

Sterioisomers that differs in their behaviour in rotating the plane of polarisation of plane-polarised light either in magnitude or direction, called as Optical isomers. The phenomenon of existence of optical isomers is known as Optical isomerism.

Plane-Polarised Light

Ordinary light consists of electromagnetic waves which oscillate in all directions perpendicular to the direction of propagation of light. A beam of light which has oscillations only in a single plane is called a **plane-polarised light**. Plane-polarised light is produced by passing a beam of ordinary monochromatic light through a polariser such as **Nicol-prism** or a polarised lens. A nicol prism is constructed of two prism of calcite hekd together by a thin film of Canada balasm, a transparent liquid having refractive index of 1.4865. Calcite (Iceland Spar) is a naturally occcuring transparent crystalline form of calcium carbonate.

EDUBULL KEY POINTS

Canada Balasm - A yellowish resin obtained from the balsam fir and used for mounting preparations on microscope slides.

When plane-polarised light produced by a Nicol prism is passed through a second Nicol prism having the same orientation as the first (**Parallel Nicols**) the polarised light is entirely transmitted through the second Nicol prism. On the other hand, if the second Nicol prism is turned 90° with respect to the first (**Crossed Nicols**), no light is transmitted at all. With any other relative orientation of two prisms, the light is partially blocked. Thus the second Nicol prism is able to stablish the plane of polarisation of the polarised light in relation to the first prism. The second Nicol prism is accordingly called the **analyser** while the first prism is called **polariser**.



Optical Activity : The ability of optically active substances to cause rotation in the plane of oscillations of polarized light is called **optical activity**. The substances which do not have any interaction with plane polarized light are called optically inactive substances.



- (a) Under ordinary conditions, the light waves oscillate in infinite number of planes passing through the line of propagation at **right angle**.
- (b) Plane polarized lights are light whose vibrations take place in only one of these possible planes.
- (c) Ordinary light can be turned into plane polarized light by passing it through **Nicol prism** (made up of calcite, a special crystalline form of CaCO₃)
- (d) When plane polarize light is passed through the liquid or dissolved state of such substances.
- (e) The plane of oscillation gets rotated through some angle towards left or right of the original plane of oscillations. The substances which rotate the plane of polarized light are called **optically active substances**.
- (f) The substances which rotate the plane of polarized light in the clockwise direction, i.e., towards right are, called dextrorotatory substances (Latin : dextro means right). This is indicated by putting a better d or (+) sign before the name of the substances.
- (g) The substances which rotate the plane of polarized light in the anticlockwise direction, i.e., towards left are called leavorotatory substances (Latin : laevus means left). This is indicated by putting letter 'l' or (-) sign before the name of the substance.
- (h) The angle through which the plane of polarized light is rotated is represented by α and is called **observed angle of** rotation.



POLARIMETER

The observed rotation of the plane of polarized light [determined with the help of polarimeter] produced by a solution depends on :

- (a) the amount of the substance in tube
- (b) on the length of the solution examined
- (c) the temperature of the experiment and
- (d) the wavelength of the light used.

The instrument used to measure angle of rotation is called polarimeter. The measurement of optical rotation is expressed in terms of specific rotation $[\alpha]_D^t$.

Specific Rotation

Sp. Rotation of optically active compound defined as the amount of optical rotation observed when plane polarized light passed through a solution of 1 gm per ml concentration solution in a 1 dm long tube.

Sp. Rotation =
$$[\alpha]_{\lambda}^{t} = \frac{\alpha}{1 \times c}$$

Cause of Optical Activity

(a) In order to exhibit optical activity, an object or molecule must be chiral.

Chirality: This term has been recently used to described such molecules as have no elements of symmetry, thus asymmetrical molecules are also called chiral molecules and optical activity is attributed to certain chiral centres in them. An asymmetrical carbon is a chiral centre.



Chirality is lost when the two atoms bonded to an asymmetric carbon become similar thus lactic acid is optically active but propionic acid is inactive.

(b) Those molecules which have asymmetric or dissymmetric molecular structure in tetrahedral perspective are called asymmetric molecules or chiral. The two features of such structures are :-

(i) No plane of symmetry : A 'Plane' of symmetry' is a plane which divides an object in such a way that the part of it on one side of the plane is the mirror image of that on the other side for eg. a ball is symmetrical while a hand is asymmetric.



Similarly, an organic molecule is asymmetric if there is no plane (or centre) of symmetry for example.



(ii) Non superimposable on its image

An asymmetric object cannot be superimposed on its mirror image thus right hand produces a mirror image which is identical with your left hand. The two hands are non superimposable which is clearing evident if your right and in the left handed glove. On the other hand, asymmetric object like a ball can be superimposed its mirror image which is another similar ball.



Chiral Centre

- (i) A carbon atom bonded to four different atoms/groups in the molecule is called Chiral centre.
- (ii) The chiral centre is the molecule is represented by asterisk (*). For example, the second carbon in lactic acid is chiral centre because it is bonded to four different groups.
 (ii) CH CH CH and COOH)

 $(-H_2, -CH_3, -OH \text{ and } -COOH).$

(iii)

Some more examples of molecules having one chiral centre are





Enantiomers

Enantiomers are molecules which are mirror images of each other i.e. They should be non superimposable.



Properties of Enantiomers

S.No.	Properties	Remarks
1	Molecular formula	Same
2	Structural formula	
3	Stereochemical formula (str. Formula with orientation)	Different
4	Physical properties (m.p., b.p. density, solubitliy,) refractive	
	Chemical properties	
5	(a) with optically inactive compound	
	(b) with optically active compound	Different

Representation of Enantiomers

(a) Wedge and dash formulae

(b) Fischer Projection Formulae

(a) Wedge and dash formulae

(i) In this method, the four groups bonded to the chiral centre are represented by different means.

(ii) A normal line represents the bond lying in the plane of paper.

(iii) A broken line represents the bond going behind the plane of the paper and a solid wedge represents the bond projected out towards the viewer.



(b) Fischer Projection Formulae

(i) Emily Fischer devised a most simple and convenient method to represent the three dimensional arrangement of groups bonded to chiral centre.

(ii) He used the point of intersection of two perpendicular lines to represent the chiral centre.

(iii) Horizontal lines represent the bonds projected out of the plane of the paper towards viewer.

(iv) Vertical lines on the other hand, represented the bonds projected back from the plane of the paper away from the viewer.

(v) The Fischer projection formulae of enantiomers of 2-butanol and lactic acid are as under



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Important Point About Fischer Projection Formula

(1) Fischer projection of stereoisomer must not be lifted from the plane of the paper and turned over. Such an operation would result into an arrangement which is enantiomer of the original stereoisomer.



(2) Fischer's projection can be rotated in the plane of the paper about the chiral centre through 180° or its whole number multiple. Such an operation products the same arrangement



(3) Fischer projection should not be turned in the plane of the paper through angle of 90° about the chiral centre. Such an operation also produces enantiomer of the original compound.



(4) Keeping one group as steady, the other groups in the Fischer projection can be rotated clockwise or anticlockwise simultaneously. Such operation would give same arrangement as the original.





DIASTEREOMERS

Such configurational isomers which are neither be mirror image nor be superimposable on each other, called diastereoisomers.

For example, a compound having two asymmetric carbon atoms can have four stereoisomers as shown below in the case of tartaric acid :



(I) is mirror image of (II); similarly (III) and (IV) are mirror images of each other. Thus, the four isomers are two pairs of enantiomers. Now compare (I) with (III); they are neither superimposable nor they are mirror images. They are called *diastereomers*. (I) and (IV) are also diastereomers, as are (II) and (III) and (II) and (IV).

• Cis-trans isomer are geometrical isomer but they are not the mirror image thus, they are said to be diastereomer.

Characteristics of Diastereomers

(1) They are generally optical active, however geometrical isomers are exception.

- (2) They have different physical properties like MP, BP, density, solubilities & value of specific rotation.
- (3) They are separated by fractional distillation, fractional crystallisation & chromatography etc.
- (4) They exhibit similar but not identical chemical behaviour.

MESO COMPOUND

(a) The compounds containing two or more chiral centres but possessing achiral molecular structure because of having plane of symmetry, are called meso compounds.



Meso Compound Plane of symmetry is represented by dotted line

- (b) Meso compounds do not rotate the plane of polarized light in any direction, i.e., they are optically inactive.
- (c) This is because of achiral nature of their molecules. Because of the presence of plane of symmetry the optical rotation caused by half of the molecule is compensated by the rotation caused by the other half.
- (d) This cancellation of rotation within the molecule is referred to as internal compensation.
- (e) In short, the meso compounds are optically inactive due to internal compensation.



Internal compensation

In meso tartaric acid the inactivity is due to effects within the molecule and not external. The force of rotation due to one of the molecule is balanced by the opposite and equal force due to the other half. The optical inactivity so produced is said to be due to internal compensation. It occurs whenever a compound containing two (or) more asymmetric carbon atoms has a plane (or) point of symmetry. Since the optical inactivity of such a compound arised within the molecule, the question of separating into active components does not arise.

Ex.



Ex.

I and II are identical

Racemic Mixture

A racemic mixture contains equimolar amounts of enantiomers. It is optically inactive due to external compensation. **External compensation**

- If equimolar amounts of d and ●-isomers are mixed in a solvent, the solution is inactive. The rotation of each isomer is balanced (or) compensated by the equal but opposite rotation of the other. Optical inactivity having this origin is described as due to external compensation. Such mixtures of (+) and (-) isomer (Racemic mixtures) can be separated into the active components.
- A meso compound is optically inactive due to internal compensation.

Racemization

It is a process of conversion of an optically active compound into the racemic modification. Both (+) and (-) forms of the compound are capable of racemizations under the influence of heat, light or chemical reagents.

Resolution

The process of separation of constituent enantiomeric forms from the racemic mixture is known as resolution.

- 1. Chemical method : This is probably the best method of resolution. The racemic mixture is to combine with another optically active compound and the resulting products (salt formation) differ in properties, particularly in various. By fractional crystallization from a suitable solvent, they can be separated.
- 2. Mechanical method : If the d and *l*-forms of a substance exist in well defined crystalline forms, the separation can be done by hand picking with the help of magnifying lens and a pair of tweezers.



3. Biochemical method : In this method, the resolution is done by use of micro-organisms, when certain bacteria or moulds are added to a solution of a racemic mixture, they decompose one of the optically active forms more rapidly than the other.

Configuration

Arrangement of groups in three dimensional manner about the chiral centre is called as configuration. Two method for assigning configuration to a molecule :-(a) Relative Method

(b) Absolute Method

Relative Method or Configuration (D, L system) (1)

It is applicable for Fischer projection formula. **(i)**

It represents relative configuration with respect to glyceraldehydes.

Following configuration of glyceraldehyde is considered as standard configuration.



(ii) This method was found suitable for the study of optically active sugars as the sugars are defined as *poly hydroxy* aldehydes and ketones.

Glyceraldehyde also contains hydroxy and aldehyde groups but this method cannot be used for those molecules which do not process hydroxy aldehyde groups like CFCI BrI.

If two or more than two-OH groups are present then D, L configuration is decided on basis of -OH group of lowest chiral in the Golden rule following fischer projection.

(iii) All molecules which could be chemically relative to D-glyceraldehyde are assigned the D-configuration and those related L-glyceraldehyde are designated L-configuration as illustrated below -





(iv) Golden Rule

Usually, the Fischer projection is drawn, so that the longest carbon chain in the molecule is vertical with the highly oxidised function at the top.

The method of separating a racemic mixture into its enantiomeric constituents is called as **Resolution**. There is no direct relation between D, L-configuration with d, l or (+), (-) configuration.

(2) Absolute Configuration (R – S system)

System which indicates the absolute configuration was given by three chemists R.S. Cahn, C.K. Ingold and V. Prelog. This system is known as (R) and (S) system or the Cahn-Ingold system. The letter (R) comes from the latin rectus (means right) while (S) comes from the latin sinister (means left).

It is better system because in many cases configuration to a compound cannot be assigned by D, L method.

(R) (S) nomenclature is assigned as follows :

- $R \rightarrow Rectus (Right)S \rightarrow Sinister (Left)$
- R-S nomenclature is assigned as follow :
- Step I: By the set of sequence rule, we give the priority order of atom or group connected through the chiral carbon.
- **Step II**: If atom/group of minimum priority present on the vertical line, then put arrow $\rightarrow 1 \rightarrow 2 \rightarrow 3$.

If it is clockwise \Rightarrow R but Anti clockwise \Rightarrow S



Step - III: If minimum priority group present on the horizontal line, then put arrow $1 \rightarrow 2 \rightarrow 3$

If it is clockwise \Rightarrow S but Anti clockwise \Rightarrow R



1. Each group attached to stereocentre is assigned a priority on the basis of atomic number. The group with the directly attached atom with highest atomic number out of the four groups gets top priority while the group with the atom of least atomic number gets the least priority.



- 2. If out of the four attached atom in consideration, two are isotopic (like H and D), then priority goes to higher atomic mass i.e. D.
- 3. If out of the four attached atoms in consideration, two or more are same, then priority is decided on the basis of the atom attached next to it in its group. e.g. out of CH₃ and COOH, COOH gets priority.



4. While deciding the primority, if the atom in consideration is attached is further to an atom through a double bond then it is treated as if it is attached two such atoms. For example :



5. After assigning priorities, the least priority group is written at remotest valency (going away), while the top priority group is written at the top directed valency (towards viewer).



If lowest priority group is not on the dash position then,

Step 1 : Bring the lowest priority group to dash by even simultaneous exchanges.

Step 2 : Draw an arrow from first priority group to second priority group till third priority group.

Step 3 : If the direction of arrow is clockwise the configuration is R and if anticlockwise it is S.

Step 4: Draw the Fisher projection formula having equivalent configuration to the wedge-dash formula.



Now the order from top priority to the one of second priority and then to the one of third priority is determined. If this gives a clockwise direction then it is termed R configuration and if the anticlockwise direction is obtained then it is assigned S configuration.

Optical Isomerism in Compound having no chiral carbon atoms

Various compounds belonging to this are allenes, alkylidenes, cycloalkane, spiro compound (spiranes) and properly substituted biphenyls.

(i) Allenes : An sp-hybridized carbon atom possess one electron in each of two mutually perpendicular p orbitals. When it is joined to two sp²-hybridized carbon atoms, as in allene two mutually perpendicular π -bonds are formed and consequently the π -bonds to the sp²-carbons are in perpendicular planes. Allenes of the type abC=C=Cab (a \neq b) are therefore not superimposable on their mirror images and despite the absence of any asymmetric atoms, exist as enantiomers and several optically active compounds have been obtained.

(Ex. a = phenyl, b = 1-naphthyl)

They are optically active compounds.



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(ii) Alkylidene, cycloalkanes and spiro compounds : When one or both of the double bonds in allenes are replaced by one and two rings, the resulting systems are respectively known as alkylidene cycloalkanes and spiranes.



(iii) **Biphenyls**: Suitably substituted diphenyl compounds are also devoid of individual chiral carbon atom, but the molecules are chiral due to restricted rotation around the single bond between the two benzene nuclei and hence they must exist in two non-superimposable mirror images of each other.



(iv) Special Point :

Chiral nitrogen containing tetra alkyl ammonium ion show optical isomerism.



I and II enatiomers

Chiral nitrogen containing tertiary amine do not show optical isomerism Reason : Rapid umbrella inversion.



Chiral C containing carbanion do not show optical isomerism. Reason : Rapid umbrella inversion.



Energy required for this interconversion is available at room temperature. So, I and II are identical.

NUMBER OF OPTICAL ISOMERS

Numbers of optical isomers of an organic compound depends on its structure and number of asymmetric carbon atoms. Thus, the number of optical isomer may be determined as following.

Case - 1 When the molecule is unsymmetrical. (It cannot be divided into two halves)



Number of d and \bullet isomers = 2ⁿ Number of meso form = 0 Total number of optical isomers = 2ⁿ Ex. Pentane-2, 3-diol H--C^{*}-OH H--C^{*}-OH H--C^{*}-OH Number of d and \bullet isomers = 2² = 4 $\downarrow_{C_2H_5}$ Where n is the number of chiral carbon atoms

Case - 2 When the molecule is unsymmetrical and number of chiral carbon = even number

Number of d and \bullet isomers = $2^{(n-1)}$ Number of meso isomers = $2^{(n/2-1)}$ Total number of optical isomers = $2^{(n-1)} + 2^{(\frac{n}{2}-1)}$

Ex. Tartaric acid

I	Number of d and \bullet isomers = $2^{(2-1)} = 2^1 = 2$
H — C [*] — OH	Number of meso isomers = $2^{(2/2-1)} = 2^\circ = 1$
Н−С −ОН	Total optical isomers $= 2 + 1 = 3$
Соон	

Case -3 When the molecule is sysmmetrical number of chiral carbon = odd number

Number of d and \bullet isomers = $2^{(n-1)} - 2^{\frac{(n-1)}{2}}$ Number of meso isomers = 2 Total number of optical isomers = 2^{n-1} Ex. Pentane - 2, 3, 4-triole

Number of meso isomers = $2^{\left(\frac{3-1}{2}\right)} = 2^1 = 2$ Total optical isomer = $2^{3-1} = 2^2 = 4$

Number of d & 1 isomers = $2^2 - 2^1 = 4 - 2 = 2$

PROBLEMS

1.





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3

CONFORMATIONAL ISOMERISM

The different arrangement of atoms is space that result from the free rotation of group about C - C bond axis are called conformers, and the phenomenon is called conformation isomers. There are infinite no. of conformers of any molecule.

Condition of Conformation

There should be three σ -bond present in a molecule.

Ex. Which of the following is optically active –

$$(A) CH_{3}CH = C = CH - CH_{3}$$

$$(C) \xrightarrow{Cl} C = C = C < Cl_{Br}$$

Sol. (A), (C) and (D)

Ortho substituted biphenyl compounds do not have any chiral carbon but due to chiral molecule, they are optically active.

 $(B) CH_2 = C = CH_2$

(D) $\underset{\text{Ft}}{\overset{\text{Me}}{\longrightarrow}} C = C = C \begin{Bmatrix} Cl \\ Br \end{Bmatrix}$



Projection of Tetrahedral Carbon Atom

(i) Newman projection : - In this method the molecule is observed along the central carbon-carbon bond. A circle is drawn and centre of the circle represents the from carbon. The bonds of the front carbon are drawn from the centre of the circle while the bonds at the back carbon are drawn from the periphery.

(ii) Saw horse projection : In this method, central carbon-carbon bond of the molecule is represented by a straight line written in bond of the molecule is represented by a straight line written in slightly tilted manner and the molecule is observed from the right side.



Dihedral Angle:-Angle between valencies of two adjacent atoms





I = III (Eclipsed form) in this form distance between 2C - H bonds minimum so maximum repulsion or minimum stable.

II = IV (Staggered form) in this form distance between 2C-H bonds is maximum so minimum repulsion so maximum stable.

There are infinite conformers between eclipsed and staggered forms which are called as skew forms

Stability order : Staggered > Skew > Eclipsed

Dihedral Angle : Dihedral angle in eclipsed form of ethane is 0°.

Dihedral angle in staggered form of ethane is 60°.

The variation of energy with rotation about the C-C bond in ethane has been shown in figure below :





The difference in the energy of various conformers constitutes an energy barrier to rotation. The energy required to rotate the ethane molecule about carbon-carbon single bond is called **torsional energy**. But this energy barrier is not large enough to prevent the rotation. Even at ordinary temperature the molecules possess sufficient thermal and kinetic energy to overcome the energy barrier through molecular collisions.



Thus, conformations keep on changing form one form to another very rapidly and cannot be isolated as separate conformers.

• **Torsional energy** : The energy required to rotate the ethane molecule about 'C-C' bond is called torsional energy.

Conformation of Propane



CH₃

Partially Eclipsed

CH,

Η

Н

Conformation of butane



Η

Η



Fully Eclipsed

H Partially staggered (Gauche form)

CH,

CH₃

Н

Η



Partially Eclipsed



H

Partially staggered (Gauche form)







Fully staggered or Anti form Stability order : Anti form > Gauche > Partial eclipse > fully eclipsed

Dihedral angle : Angle between two planes.

Angle of rotation to get minimum stable to maximum stable form in butane is 180°.

Angle of rotation to get maximum stable to maximum stable form in butane is 360°.

The energy profile diagram for the conformation of butane is given below along with the difference of energy between various conformation of butane.



Energy changes that arises from rotation about the C2-C3 bond of butane

Some Important Example :-

Ethylene glycol :

H Gauche form is most stable due to intramolecular H-bonding.

Н

$$Z - CH_2 - CH_2$$

 QH $Z = -OH, -NH_2, -F, -CHO -COOH, OCH_3$

Η

Gauche in all cases due to H-bonding.

Gauche effect : In a lone pair containing compound bulkier group should be placed in Gaucher (60°) from l.p. As l.p. has minimum steric repulsion.

CH₃CH₂NH₂





(i)

(ii)
$$CH_3 - CH - \overset{\circ}{O} - H$$



Q. Write stable conformer for Z-CH₂-CH₂-Z in Newman's projection. If $\mu_{solution} = 1.0$ D and mole fraction of anti form = 0.82, find μ_{Gauche} .



Sol.

Mole fraction of anti form = 0.82 Mole fraction of Gauche form = 0.18 μ_{ob} . = 1 $1 = \mu_{(anti)} \times 0.82 + \mu_{(Gauche)} \times 0.18$ $\mu_{(anti)} = 0$ $\therefore 1 = \mu_{(Gauche)} \times 0.18$ $\mu_{(Gauche)} = \frac{1}{0.18} = 5.55 \text{ D}$

Conformational analysis of Cyclo alkane

Baeyer's strain theory : According to Baeyer's strain theory, the amount of the strain is directly proportional to the angle through which a valency bond has deviated from its normal position. i.e.

Amount of deviation
$$d = \frac{1}{2} (109^{\circ} 28' - \text{Valency} \text{ angle})$$

in cyclopropane d =
$$\frac{1}{2}(109^{\circ}28' - 60^{\circ}) = 24^{\circ}44'$$

in cyclobutane d = $\frac{1}{2}$ (109° 28' – 90°) = 9°44'

in cyclopentane d =
$$\frac{1}{2}$$
 (109° 28' – 108°) = 0°44'

in cyclohexane d =
$$\frac{1}{2}$$
 (109° 28' – 120°) = -5°16'

Heat of combustion

Cyclohexane > Cyclopentane > Cyclobutane > cyclopropane

Heat of combustion per -CH₂-

Cyclopropane > Cyclobutane > Cyclopentane > Cyclohexane



Orbital picture of angle strain



In cyclopropane however, the C–C–C bond angle cannot be 109° 28' but instead must be 60° . As a result the C–atom cannot be located permit their sp³ orbitals to point towards each other. There is less overlap and the bond is weaker than the usual C–C bond.

Conformation of cyclohexane : Cyclohexane exists in different forms, they are as follows :

Chair form, Boat form, twist boat form, half chair form.

(A) Chair form

(i) Experimental evidence show that cyclohexane is non-planar. If we look to the models of the different conformations that are free of angle strain first there is chair conformation. If we sight along each of the carbon-carbon bonds in turn we see in every case perfectly staggered bonds.



Chair conformation



Chair conformation(all staggered bonds)

The conformation is thus of all the strains, it lies at energy minimum and is therefore a conformational isomer. The chair form is the most stable conformation of cyclohexane.

(ii) There are two type of hydrogen in cyclohexane :

(a) Axial hydrogen (Ha) (b) Equatorial hydrogen (He)



(iii) The 12 hydrogen atoms of chair conformation of cyclohexane can be divided into two groups. Six of the hydrogens, called axial hydrogen, hence their bonds parallel to a vertical axis that passes through the rings centre. These axial bonds are directed up & down on adjacent carbons. The second set of six hydrogen called equatorial hydrogens are located approximately along the equator of the molecule.



(B) Boat form : Another conformation which is known as boat conformation has exactly eclipsed conformations.



In boat form of cyclohexane 6 hydrogens are equatorial, 4 hydrogens are axial and two hydrogens are flagpoles. It is an unstable conformation of cyclohexane due to torsional strain among axial hydrogens and due to vander waals caused by crowding between the "flagpole" hydrogens.

Conformational Inversion (Ring Flipping) in cyclohexane

In cyclohexane all carbon maintain tetrahedral geometry so that cyclohexane is most stable cycloalkane. At room temperature one chair form flips to another chair form during flipping axial bonds converts to equatorial & equatorial bonds converts to axial.



(vi) By ring flipping all axial bonds convert to equatorial and vice-versa. The activation energy for cylohexane ring inversion is 45 kJ/mol. It is a very rapid process with a half-life of about 10^{-5} sec at 25°C.



Conformation of mono substituted cyclohexane



(1, 3-1,5 interaction)

When methyl group is add axial position than their will be more 1,3-1,5 interaction so that this conformation will be least stable. By ring flipping methyl group occupied equatorial position so that new reverse chair form will be more stable.



1,3-diaxial repulsion

A methyl group is less crowded when it is equatorial that when it is axial. The distance between the axial methyl groups at C-1 and two hydrogens at C-3 and C-5 is less than the sum of their vander waal radii which causes vander waal strain the axial conformation this type of crowding is called 1,3-diaxial repulsion. When the methyl group is equatorial, it experience no significant crowding.



Write the orders of equilibrium constant for following equilibrium.





(iv) On the other hand, the double bond is assigned the configuration Z (From zusamenn, the German word for together) if the two groups of higher priority are on the same side of the double bond.



(c) Syn-anti isomers : This type of isomerism exhibit by oximes and Azo compound. Oximes are the compounds formed by the reaction of aldehydes or ketones with hydroxyl amine. The products obtained have all the necessary conditions for Geometrical isomerism. i.e, restricted rotation they can be represented by the general formula





Aldoximes



(II) **Optical Isomerism**: Compounds having similar physical and chemical properties but differing only in the behaviour towards plane polarised light are called optical isomers and this phenomenon is called optical isomerism.

The carbon atom linked to four different groups is called chiral carbon.

Non-superimposable mirror images are called **enantiomers** which rotate the plane polarised light up to same extent but in opposite direction.

Stereoisomers which are not related as mirror images of each other are called **diastereomers**. They have different physical and chemical properties.

Specific Rotation : Sp. Rotation of optically active compound defined as the amount of optical rotation observed when plane polarized light passed through a solution of 1 gm per ml concentration solution in a 1 dm long tube.

Sp. Rotation =
$$[\alpha]^t_{\lambda} = \frac{\alpha}{1 \times c}$$

Fischer projection : An optically active compound can be represented by Fischer projection which is planar representation of three dimensional structure.

The Fischer projection formulae of enantiomers of 2-butanol and lactic acid are as under





Absolute configuration : It is a three dimensional representation of optically active compound. It is also said to be R, S– system. (R-Rectus, S-Sinister).



- 2. Determination of R, S configuration : It involves the following steps :
- (i) Assignment of priority sequences of the group. Let the priority sequence among the given groups A, B, C and D are A > B > C > D.
- (ii) Rotation of eye from higher to lower priority sequence by keeping eye towards opposite side of lowest priority group i.e. rotating eye from 1 to 3 (A to C) via 2(B), while doing so if eye is rotating in clockwise then it is R-configuration and if in anticlockwise, then its is S-configuration.
- 3. **CIP Sequence rule** : The following rules are followed for deciding the precedence order of the atoms or groups.
- (i) Highest priority is assigned to the atoms of higher atomic number attached to asymmetric carbon atom.
- (ii) If the first atom of a group attached to asymmetric carbon atom is same then we consider the atomic number of 2^{nd} atom or subsequent atoms in group.
- (iii) If there is a double bond or triple bond, both atoms are considered to be duplicated or triplicated.
- 4. **Diastereomers** are stereoisomers which are not mirror images of each other. They have different physical and chemical properties.
- 5. Meso compounds are those compounds whose molecules are superimposable on their images in spite of the presence of asymmetric carbon atom.

An equimolar mixture of the enantiomers (d & \bullet) is called **racemic mixture**. The process of converting of d-and \bullet - form of an optically active compound into racemic form is called **racemisation**.

The process by which $d \bullet$ mixture is separated into d and \bullet form with the help of chiral reagent or chiral catalyst is known as **resolution**.

Compound containing chiral carbon my or may not be optically active but show optical isomerism.

For optical isomer chiral carbon is not the necessary condition.

Case - 1 When the molecule is unsymmetrical. (It cannot be divided into two halves)

Number of d and \bullet isomers = 2^n Number of meso form = 0 Total number of optical isomers = 2^n

Where n is the number of chiral carbon atoms

Case - 2 When the molecule is unsymmetrical and number of chiral carbon = even number

Number of d and \bullet isomers = $2^{(n-1)}$ Number of meso isomers = $2^{(n/2-1)}$ Total number of optical isomers = $2^{(n-1)} + 2^{(\frac{n}{2}-1)}$

Case -3 When the molecule is sysmmetrical number of chiral carbon = odd number

Number of d and \bullet isomers = $2^{(n-1)} - 2^{\frac{(n-1)}{2}}$

Number of meso isomers = 2

Total number of optical isomers = 2^{n-1}



Conformational isomerism: The different arrangement of atoms in space that results from the carbon-carbon single bond free rotation by 0-360° are called conformations or conformational isomers or rotational isomers and this phenomenon is called conformational isomerism.

Newman projection: Here two carbon atoms forming the σ bond are represented one by circle and other by centre the circle. Circle represents rear side C and its centre represents front side carbon. The C-H bonds of front carbon are depicted from the centre of the circle while C-H bond of the back carbon are drawn from the circumference of the circle.





eclipsed form (least stable) Conformations of butane : Staggered form (most stable)

 ${\stackrel{1}{C}}{\stackrel{2}{C}}{H_3} - {\stackrel{2}{C}}{H_2} - {\stackrel{3}{C}}{\stackrel{4}{H_2}}{\stackrel{4}{C}}{H_3}(C_2 - C_3 \text{ bond rotation})$





H H H Partially staggered (Gauche form)

Н





CH₃ H H CH₃ H H Partially Eclipsed

H H Partially staggered (Gauche form)

CH₃

The order of stability of conformations of n-butane. Anti > Gauche > Eclipsed > Fully eclisped. Relative stability of varous conformance of cyclohexane is Chain > twist boat > boat > half chair

CH:

