

ISOMERISM

⇒ (I) Chain isomerism: differ in length of parent chain

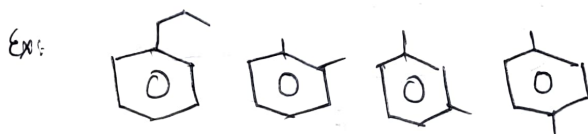
Ex: 

Alkyl alkanes exhibits only chain isomers but not positional isomers

H·C	Min of C's
alkane	4C
alkene	4C
alkyne	5C

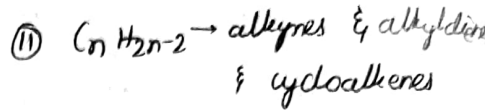
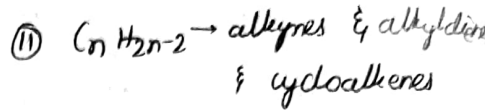
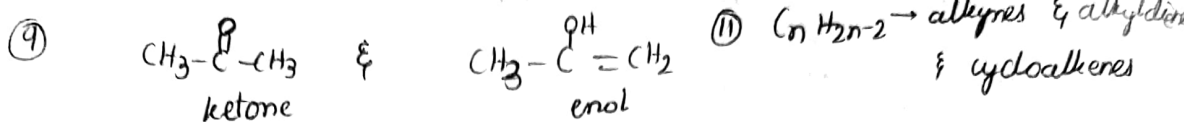
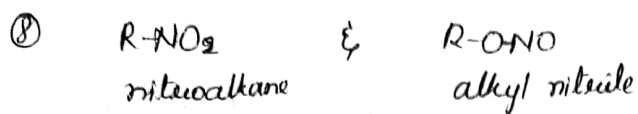
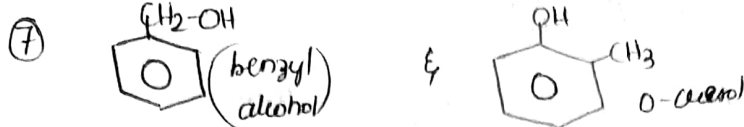
<u>Alkane</u>	<u>No. of chain isomers</u>
C_4H_{10}	2
C_5H_{12}	3
C_6H_{14}	5
C_7H_{16}	9
C_8H_{18}	18
C_9H_{20}	35
$C_{10}H_{22}$	75
$C_{15}H_{32}$	375

⇒ (II) Positional isomerism: differ in position of functional grp (or) substituent.

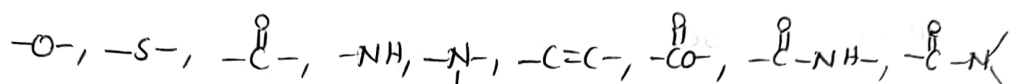


⇒ (III) Functional isomerism: same molecular formulae but differ in functional grp.

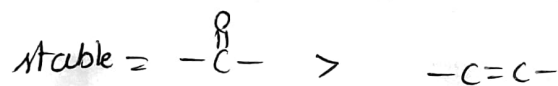
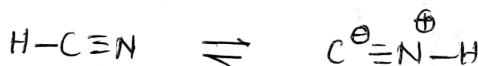
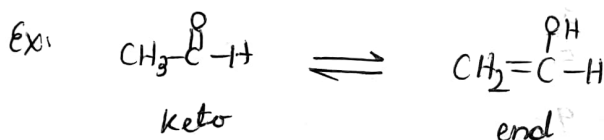
- ① $C_nH_{2n+2}O \rightarrow$ Alcohols & ether
- ② $C_nH_{2n}O \rightarrow$ aldehydes & ketones
- ③ $C_nH_{2n}O_2 \rightarrow$ carboxylic acids & esters
- ④ $C_nH_{2n+3}N \rightarrow$ 1, 2, 3 amines (aliphatic only)
- ⑤ $R-CN \text{ \& } R-NC$
- ⑥ $CH_3-CH_2-N=O$ & $CH_3-CH=N-OH$
nitrosone oxime



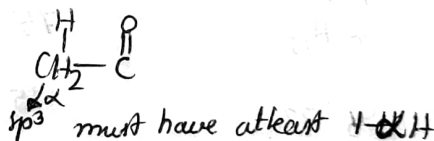
④ Metamerism: f.g attached to different alkyl grps.



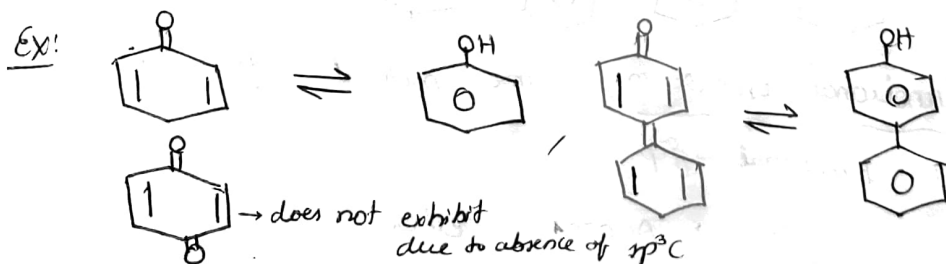
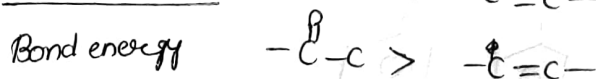
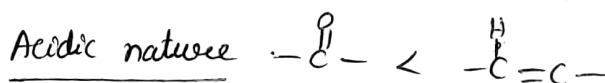
⑤ Tautomerism: It is due to arise of carbonyl compounds containing α -H atom. eg



to exhibit tautomerism



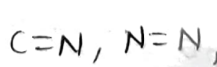
\Rightarrow enol content & acidity of hydrogen & no. of $-C(=O)-$ grps & hydrogen bond



Geometrical isomerism:

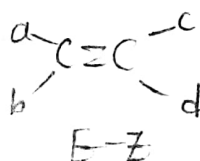


cis-trans

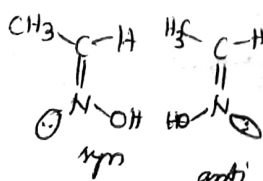


syn-anti

cis-trans



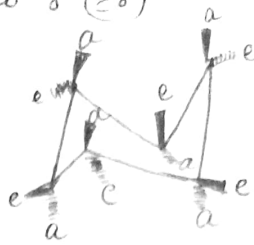
oppo same



priority & mol. wt

Geometrical isomerism \rightarrow min. no. of C equal to 8 (≥ 8)

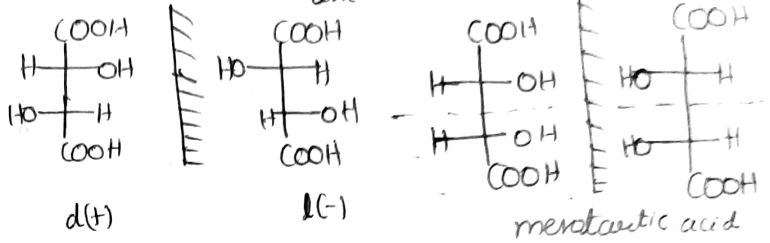
G.I	Cis	trans
1,2 & 1,4	a, e	a, a (R)
1,6	e, a	e, e
1,3 & 1,5	a, a	a, e
	e, e	e, a



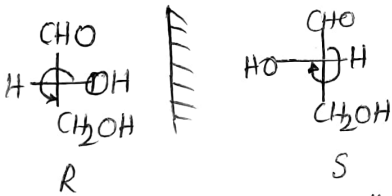
a = axial
e = equatorial

Optical isomerism: $[\alpha]_D^{25} = \frac{\alpha_{obs}}{c \times l}$
 where c is concentration and l is path length.

Tartaric acid



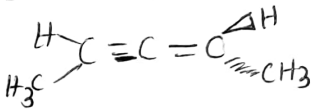
Racemic mixture: The equimolar mixture of enantiomers;



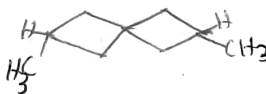
50% of R + 50% of S = Racemic mix

Optical active compounds without chiral centres

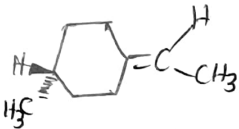
① even no. of allenes



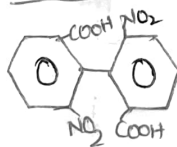
② even no. of spiranes



③ even no. of cycloalkylenes



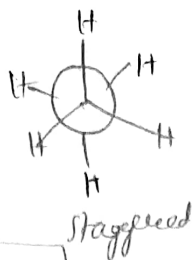
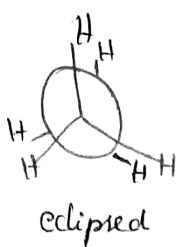
④ Biphenyl compounds



	Cis	trans
B Boiling	↑	↓
D Dipole moment	↑	↓
S Solubility	↑	↓
M Melting	↓	↑
S Stability	↓	↑

Erythro & threo system:





stability more for staggered.

$$\text{energy} \propto \frac{1}{\text{stability}}$$

staggered

→ Bayer Stearic theory

$$\text{Stability} \propto \left(\frac{1}{\text{heat of combustion values}} \right)$$

R-S Notation

H — horizon. → CW R → S ✓ R-C.W

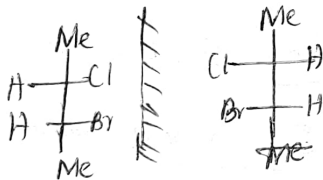
H — vertical → CW R → R ✓ S-A.C.W

D-L Nomenclature: In optical isomers, if H is present on left it is

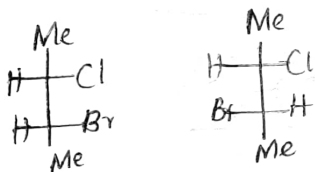
D-form, if H is present towards right & other grp occupy left position it is L-form.

Enantiomers: Non-superimposable mirror images.

Ex:



Diastereomers: Isomers which are non-superimposable & not related to each other as mirror image.

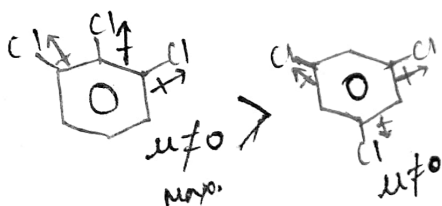


differs in physical & chemical properties

Priority for S.I — Ring chain > Tautomerism > F.G > Metamerism >

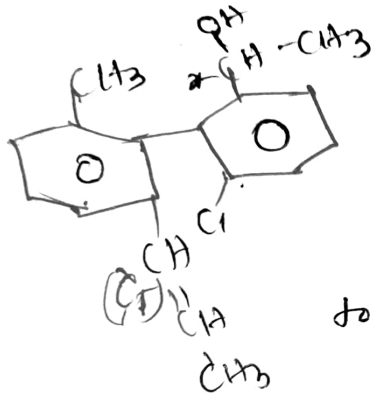
Chain isomerism > positional isomerism.

$$\text{Optical purity} = \frac{[\alpha]_{\text{obs}}}{[\alpha]_D}$$



Stability of compound:

① Neutral > ② $\text{E}^{\ominus}\text{N}$ > ③ $\text{E}^{\oplus}\text{N}$



if 4 different functional groups are present on biphenyl group
it acts as chiral carbon

total no. of isomers = 8 = $2^3 \rightarrow$ chiral carbon