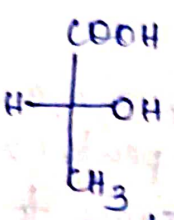
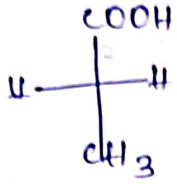
Chirality

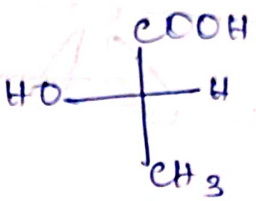
Most of the structure of several optically active compounds contain at least one chiral carbon atom. A carbon atom having four monovalent atoms or groups is known as chiral carbon / chiral centre.



D-lactic acid (chiral)

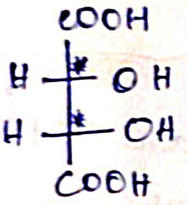


Propionic acid (achiral)



L-lactic acid (chiral)

Some molecules that although contain chiral centres yet are achiral.



Meso tartaric acid (achiral)

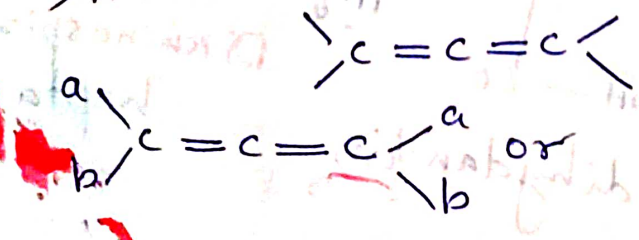
$CH_3 - CH = C = CH - CH_3$

2, 3 - pentadiene (no chiral atom, but the molecule is chiral.)

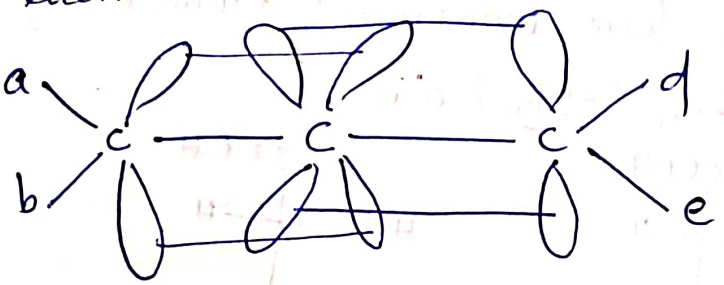
So, chirality of a compound means a phenomenon of a molecule which is optically active, that means a molecule rotates the plane polarized light either towards right or left.

Optical isomerism in compounds containing no chiral carbon atom.

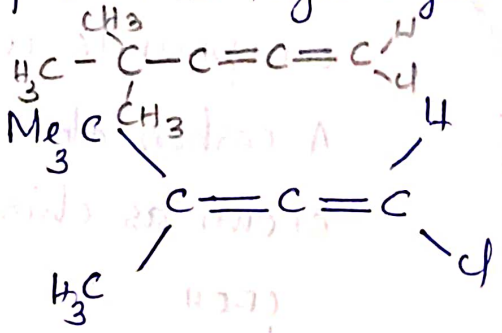
a) Allenes



In allenes, the two terminal carbon atoms are in sp^2 hybridised state and the central carbon atom sp hybridised. The two π bonds are in planes at right angles to each other.



eg:-

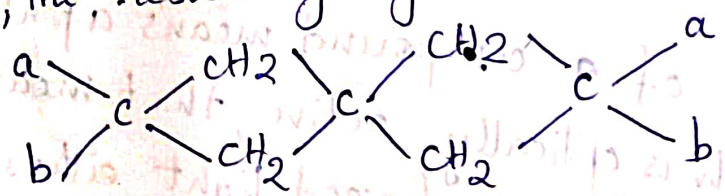


1-chloro 3,4,4-trimethyl penta 1,2-diene.

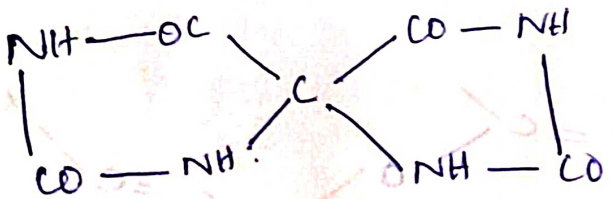
In trigonal state the π bonds is at right angle to plane of the σ bonds, the terminal grps attached to trigonal carbon atom lie in planes perpendicular to each other. The molecules thus possess neither plane nor a centre of symmetry and forms a non-superimposable mirror image hence it is assymmetric and optically active.

b) Spiro compounds:

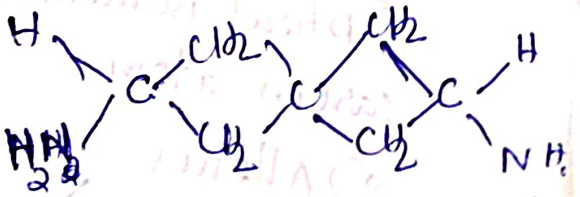
Both the double bonds in allenes are replaced by rings, the resulting system is known as spirans.



Since the two rings are perpendicular to each other and hence suitable substitution at either of the ends of the system or within the rings will make the molecule dyssemmetric ie, optically active.



Spiro-5,5'-dihydantoin

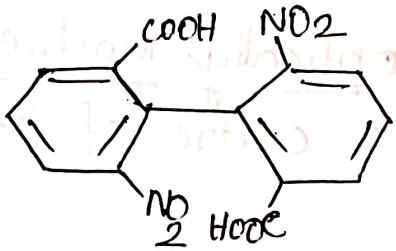


Diaminospirocyclo heptane.

Biphenyl Compounds:

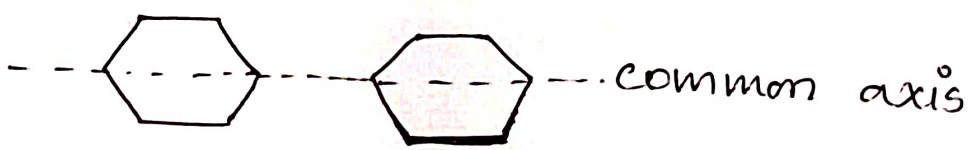
Suitable substituted biphenyl compounds are devoid of individual chiral carbon atom, but the molecules are chiral due to restricted rotation around the single bond between the two benzene nuclei and hence they must exist in two forms which are non superimposable mirror images of each other; such type of stereoisomerism which is due to restricted rotation about single bond is known as atropisomerism and the stereoisomers are known as atropisomers.

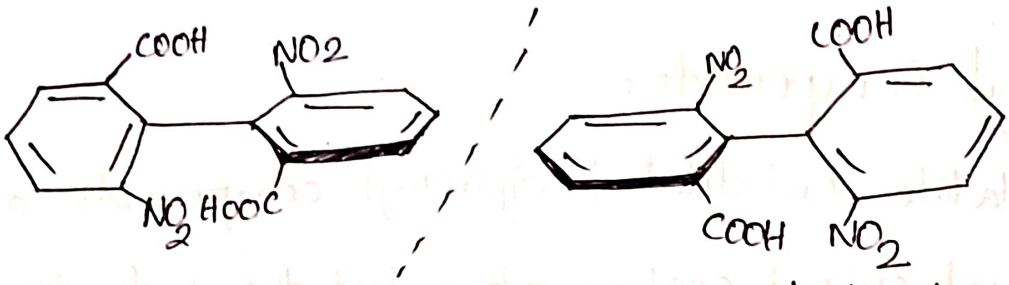
Kenner et al synthesised 6, 6'-dinitro diphenic acid which was the first biphenyl compound to show atropisomerism.



6, 6'-dinitro diphenic acid

Turner et al postulated that in biphenyl molecule the two benzene nuclei are collineas and the introduction of bulky groups in the o-positions prevent the free rotation of the benzene nuclei about the coaxis, and hence the two benzene nuclei in o-substituted derivatives cannot be planar; ie; the molecule is dissymmetric.

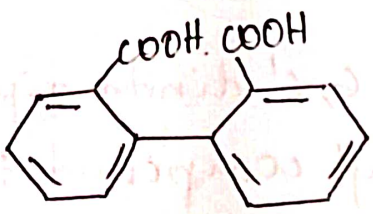




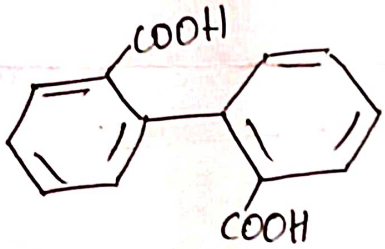
Enantiomers of 6,6'-dinitro diphonic ā

Two conditions for the biphenyl compounds to exhibit optical isomerism :

i) Neither of the two rings must have a vertical plane of symmetry ie; each ring should be unsymmetrically substituted.



} optically inactive due to plane of symmetry



} optically inactive due to centre of symmetry

ii) The o-positions (at least two) must be substituted by large groups (NO_2, SO_3H, CH_3 etc) in orders to prevent coplanarity and free rotation of the two benzene rings. If the groups are smaller in size, the two benzene nuclei become planar ie; free rotation occurs and thus the compound cannot show optical activity.