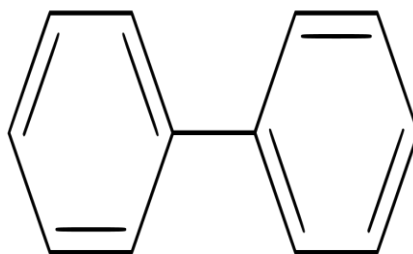


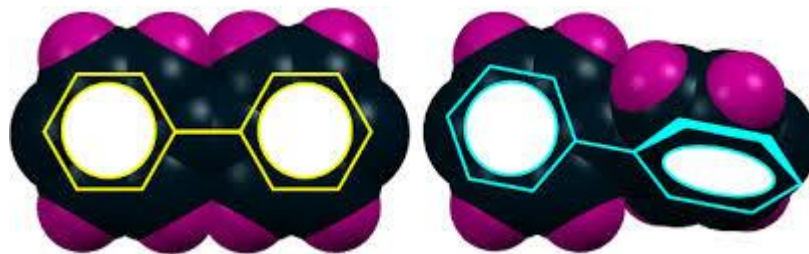
TY BSC (USCH-503)
Revised syllabus of University of Mumbai
Semester V
Stereochemistry of Biphenyl compound



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Introduction

- Biphenyl/diphenyl/phenyl benzene/ 1,1'-biphenyl / lemonene is an aromatic hydrocarbon ($\text{MW}(\text{C}_6\text{H}_5)_2$) compound that forms **colorless crystals**. It has distinctively pleasant smell. insoluble in water, but soluble in typical organic solvents. It is naturally occur in **coal tar, crude oil** and natural gas isolated from these sources via **distillation**.
- It can also be synthesized by using a **Grignard reagent** such as phenylmagnesium bromide and reacting it with bromobenzene.



Reactivity of Biphenyl

The biphenyl molecule consists of two connected phenyl rings.

Lacking functional groups, it is fairly non-reactive. It will, however, participate in many of the reactions that are typical for benzene, e.g substitution reactions upon treatment with halogens in the presence of a Lewis acid.

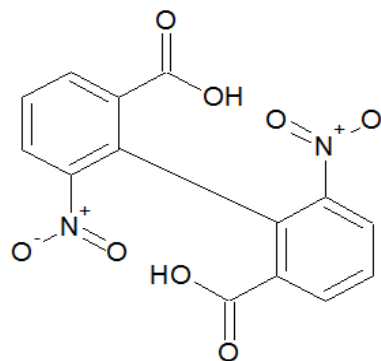
Biphenyl **do not show geometrical isomerism.** it shows **conformational isomerism** the rotation around the single bond is possible in biphenyls .

Plane of symmetry in biphenyls

- Biphenyls containing **four large groups in the ortho position cannot freely rotate about the central bond because of steric hindrance**. In such compound the **two rings are in perpendicular planes**. Three cases may be distinguished:
 - Both rings symmetric
 - One symmetric
 - Neither symmetric

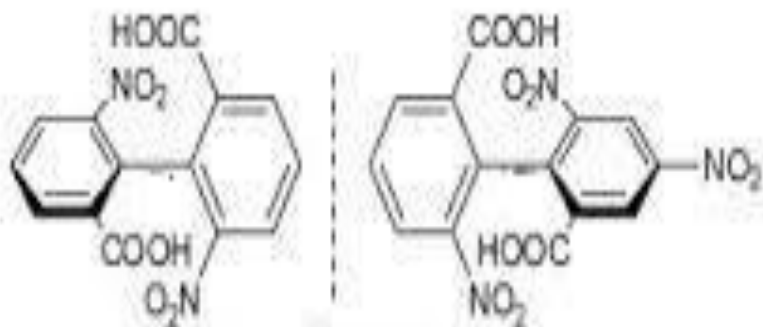
1ST CASE OF PLANE OF SYMMETRY

The molecule has two planes of symmetry. If a plane is drawn containing all atoms or groups in either ring, it is a **symmetrical perpendicular bisector** of the other ring such molecules are **not optical active**.



2nd case of Plane of symmetry

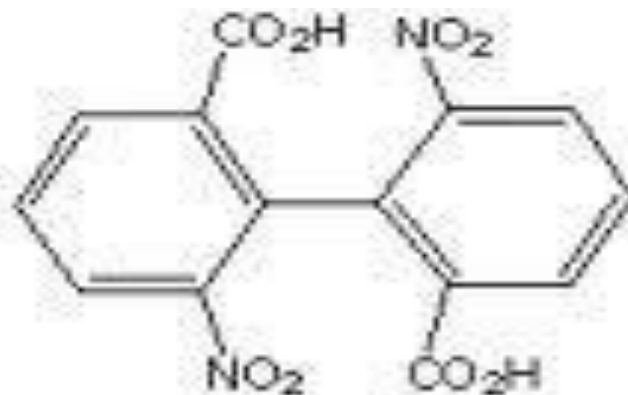
- In the second case only **the one ring is symmetric**. One **plane of symmetry** is sufficient to make the compound optically inactive, and it is . The case may be symbolized as AB....CC



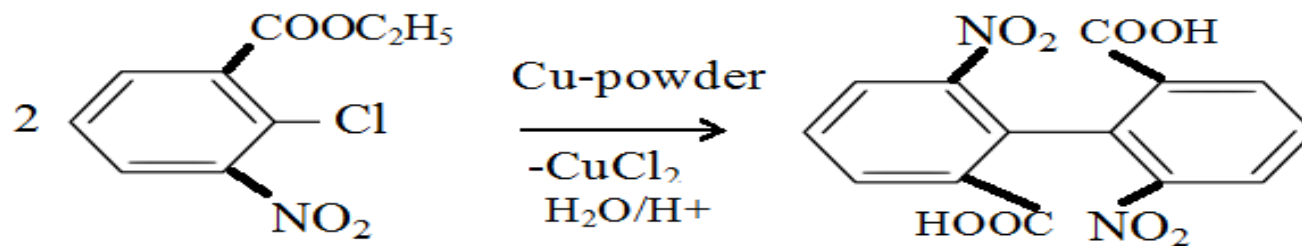
biphenyls

3rd case of Plane of symmetry

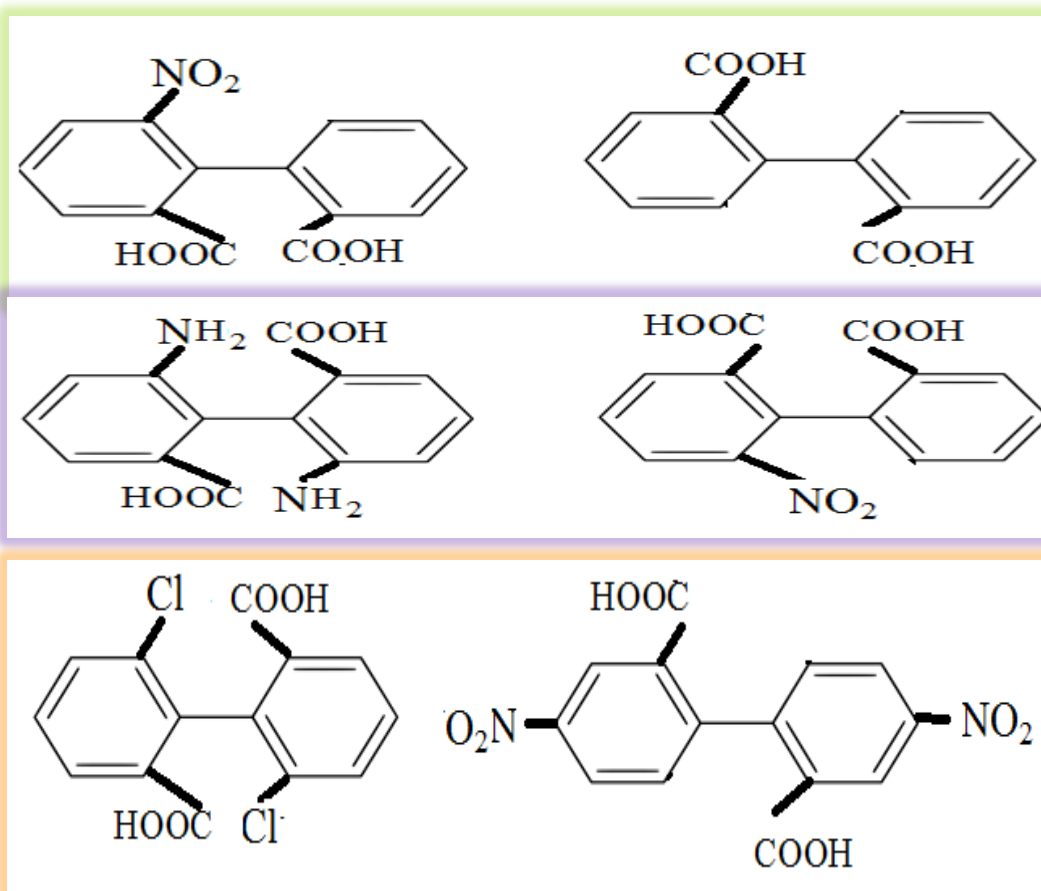
- In the third case **neither ring is symmetric** there is **no plane of symmetry**, and many such compounds have been resolved. This corresponds to AB.....AB.



Resolution of 6,6' dinitro -diphenic acid prepared through Ullmann reaction.



resolution



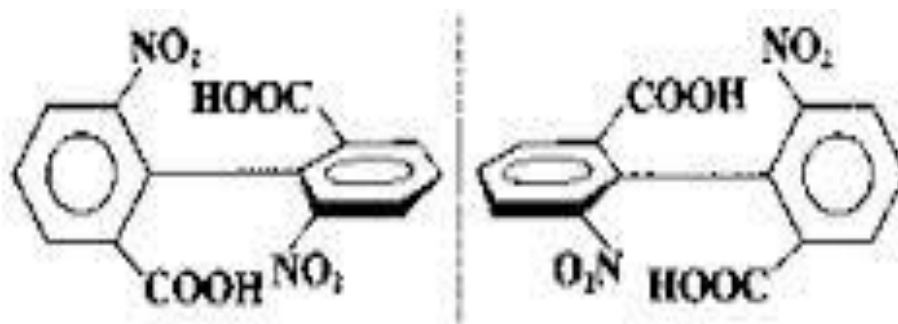
No resolution

How Biphenyl show optical activity ?

- Optical activity was caused by the presence of a chiral center and non superimpossibility of mirror images. Certain molecules however, are still optically active even if they **do not contain a chiral center**. Biphenyls do not possess stereogenic centers but still they are optically active. Substituted biphenyl exist in enantiomeric forms.
- Biphenyls can be chiral if two conditions are met.
 - If bulky groups are present on **ortho_position** .
 - Plane of symmetry **absent** in rings of biphenyls.

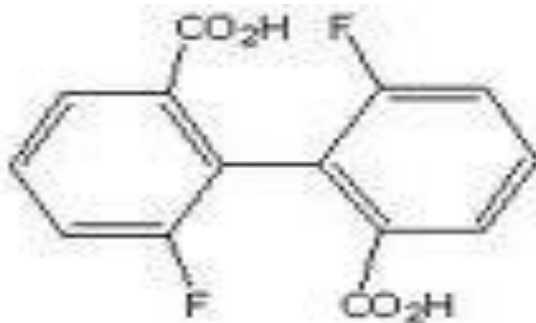
1st condition for optical activity of Biphenyls

- The substituent in the ortho_position must have a large size. **If three bulky groups present on ortho position they cause restriction. The groups are large enough to interfere mechanically i.e. to behave as obstacles then free rotation about the single bond is restricted. Thus the two benzene rings cannot be co-planar.**



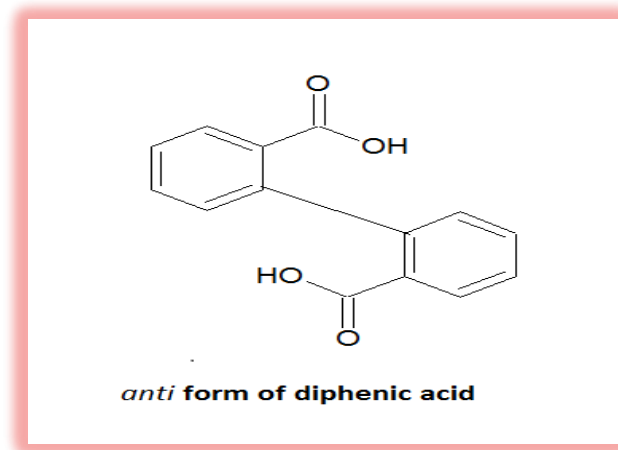
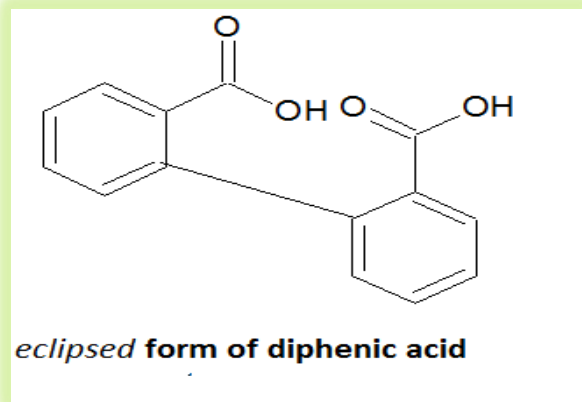
2nd condition for optical activity of Biphenyls.

- Resolvable biphenyls **must contain different ortho substituted on each ring** if one or both rings contain **two identical substitution** the molecule is **not chiral**, in other words **plane of symmetry must be absent in biphenyls**.



Conformation in biphenyls

- Conformational forms also exist in biphenyls take example of 2,2-diphenic acid. Both the forms of 2,2-diphenic acid will have a plane of symmetry but molecule prefer the **anti-configuration** because the **two large polar carboxylic groups**.



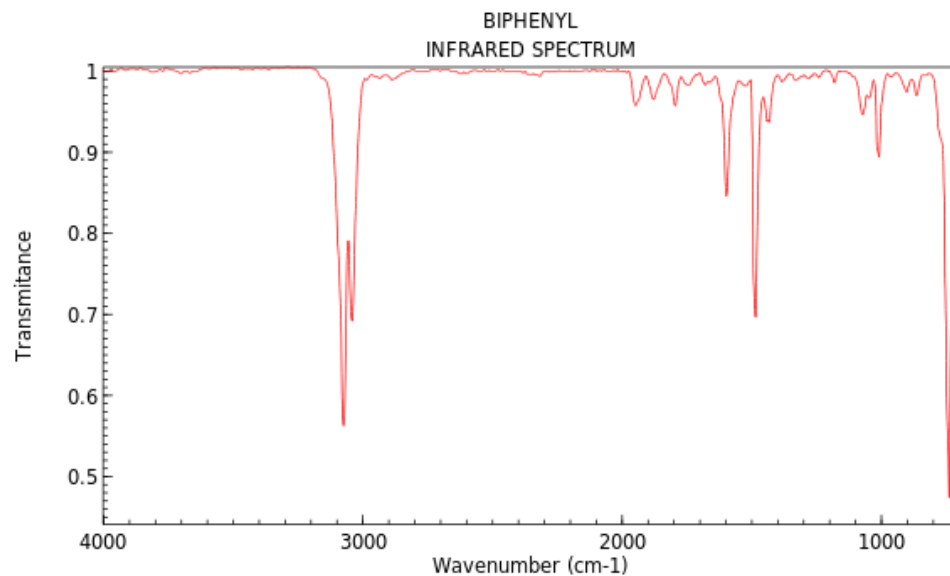
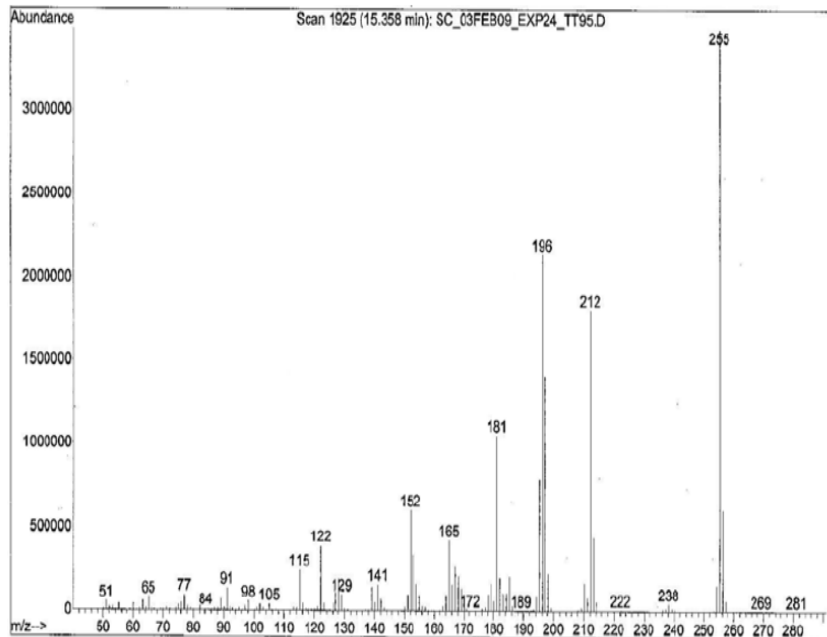
Recamization in Biphenyls

- The phenomenon of recamization in biphenyls is not yet discovered clearly. But it was assumed that when biphenyls are heated increase the amplitude of vibrations of substituent groups and also the amplitude of two benzene rings with respect to each other the substituent groups to slip by one other. Nuclei pass through a common plane and hence the probability is that the final product will an equimolecular amount of (+) and (-) forms.

So it concluded that the recamization process in biphenyls is completely a physical phenomenon.

Spectra of Biphenyl

- **Biphenyl shows an intense peak at 248nm.** This is due to the conjugation between the two benzene rings which can readily achieve co planarity. However, in ortho-substituted biphenyls the two rings pushed out of coplanarity , and **red leads towards the blue shift.**



Uses of Biphenyl

- Notably use as starting materials/primer for the production of polychlorinated biphenyls (PCBs) which widely used as dielectric fluids and heat transfer agents.
- Biphenyls is also the intermediate for the production of host of other organic compounds such as emulsification, optical brightness.
- Crop production, products and plastics.
- Biphenyl is used in organic syntheses, heat transfer fluids, dye carriers, food preservatives, as an intermediate for polychlorinated biphenyls, and as a fungistat in the packaging of citrus fruits.