STEREOCHEMISTRY- II

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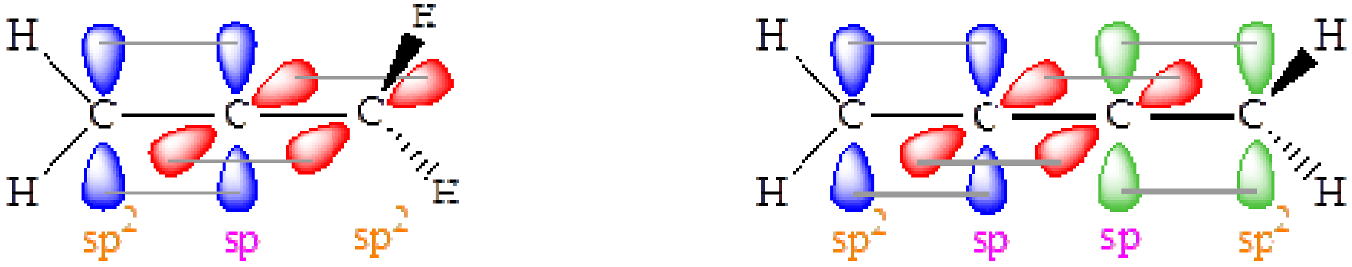
Cumulenes:

Cumulenes are the compounds having a cumulated system or adjacent double bonds and the simplest cumulene is Allene ($CH_2=C=CH_2$), which is having only two cumulated double bonds. Hence they form two pi-bonds by overlapping laterally with the 'p' orbitals on the adjacent carbon atoms. Unlike most alkanes and alkenes, cumulenes tend to be rigid, comparable to alkynes. By convention, if the number of cumulated double bond is n, then the number of carbon atom is n+1. Cumulenes containing heteroatoms are called heterocumulenes, e.g. carbon suboxide ($O=C=C=C=O$).

The rigidity of cumulenes arises from the fact that the internal carbon atoms carry two double bonds. Their sp hybridization results in two π bonds, one to each neighbor, which are perpendicular to each other. This bonding reinforces a linear geometry of the carbon chain.

Containing even no. of double bonds
(non-planar)

Containing odd no. of double bonds
(planar)



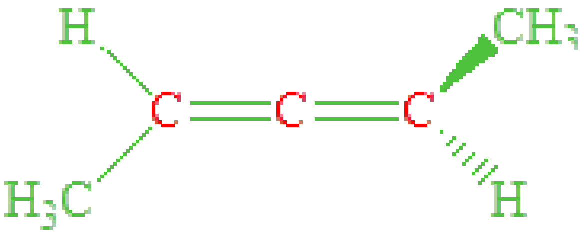
Stereochemistry of Cumulenes

Here the hydrogen atoms at one end of the system lie in a plane at right angles to those at the other end. Such spatial arrangement can be explained in the following way:

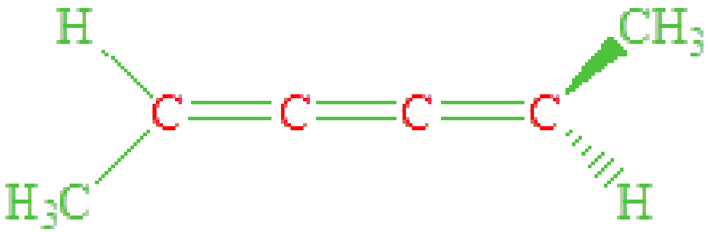
- The central carbon atom is in sp hybridized state and the terminal carbon atoms are in sp^2 hybridized state.
- The central carbon atom forms two π-bonds by using its two p-orbitals which are mutually perpendicular to each other. So the planes containing two π-bonds are commonly perpendicular to each other.
- The plane containing π-bond is perpendicular to the plane containing σ-bonds. Thus the plane containing σ-bonds at the two terminals are mutually perpendicular to each other.

Cumulenes containing even no. of double bonds is non-planar in geometry and hence if suitably substituted show enantiomerism i.e. optical isomerism (dextro and levo) that should be non-superimposable with its mirror image. Cumulenes containing odd no. of double bonds is planar in geometry and hence if suitably substituted show diastereomerism i.e. geometrical isomerism or cis-trans isomerism.

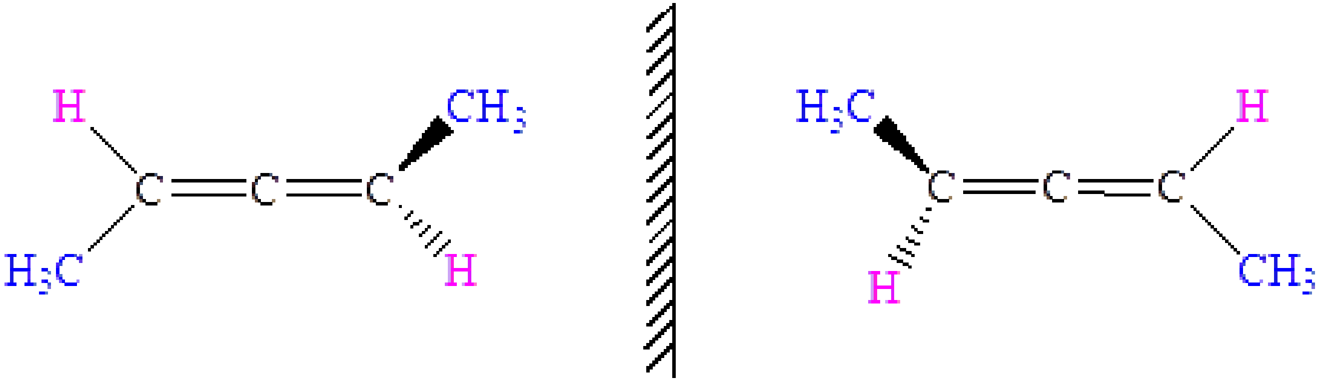
But the most important fact is that there should be different groups on terminal carbon atoms.



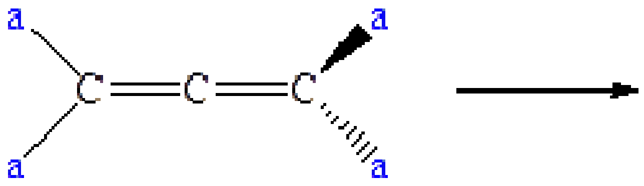
2,3-Pentadiene
(shows optical isomerism)



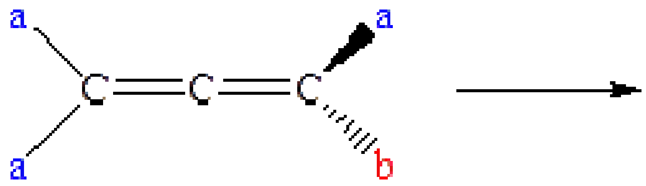
2,3,4-Hexatriene
(shows geometrical isomerism)



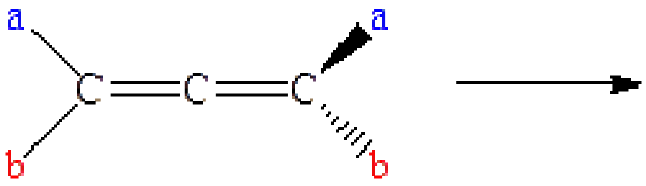
Pair of Enantiomer
Non-superimposable mirror image
They can be separated into (−) & (-) isomer. So resolvable



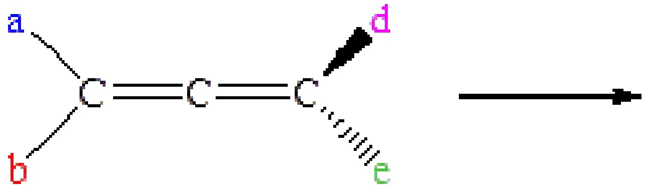
no cis-trans isomers



no cis-trans isomers (a ≠ b)



Shows enantiomerism due to presence of chiral axis (a ≠ b).
Optically active. Resolvable



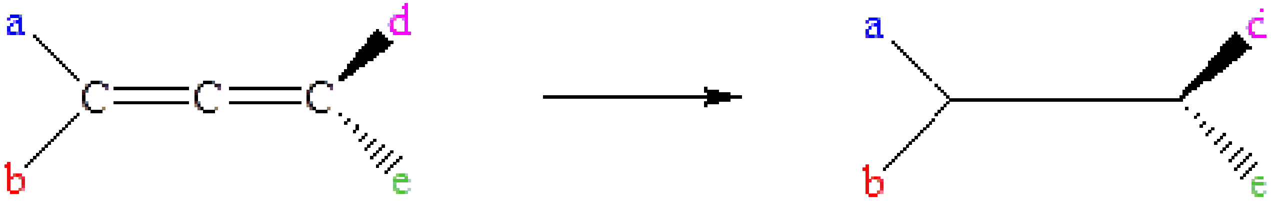
Shows enantiomerism due to presence of chiral axis (a ≠ b ≠ d ≠ e).
Optically active. Resolvable

Allenes:

Molecules with Axial Chirality:

Allenes are organic compound in which carbon atom has double bonds with each of its two adjacent carbon centers. Allenes are classified as polyenes with cumulated dienes. The parent compound of this class is propadiene, which is itself also called allene. Allenes are much more reactive than most other alkenes.

The central carbon atom of allenes form two σ-bonds and two π-bonds. The central carbon is sp-hybridized, and the two terminal carbon atoms are sp^2-hybridised. The bond angle formed by the three carbon atoms is 180^o, indicating linear geometry for the central carbon atom. The two terminal carbon atoms are planar and these planes are twisted 90^o from each other. As shown in the following diagram, the overall configuration of allenes resembles that of an "elongated tetrahedron".

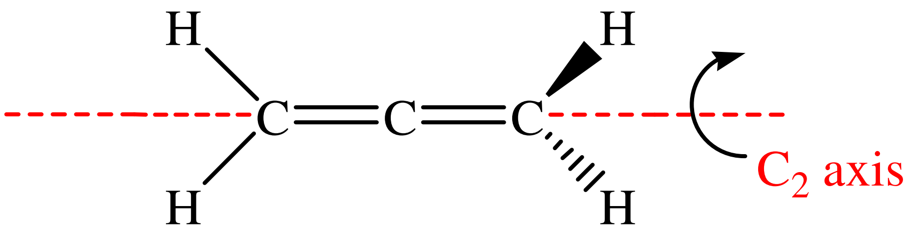


Elongated tetrahedron

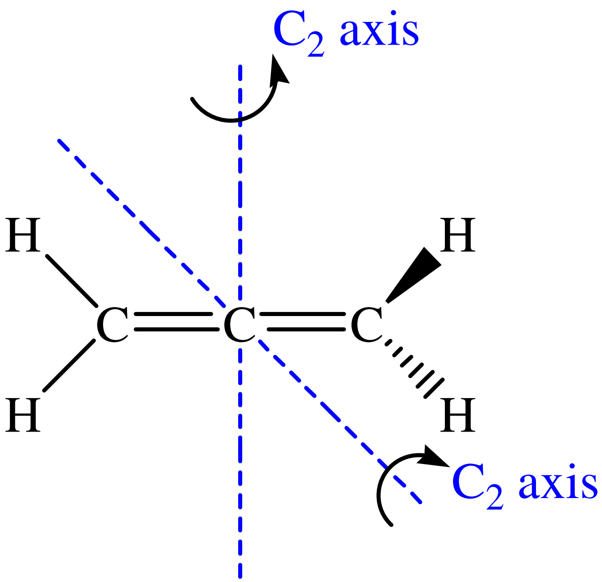
Symmetry:

The symmetry and isomerism of allenes has long fascinated organic chemists. For allenes with four identical substituents, there exist two twofold axes of rotation through the center carbon, inclined at 45° to the CH_2 planes at either end of the molecule. The molecule can thus be thought of as a two-bladed propeller. A third twofold axis of rotation passes through the C=C=C bonds and there is a mirror plane passing through both CH_2 planes. Thus this class of molecules belong to the D_{2d} point group. Because of the symmetry, an unsubstituted allene has no net dipole moment.

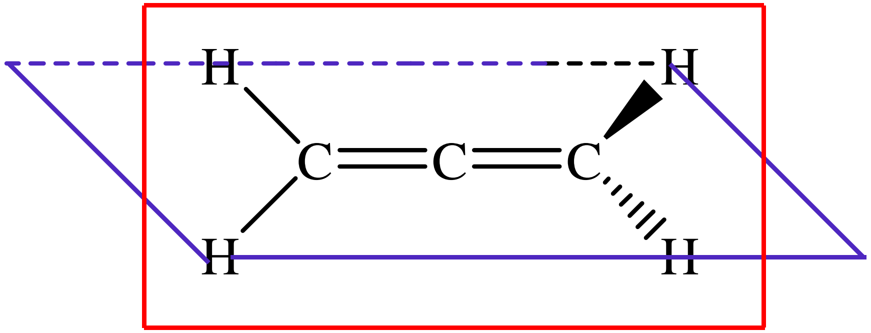
- A C_2 axis which passes the three carbon atoms as shown in the adjacent figure:



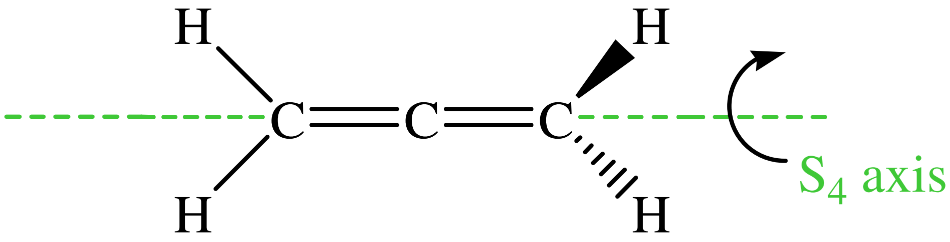
- In addition to the above it contains two other C_2 axes as shown in the adjacent figure. Obviously these two C_2 axes are mutually perpendicular to each other and perpendicular to the former one which is actually the principle axis.



- Again the molecule contains two planes of symmetry- one is on the plane of the paper and another is perpendicular to the plane of the paper as shown in the following figure. Also each of these two planes of symmetry bisects the angle between the above two C2 axes and thus these can be designated as σ_d planes.

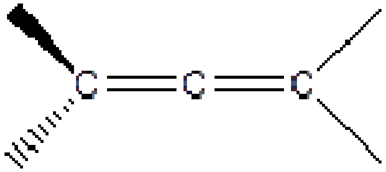


- Up to this study it appears that simplest allene is a molecule in D_{2d} point group. In addition to the above the molecule contains an S_4 axis which coincide the principle axis as shown below:

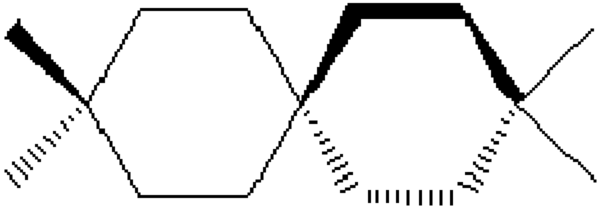


Spirans:

A spiro compound or spiran, from the Latin *spira*, meaning a twist or coil, is a chemical compound, typically an organic compound, that presents a twisted structure of two or more rings in which 2 or 3 rings are linked together by one common atom. Spirans are compounds in which it appears that both the double bonds of allene are replaced by rings. Now properly substituted spirans just as in the case of allenes give raise axial chirality.

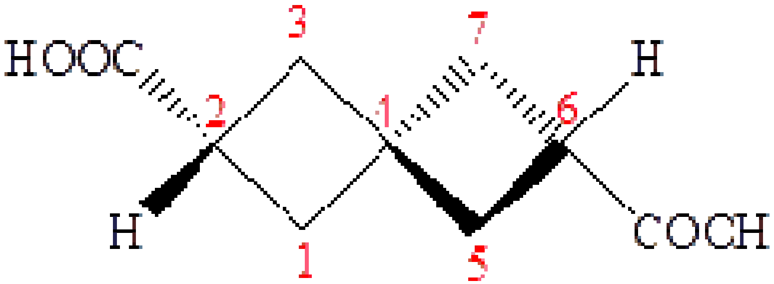


Allenes



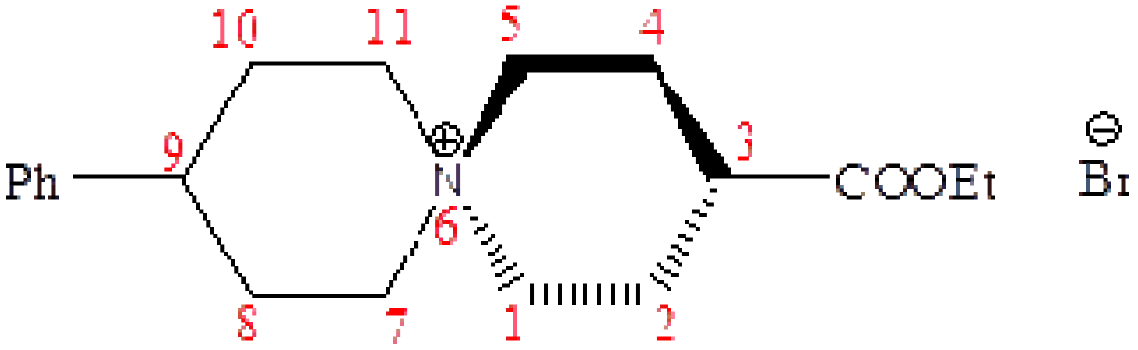
Spirans

The simplest spiro compounds are bicyclic or have a bicyclic portion as part of the larger ring system with two rings connected through the defining single common atom. The one common atom connecting the participating rings distinguishes spiro compounds from other bicycles such as isolated ring compounds like biphenyl that have no connecting atoms. E.g.



Spiro[3.3]heptane-2.6-dicarboxylic acid

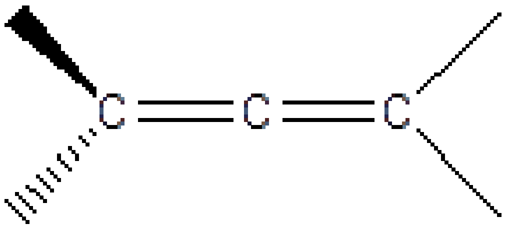
Another attractive molecule is as follows. Here we have the axial chirality and it is resolvable into two enantiomeric forms. Here the quaternary nitrogen atom acts as a common atom to the both rings.



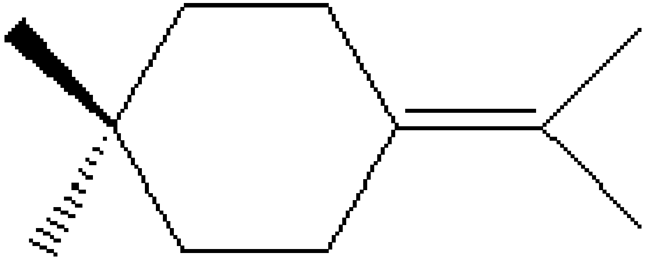
3-Ethoxycarbonyl-9-phenyl-6-azonia-spiro[5.5]undecane bromide

Alkylidenecycloalkanes:

Alkylidenecycloalkanes are the compounds in which one of two double bonds of allene is replaced by a ring. It is also called hemispirans.

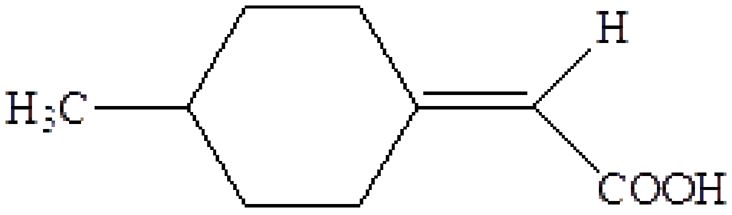


Allenes

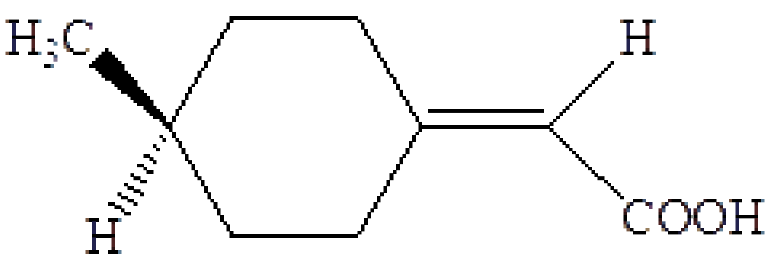


Alkylidenecycloalkanes

As in the case of allenes, properly substituted alkylidenecycloalkanes give raise axial chirality, for which that compound is resolvable into two enantiomeric forms. Thus the following compound is resolvable into two resolvable into two enantiomeric forms:



(4-Methyl-cyclohexylidene)-acetic acid



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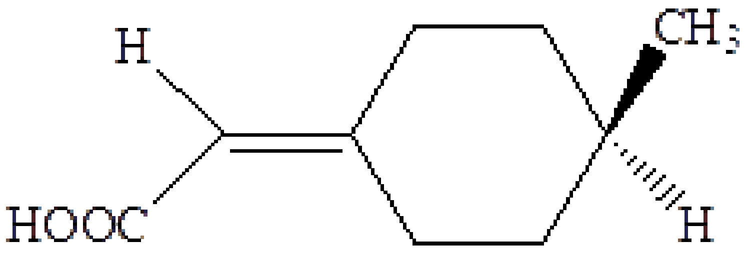
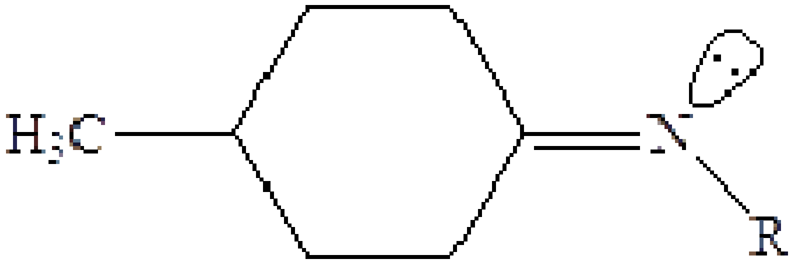


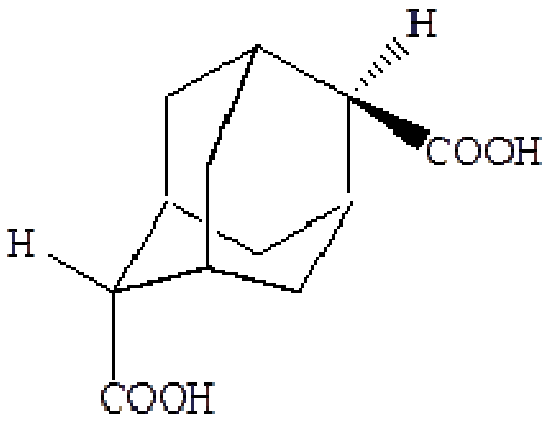
(4-Methyl-cyclohexylidene)-acetic acid is the first molecule without any asymmetric carbon was resolved. Subsequently a number of cyclic oximes, semicarbazones and phenyl hydrazones have also been resolved.



$R = OH$
$= NHCONH_2$
$= NHPh$

Adamantanes:

Adamantanes are highly rigid molecules and diametrically opposite two secondary carbons i.e. two methylene planes are in orthogonal alignment. So here axial chirality as that in allenes is originated with proper substitution. Here adamantane-2,6-dicarboxylic acid fulfills the specifications of axial chirality and thus exists in two enantiomeric forms which are as follows:



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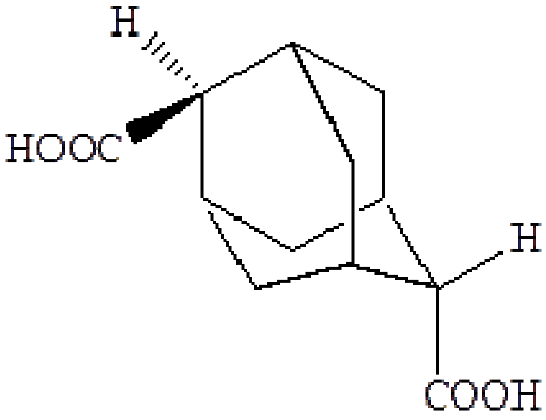


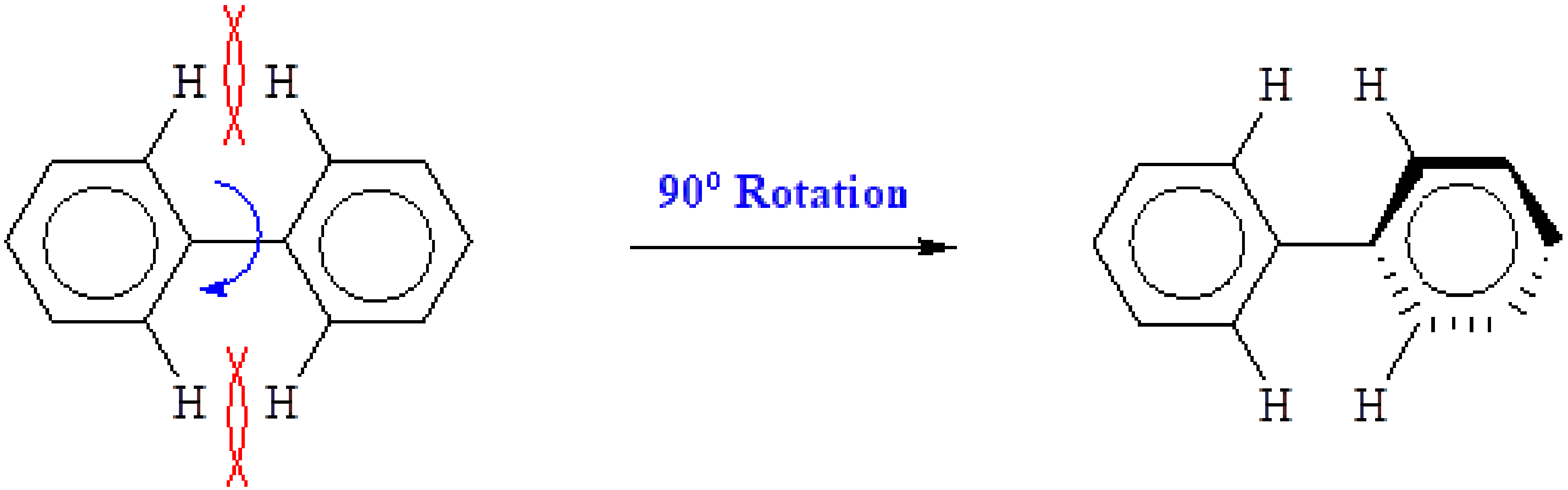
Catenanes:

A catenane with two or more dissimilar rings interlinked with each other may give rise to chirality due to secondary structure which arises out of primary structure through coiling, the most common example being the helical structure of proteins. The interlocked rings cannot be separated without breaking the covalent bonds of the macrocycles. If the two rings are held with their planes perpendicular to each other, a catenane may correspond to the following structure with respect to the arrangement of four distinguishable groups in the chains.

Biphenyl Derivatives and Atropisomerism:

In case of biphenyl the rotation of two benzene nuclei around the common axis is allowed. In biphenyl two phenyl groups are joined by a single bond (sp^2-sp^2), called the pivotal bond. The distance between *ortho* H's in adjacent rings in the planar conformation is greater (0.29 nm) than twice the Vander Waals radius of hydrogen (2 x 0.12 nm) so that the rotation around the pivotal bond is not impeded by steric factors.

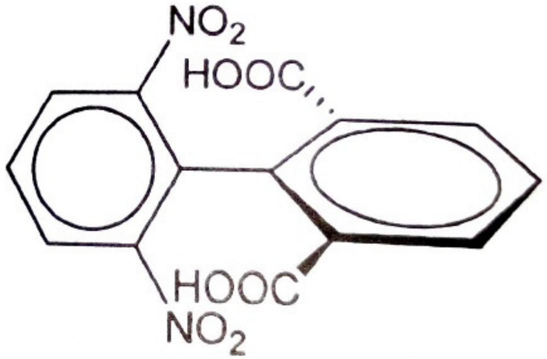
If the *ortho*-positions are substituted by bulky groups then the rotation of two benzene nuclei about the common axis is hampered, then the two benzene nuclei will be inclined to each other and the angle of inclination is actually in the vicinity of 90^o i.e. two benzene nuclei are almost in orthogonal alignment.

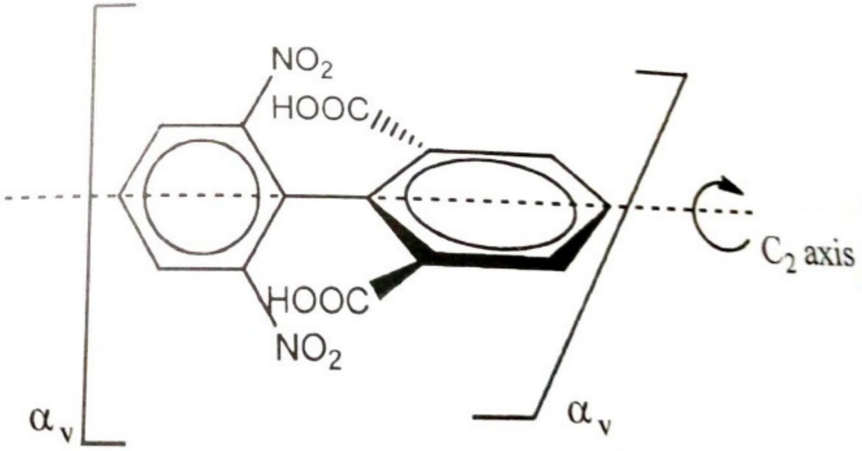


H's becomes in Vander Waal Radiation
arises Vander Waal repultion

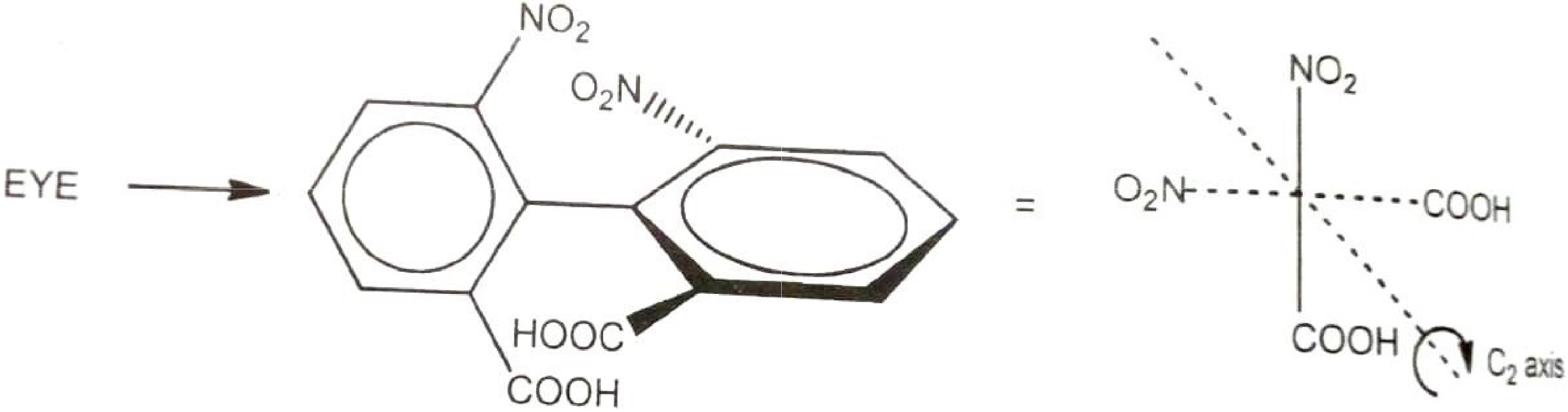
Two benzene nuclei are in
orthogonal allignments

Let us consider the following molecule. It contains two plane of symmetry, one is on the plane of the paper and other is perpendicular to the plane of the paper and a C_2 axis as shown below. Thus the molecule is of C_{2v} point group.

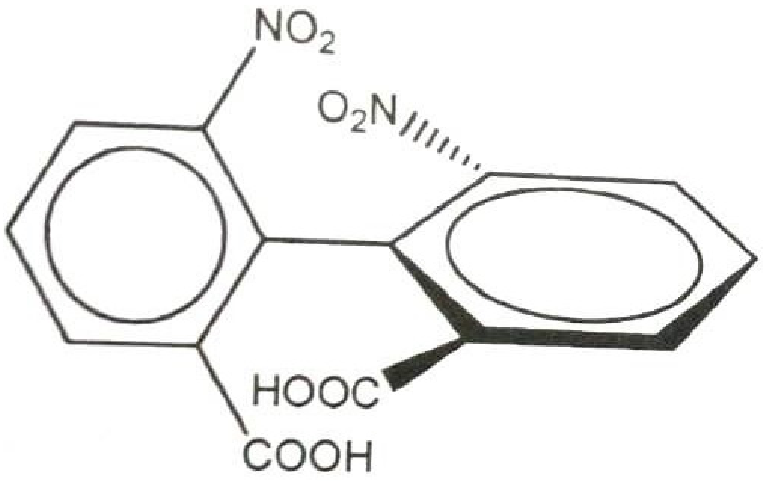




Now let us consider 2,6-dinitro-2$^{/}$,6$^{/}$-diphenic acid where no question of resolution arises t contains only C_2 axis as shown below.



hus it is a dissymmetric molecule of C_2 point group. So the compound 2, nitro-$2^{/}$,$6^{/}$-diphenic acid can exist in two enantiomeric forms which a own below:



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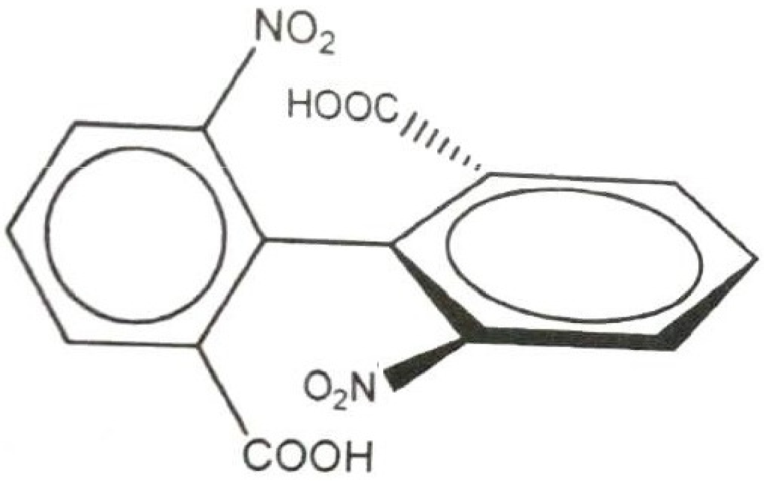
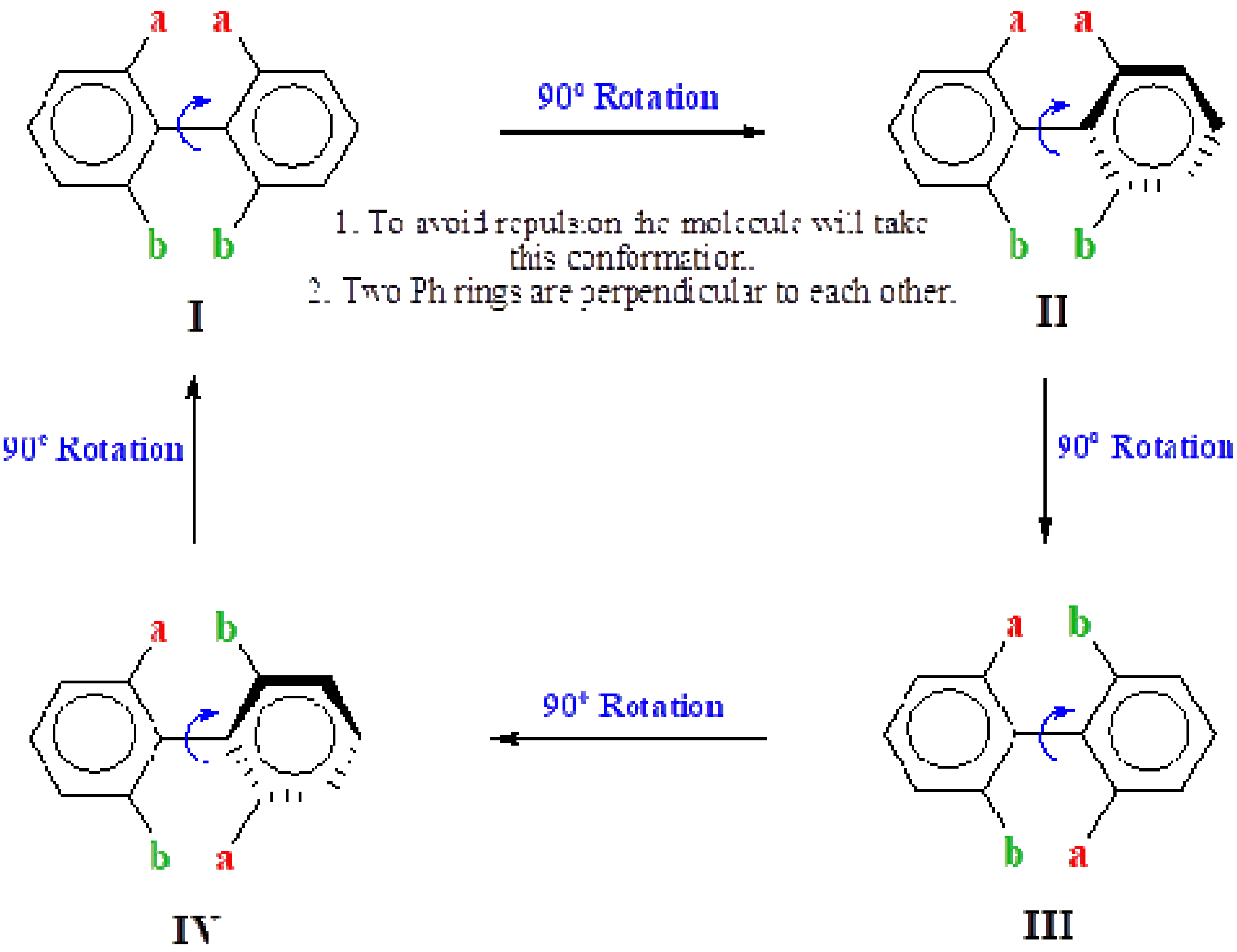


This type of isomerism arises due to restricted rotation around a single bond where the isomers are isolable under ordinary condition is known as ***Atropisomerism*** and the enantiomers are called ***Atropisomers***. They are actually torsional isomers about single bonds.

Thus for the atropisomerism with biphenyls:

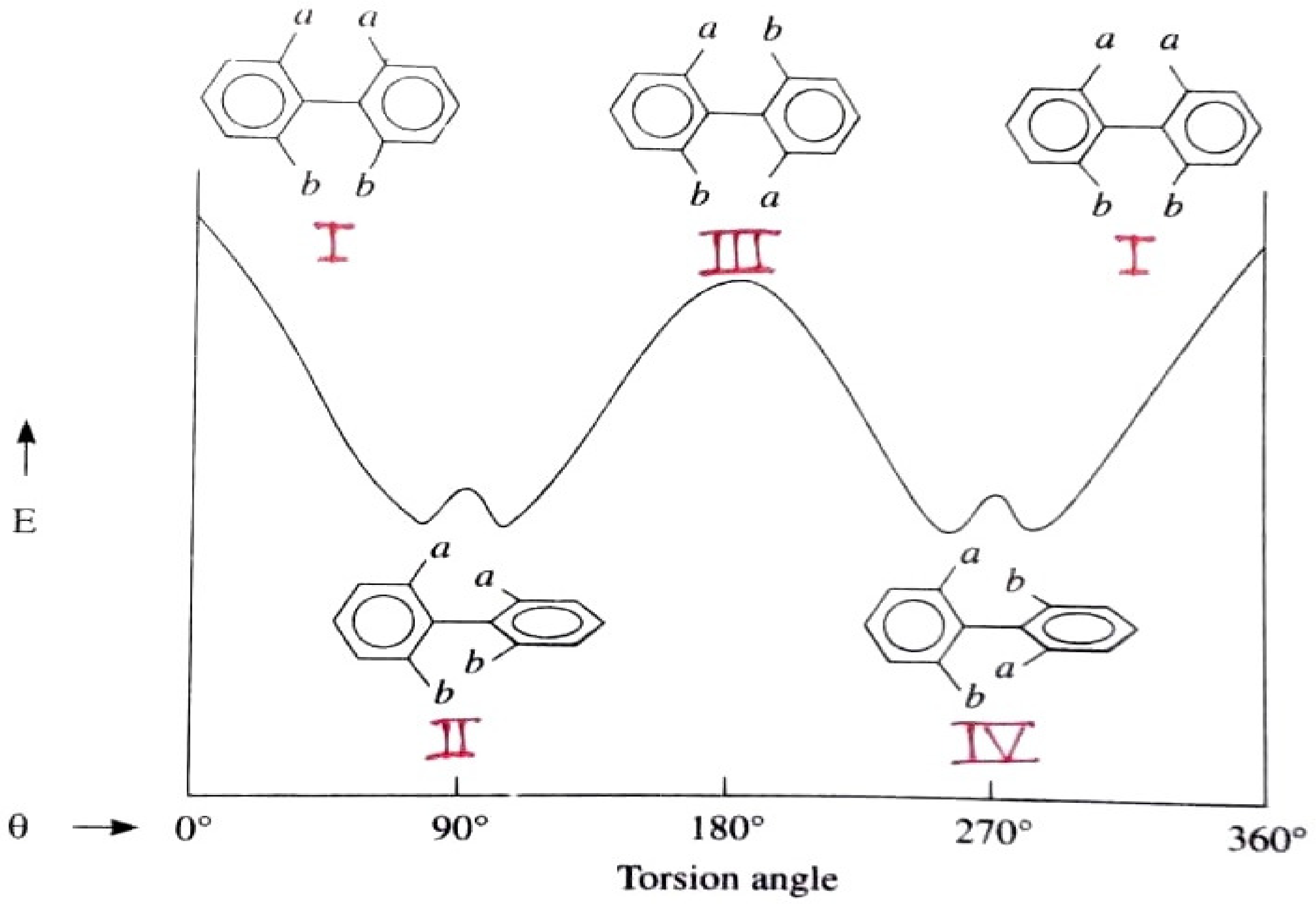
- The *ortho* substituents must be bulky enough which inhibits the rotation about carbon-carbon single bond.
- Two benzene nuclei must be properly substituted.



1. To avoid repulsion the molecule will take this conformation.
2. Two Ph rings are perpendicular to each other.

Co-planar structure.
It again suffers repulsion.

An approximate energy profile diagram is shown in the following figure for a 360° (θ) rotation around the pivotal bond.



Energy profile diagram of biphenyls

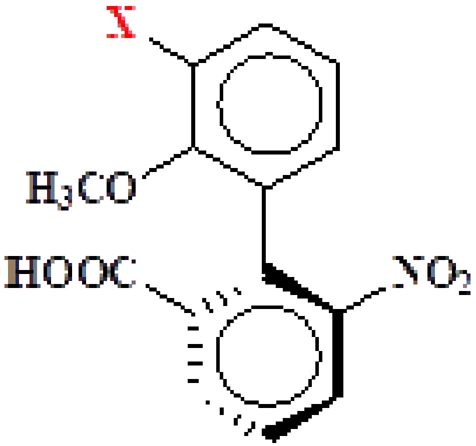
From the diagram it has been seen that stability of II and IV are equal. Also they exist in same energy level. II and IV are non-superimposable mirror images. This type of isomerism which owes its existence to restricted rotation around a single bond is known as **Atropisomerism**. Because they are interconvertible by the exact amount of energy supply, they are not real enantiomer. They are atropisomers.

It may be noted that two diastereomeric planar conformations I and III represent maximum energy. I with similar groups on the same side (cisoid) has higher energy than III with similar groups on opposite sides (transoid).

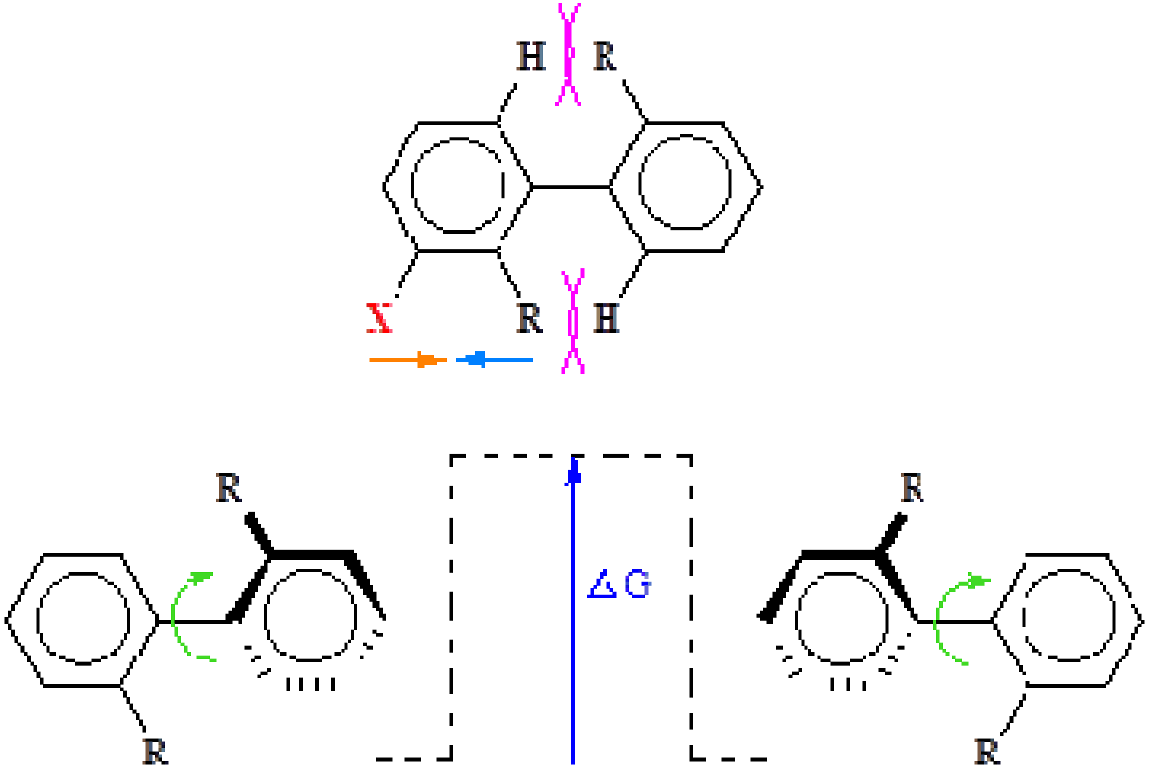
Buttressing Effect:

ome organic molecules are chiral not because of the presence of a chiral sp3 carbon but because o estricted rotation. Typical examples are biphenyl structures. Due to the presence of *ortho*-substituents th wo rings are not only rotated out of plane but due to restricted rotation both the isomers are isolable, calle **Atropisomers**.

ater it has been observed that a meta substituted biphenyl further restricted the rotation of biphenyls. Thi ffect is called **Buttressing effect**.



The buttressing effect is explained by looking at the transition state of rotation:



In this planar transition state, the *ortho*-groups are close to each other which causes steric strain. In order to overcome the steric strain, the *ortho*-groups will try to move away i.e. the bond will bend to overcome the rotational barrier. The extra *meta*-group prevents that the ortho group can bend and therefore makes the transition state higher in energy.

THANK YOU