Study Material: 2

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Subject- Chemistry

Semester- II

Course Code- CC4

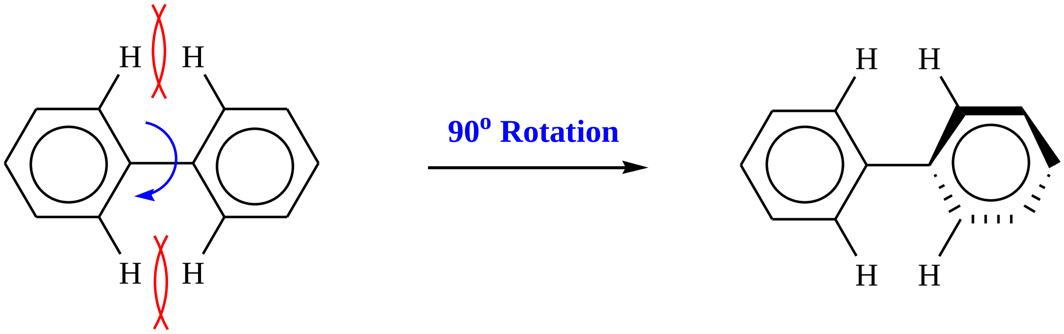
Topic- Organic Chemistry, Stereochemistry

STEREOCHEMISTRY- 2

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.

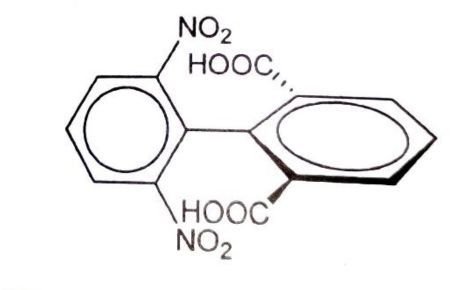
If the *ortho*-positions are substituted by bulky groups then the rotation of two benzene nuclei about the common axis is hampered, then the two benzene nuclei will be inclined to each other and the angle of inclination is actually in the vicinity of 90^o i.e. two benzene nuclei are almost in orthogonal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

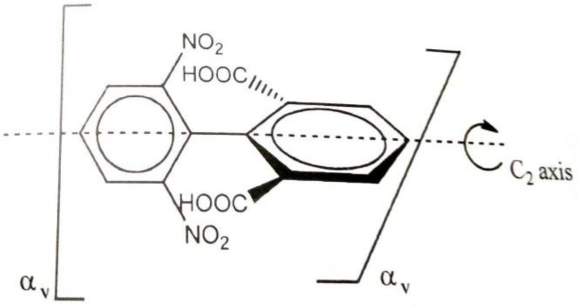


H's becomes in Vander Waal Radiation arises Vander Waal repultion

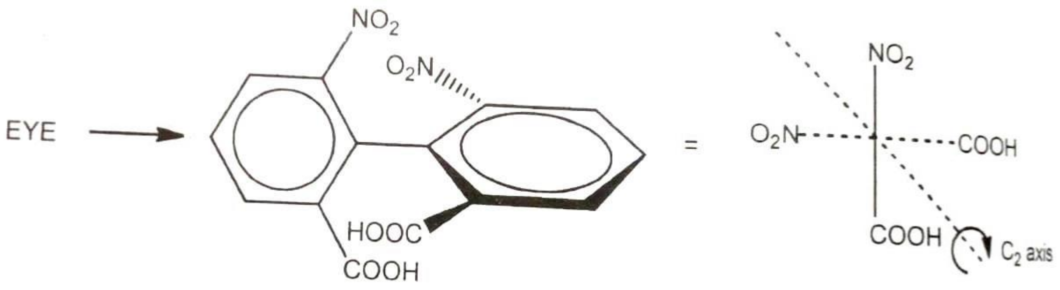
Two benzene nuclei are in orthogonal allignments

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.

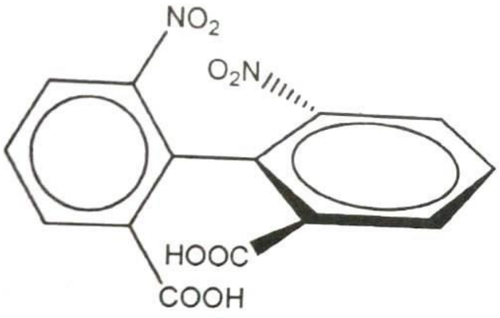




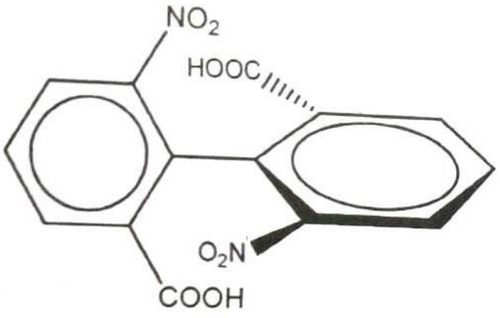
Now let us consider 2,6-dinitro-$2^{/}$,$6^{/}$-diphenic acid where no question of resolution arises. It contains only C_2 axis as shown below.



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



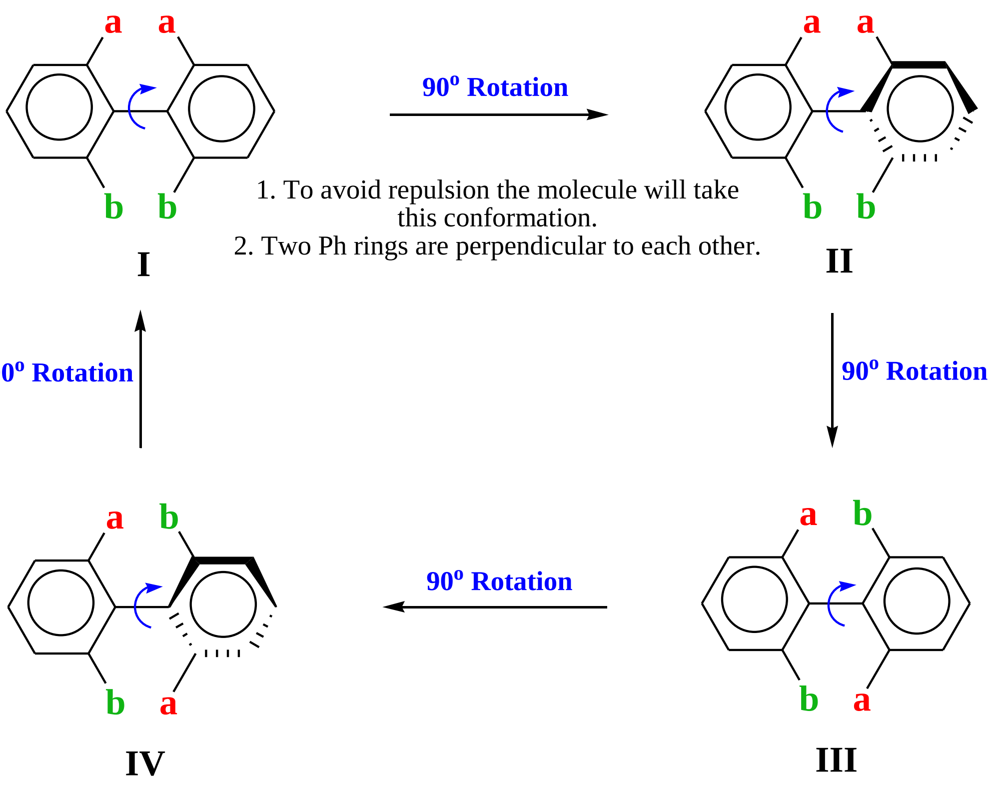
and



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:

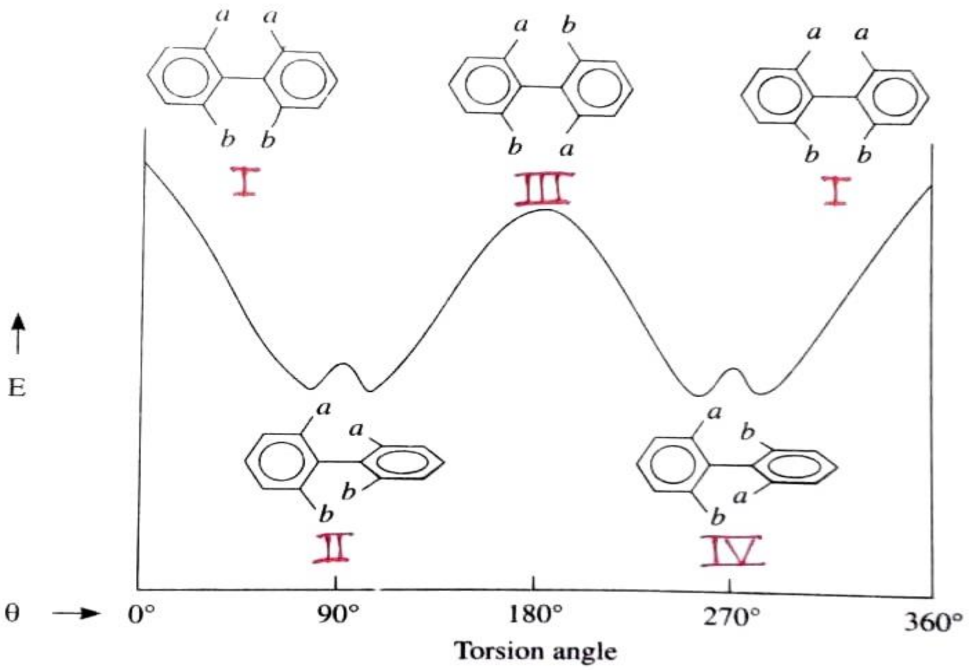
- The *ortho* substituents must be bulky enough which inhibits the rotation about carbon-carbon single bond.
- Two benzene nuclei must be properly substituted.



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^o (θ) rotation around the pivotal bond.

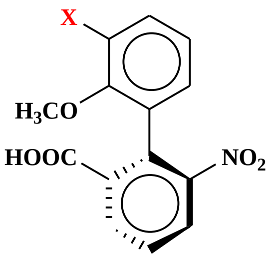


Energy profile diagram of biphenyls

From the above 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).

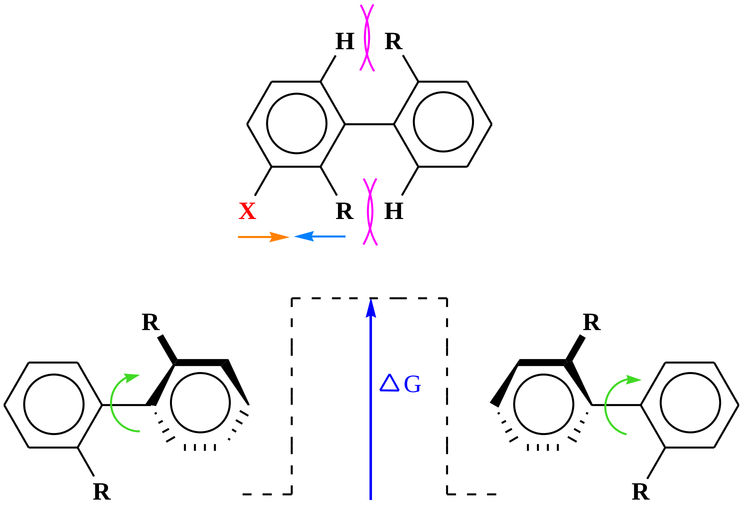
Buttressing Effect:



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

Later it has been observed that a meta substituted biphenyl further restricted the rotation of biphenyls. This effect 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.