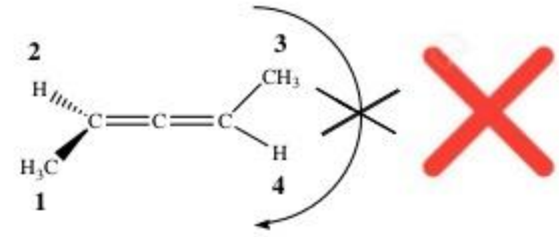
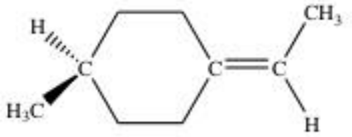


R

Hemispiranes or Alkylidenecycloalkanes:

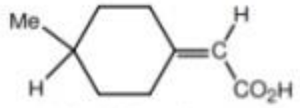
The replacement of one double bond in an allene by a ring gives alkylidenecycloalkanes referred to as hemispiranes, does not alter the basic geometry of the allene and exists as optical form if suitabley substituted.



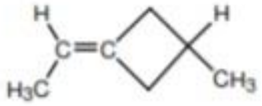
For such a system, Optical activity arises if

(1) Number of **ring + double bonds** should be **even**.

(2) **Proper substitution** i.e. two different substituents at either end and also on carbon.



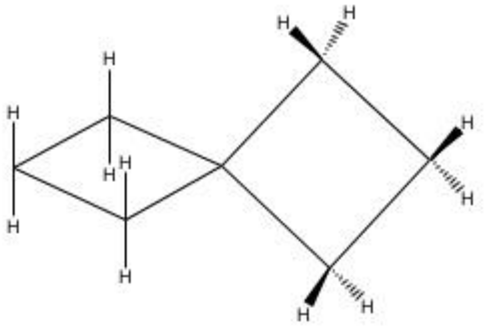
→ 1 double bond + one ring = 2 = even
→ Properly substituted
→ Chiral and hence optically active.



→ 1 double bond + 1 ring = even
→ Properly substituted
→ Chiral, optically active.

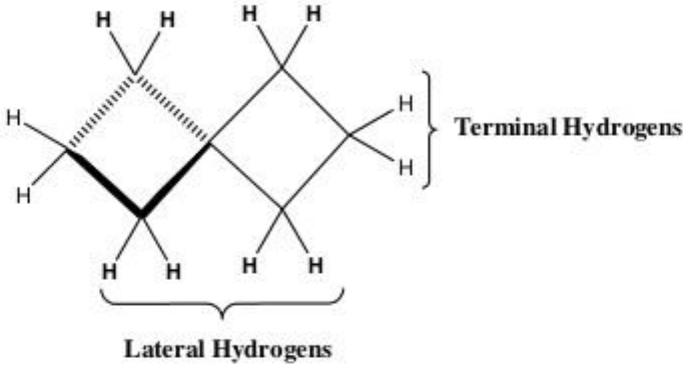
Spiranes:

If both double bonds in the allene system are replaced by rings the resulting molecules are spiranes. In spirane molecule two rings are perpendicular to each other due to steric crowding by the hydrogen atoms.



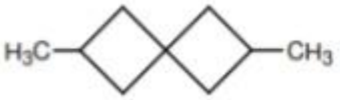
Spiranes has two types of hydrogen

1. **Lateral** - 8 hydrogens are lateral
2. **Terminal** – 4 hydrogens are terminal

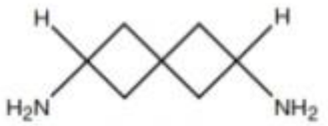


Essential criteria for exhibiting optical activity

1. Even number of ring in spiro compound (Odd number of spiro carbon)
2. Proper substitution at only terminal H.

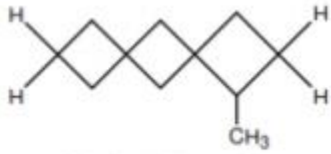


→ Number of rings = even
→ Properly substituted
→ Chiral, optically active.



→ Number of rings = even
→ Properly substituted
→ Chiral, optically active.

- ❖ Chirality due to chiral centre can be generated in any spirane compound (even or odd number of ring) by substitution at lateral hydrogen (Plane of symmetry should not be there).



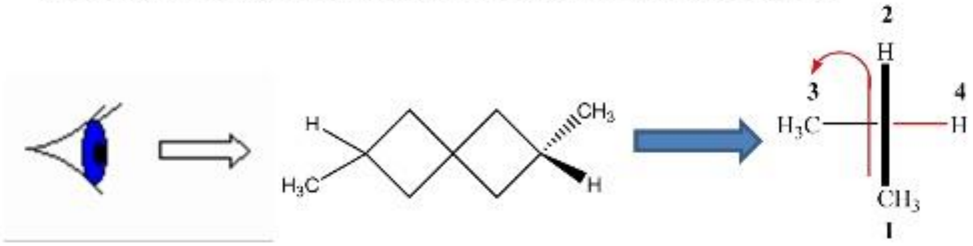
→ Number of rings = odd

→ Not properly substituted

→ But chiral due to chiral centre not due to axis.

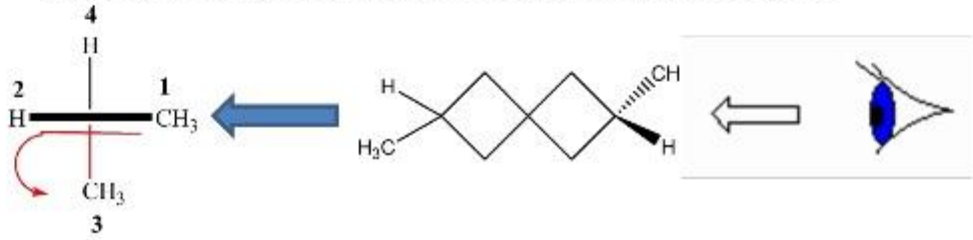
R/S nomenclature for the Spiranes:

1. **Viewing of molecule from left side**
    (a) Groups near to the observer are drawn on the bold line and away groups are on the thin line.
    (b) Priority will be given to near group according to CIP rule than far group.



S

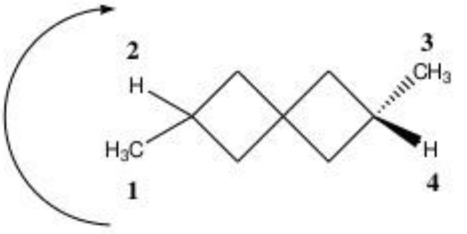
2. **Viewing of molecule from right side**
    (a) Groups near to the observer are drawn on the bold line and away groups are on the thin line.
    (b) Priority will be given to near group according to CIP rule than far group.



S

OR

- Always the groups on the solid lines are given priority then priority given to dashed and wedge lines.



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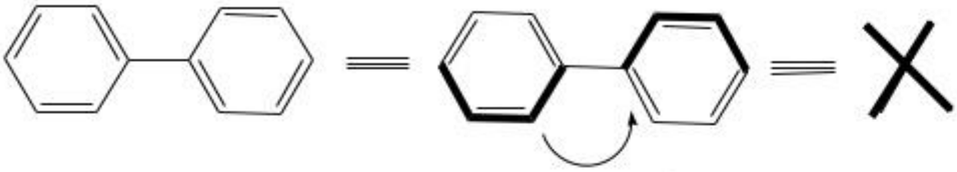
Biphenyls:

Biphenyls itself is not planar, one benzene ring being slightly twisted in relation to other as a consequence of steric crowd.



Dihedral angle 45°

Conformation having a 90° dihedral angle is achiral as a consequence of plane of symmetry. If each of the phenyl rings of biphenyl has two different ortho / meta substituent, even the twisted 90o dihedral angle conformer becomes chiral.

In order to interconvert such conformation with their mirror image structure, a rotation through the higher energy coplanar form must be made. The ease with which this interconversion occurs will depend on the size of ortho substituents.

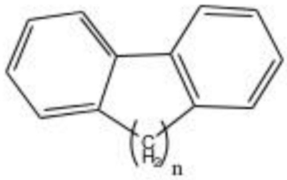
Conformational isomers that are isolable due to high energy barrier are called atropisomers (a = not, tropos = turn).

The name was introduced by Kuhn i 1933, but atropisomerism was first detected in 6, 6'-dinitro-2, 2'-diphenic acid by Cristie in 1922.

The C-C sigma bond is known as pivotal bond.

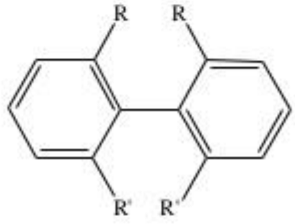
Biphenyls are classified into two categories

1. **Bridged biaryls**



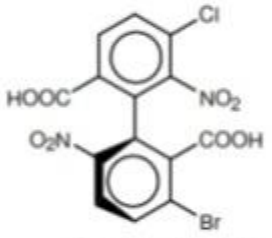
n > 2, leads to atropisomersim irrespective of bulkiness of two ortho substituents

2. **Non bridged biaryls**

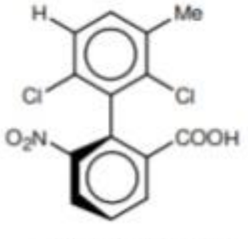


Conditions for biphenyls to be enantiomeric or resolvable:

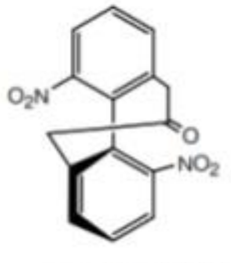
1. Two aryl ring must be non planar. This can be done by introducing bulky group in ortho position.
2. Most tetra substituted biphenyls can be resolved and quite stable to racemisation.



→ Properly substituted
→ Restricted rotation
→ So optically active



→ Properly substituted
→ Restricted rotation
→ So optically active

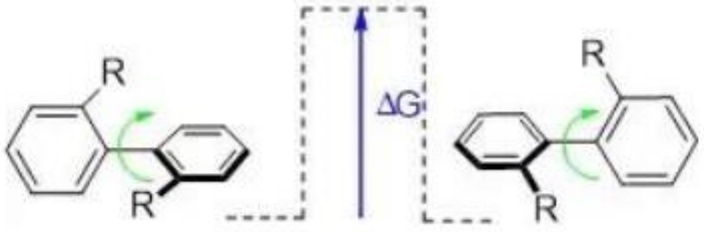


→ Properly substituted
→ Restricted rotation
→ So optically active

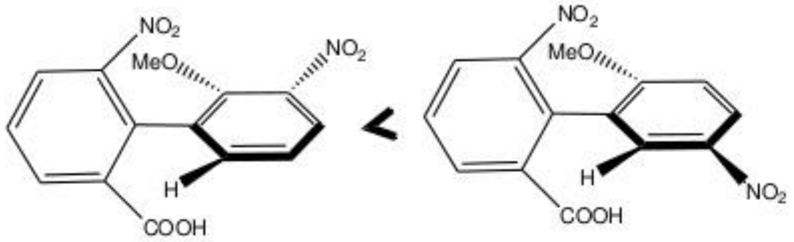
Buttressing effect (BE-effect):

The substituent in meta position tend to enhance the racemisation barrier i.e. preventing the outward bending of an ortho substituent, which could otherwise occur in the transition state for racemisation.

In simple the extra meta-group prevents that the ortho-group can bend and therefore makes the transition state higher in energy. (The meta group 'buttresses' or 'reinforces' the bond of the ortho-substituent). This is known as buttressing effect.



The rate of racemisation of the 3-nitro derivative is much lower compared to 5'-nitro derivative. The meta substituent increases the effective size of the ortho substituent.



NO_2 gp in meta increase effective size of ortho OMe hence racemization rate decreases

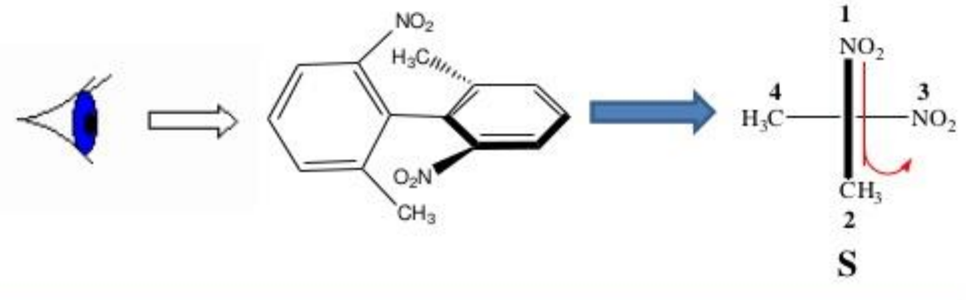
NO_2 gp in meta does not have much influence on ortho H hence racemization rate is more

R/S nomenclature for the Biphenyls:

1. **Viewing of molecule from left side**

(a) Groups near to the observer are drawn on the bold line and away groups are on the thin line.

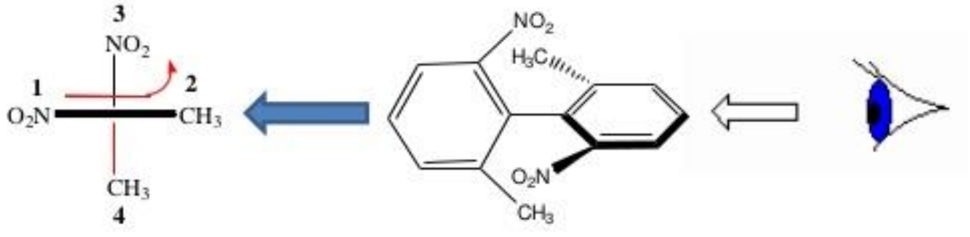
(b) Priority will be given to near group according to CIP rule than far group.



2. **Viewing of molecule from right side**

(a) Groups near to the observer are drawn on the bold line and away groups are on the thin line.

(b) Priority will be given to near group according to CIP rule than far group.



S

OR

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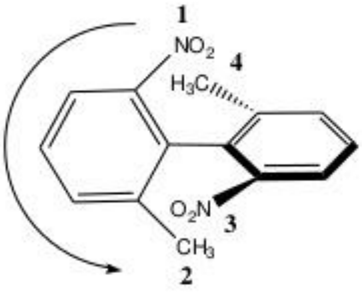

S

Classification of cyclic compounds

Cyclic compounds are classified, according to the number of atoms in the ring and properties, as small rings with 3 or 4 atoms, common rings with 5–7, medium rings 8–11, and large rings with 12 or more.

Types of strain

Conformational analysis of simple alkanes revealed two types of strain—torsional and steric. According to Hendrickson and separately Allingerthe total strain of a conformation is the sum of:

Bond strain - stretching or compression of chemical bonds. This type of strain is rather severe and is not encountered very often in organic compounds. To minimize bond strain, a molecule adopts conformations that have other, less energy-demanding, types of strain.

Torsional strain (eclipsing strain, Pfitzer strain) is caused by eclipsing interactions. Torsional strain is considerably higher compared to steric or angle strain, which are explained next.

Steric strain (Van der Waals strain, Prelog strain) is caused by atoms forced too close to each other. Transannular strain (Prelog strain) is a form of steric strain characteristic of medium rings.

Angle strain (Bayer strain, classical strain) is a result of deviation from the ideal bond angle. Compared to other types of strain, increase in energy of a conformation caused by angle strain is relatively low. As a result, a molecule can accommodate relatively large deviation from an ideal bond angle and still be stable.

Van't Hoff and Lebel proposed tetrahedral geometry of carbon. The bond angel is of 109° 28' (or 109.5°) for carbon atom in tetrahedral geometry (methane molecule). Baeyer observed different bond angles for different cycloalkanes and also observed some different properties and stability.

On this basis, he proposed angle strain theory.

The theory explains **reactivity and stability of cycloalkanes**.

Baeyer proposed that the **optimum overlap of atomic orbitals** is achieved for bond angel of **109.5°**. In short, it is **ideal bond angle** for alkane compounds. Effective and optimum overlap of atomic orbitals produces **maximum bond strength and stable molecule.** If bond angles deviate from the ideal then ring produce **strain**. Higher the strain **higher will be instability**. Higher strain produce **increased reactivity** and increases **heat of combustion**.

Baeyer proposed **"any deviation of bond angle from ideal bond angle value (109.5°) will produce a strain in molecule. Higher the deviation lesser will be instability.**

Baeyer's theory is based upon some assumptions as following.

1. All ring systems are **planar**. Deviation from normal tetrahedral angles results in to **instable cycloalkanes**.
2. The large ring systems involve **negative strain** hence do not exists.
3. The bond angles in cyclohexane and higher cycloalkanes (cycloheptane, cyclooctane, cyclononane……..) are not larger than **109.5°** because the carbon rings of those compounds are not planar (flat) but they are puckered (Wrinkled).

According to Baeyer, the relative order of stability for some common cycloalkanes is as under.

Cyclopentane > Cyclohexane >Cyclobutane> Cyclopropane

Actual observed order of stability for these cycloalkanes is as under.
Cyclohexane > Cyclopentane >Cyclobutane> Cyclopropane

According to Baeyer, the bond angle in **cyclopentane is 108° (the geometry is pentagonal)** that is very close to tetrahedral angle (109.5°), so it is almost free from ring strain.

Heat of Combustion and Relative Stability of Cycloalkanes

The **amount of heat evolved** when **one mole** of compound is burned in **carbon dioxide and water is referred as heat of combustion**.

Heat of combustion is important property to know the stability and other valuable information. The information from heat of combustion is important to understand the Baeyer's theory and its limitations.

For open chain compound heat of combustion for CH_2 group is 157.4 Kcal/Mole

Ring Size	Heat of Combustion/CH_2 Kcal/Mole	Ring Size	Heat of Combustion/CH_2 Kcal/Mole
3	166.6	10	158.6
4	164.0	11	158.4
5	158.7	12	157.6
6	157.4	13	157.8
7	158.3	14	157.4
8	158.6	15	157.7
9	158.6	16	157.2

Calculation of heat of combustion (Bomb calorimeter)

$$\text{Heat of combustion} = (\text{No. of Carbon atom in the ring}) \times (\text{heat of combustion for that ring per } CH_2) - \text{heat of combustion for normal alkane per } CH_2$$

Heat of Combustion for Cyclopropane

Number of carbon in cyclopropane = 3

Observed heat of combustion for cyclopropane = 166.6 Kcal/mole

Observed heat of combustion for n-propane = 157.4 Kcal/mole

Therefore, Heat of Combustion for cyclopropane = 3 x (166.6 – 157.4)

= 27.6 Kcal/mole