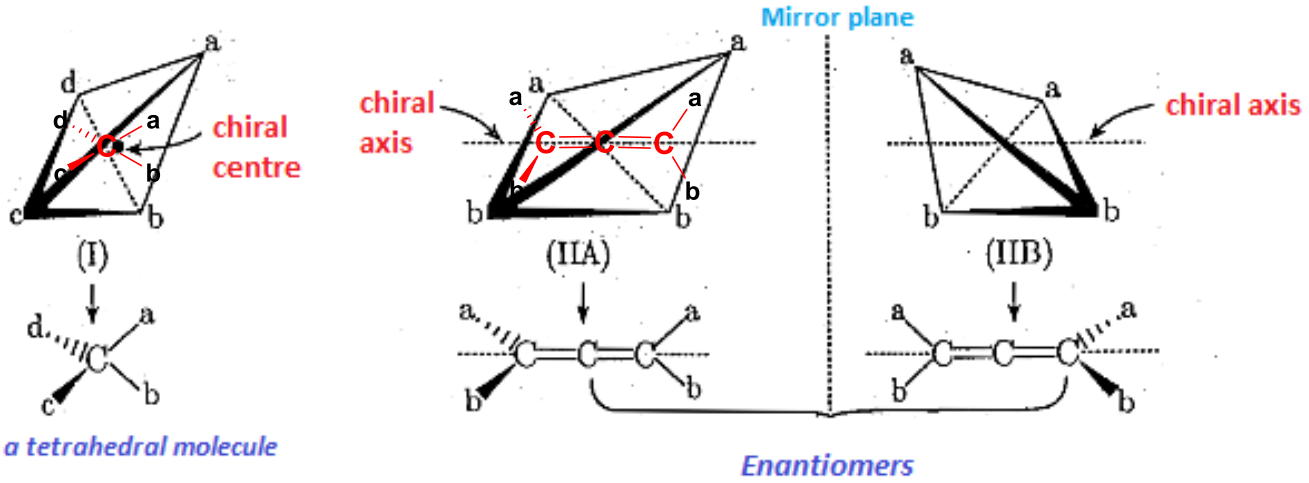
CYI101
Common CHEMISTRY(Organic)

Stereochemistry: Axial chirality

06th January 2022/Sec G & H

Axial Chirality: Chirality w/o chiral centre

Axial chirality refers to stereoisomerism resulting from the non-planar arrangement of four groups in pairs about a *chiral axis.*



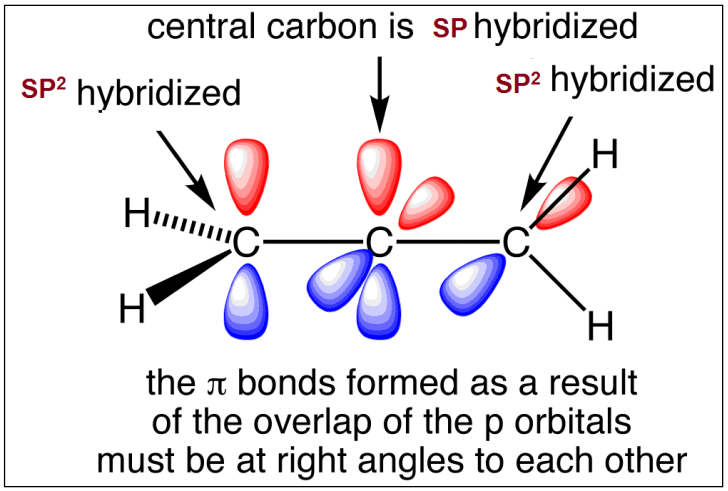
Symmetrical regular tetrahedron molecule → *Elongated tetrahedron* molecule
Desymmetrised tetrahedron of type ***Caabb***

- ***Condition for chirality:*** *two ligands at each end of the axis should be different (**a** ≠ **b**).*

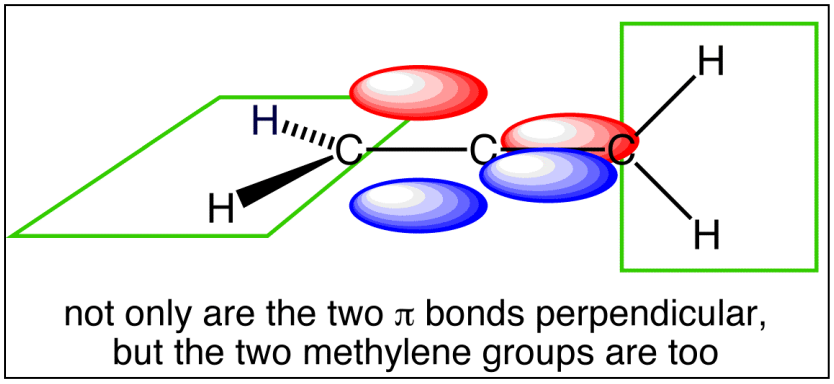
The axis along which the tetrahedron is elongated is called ***chiral axis*** or the ***stereoaxis***. The molecular chirality of this type is termed as ***axial chirality***.

Allenes: Geometry

The central carbon of allene forms *two sigma bonds* and *two π-bonds*.
The central carbon is *sp-hybridized* and the two terminal carbons are *sp²-hybridized*.
The *two π-bonds* attached to the central carbon are perpendicular to each other.
The geometry of the *π-bonds* causes the groups attached to the end carbon atoms to lie in *perpendicular plane*.

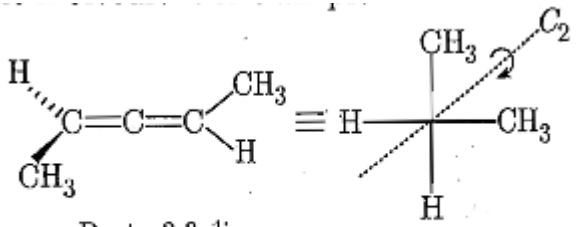


the π bonds formed as a result of the overlap of the p orbitals must be at right angles to each other



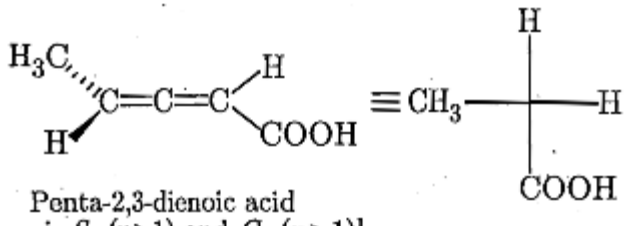
not only are the two π bonds perpendicular, but the two methylene groups are too

Chiral Allene (abC=C=Cab): Dissymmetric.



Penta-2,3-diene
[no σ, i and S_n (n>1)]

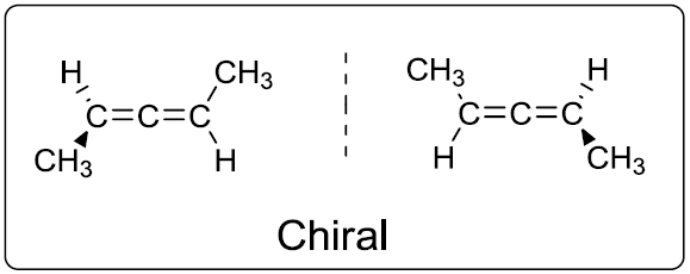
Chiral Allene (abC=C=Cde): Asymmetric.

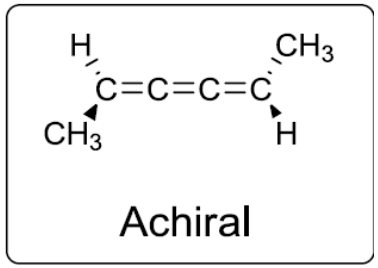


Penta-2,3-dienoic acid
[no σ, i, S_n (n>1) and C_n (n>1)]

Allenes: Geometry with cumulated bonds

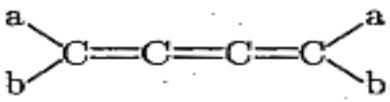
Note that allenes with *odd numbers* of cumulated bonds are *not chiral*; only those with *even numbers* are.

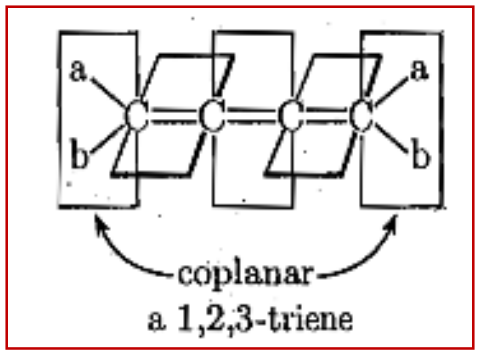




Allene (abC=(C)$_n$=Cab): when n= even

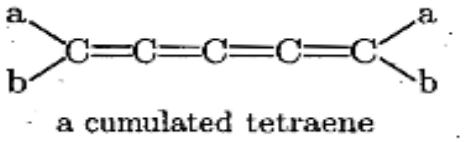
*Exhibit **cis-trans** isomerism, not **enantiomerism***

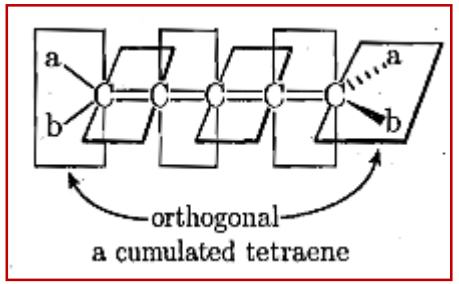




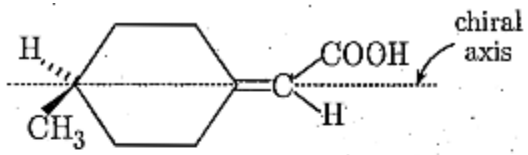
Allene (abC=(C)$_n$=Cab): when n= odd

*Exist as a pair of **enentiomers** not exhibit **cis-trans** isomerism.*

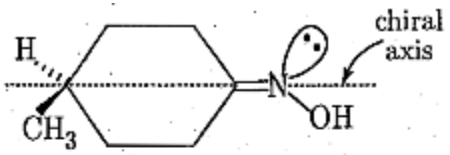




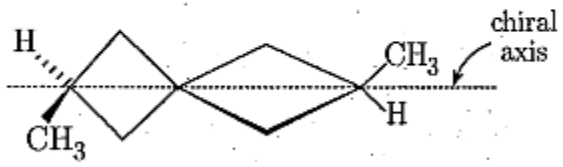
Chirality: Alkylidenecycloalkanes, Spiranes, Adamantanes



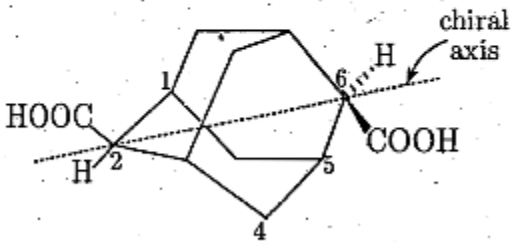
4-Methylcyclohexylidene acetic acid
(a chiral alkylidenecycloalkane)



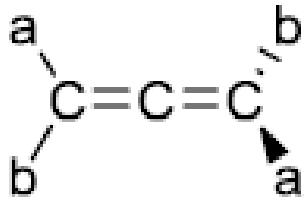
4-Methylcyclohexanone oxime
(a chiral oxime)



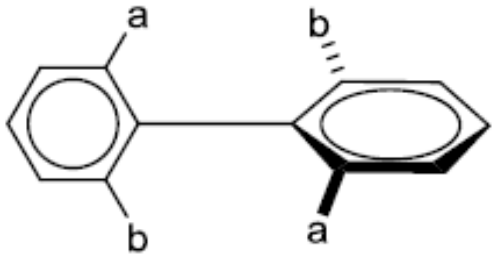
2,6-Dimethylspiro[3,3]heptane
(a chiral spirane)



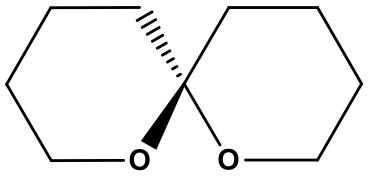
Adamantane-2,6-dicarboxylic acid
(a chiral adamantane)



Allenes



Substituted biphenyls

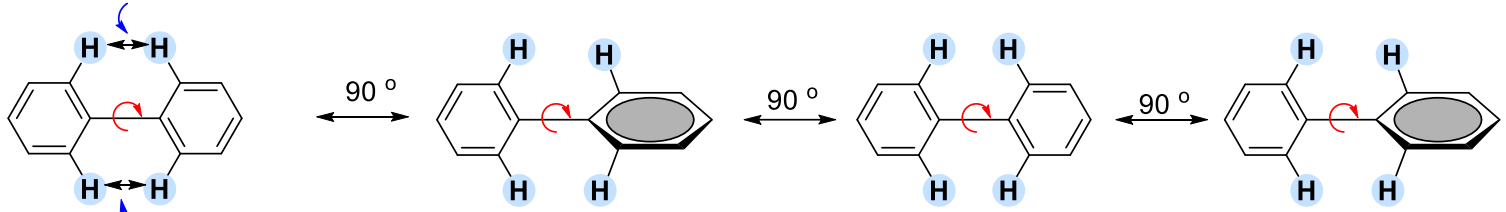


1,7-dioxaspiro[5.5]undecane

Axial Chirality: Substituted Biphenyl system

Distance greater: 2x van der Waals radius of H

Unsubstituted Biphenyl System



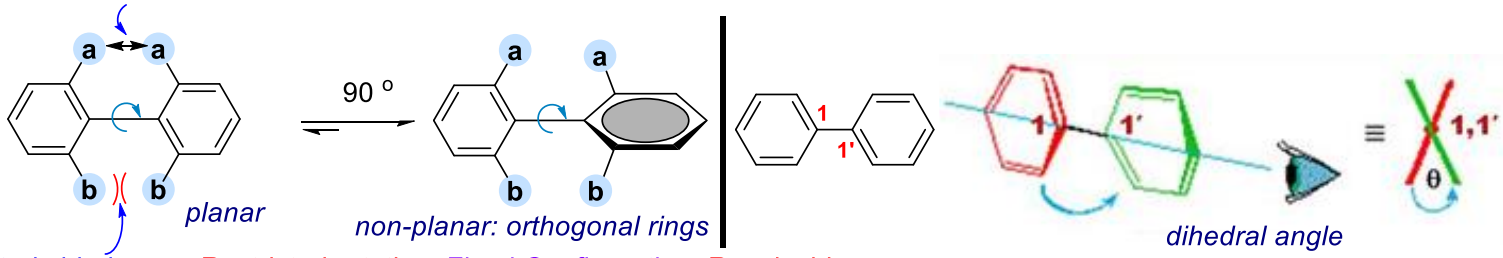
NO steric clash: NO restricted rotation: Various rotamers: Non-resolvable

planar

non-planar: orthogonal rings

Distance shorter: within van der Waals radius of **a**

2,2'-Disubstituted Biphenyl System



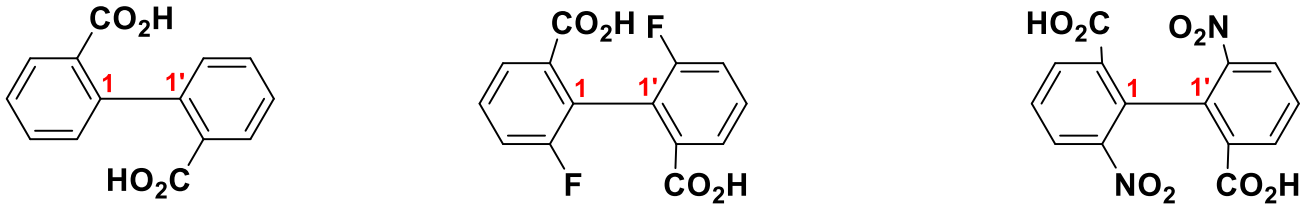
planar

non-planar: orthogonal rings

dihedral angle

Steric hindrance: Restricted rotation: Fixed Configuration: Resolvable

2,2'-Disubstituted Biphenyl System



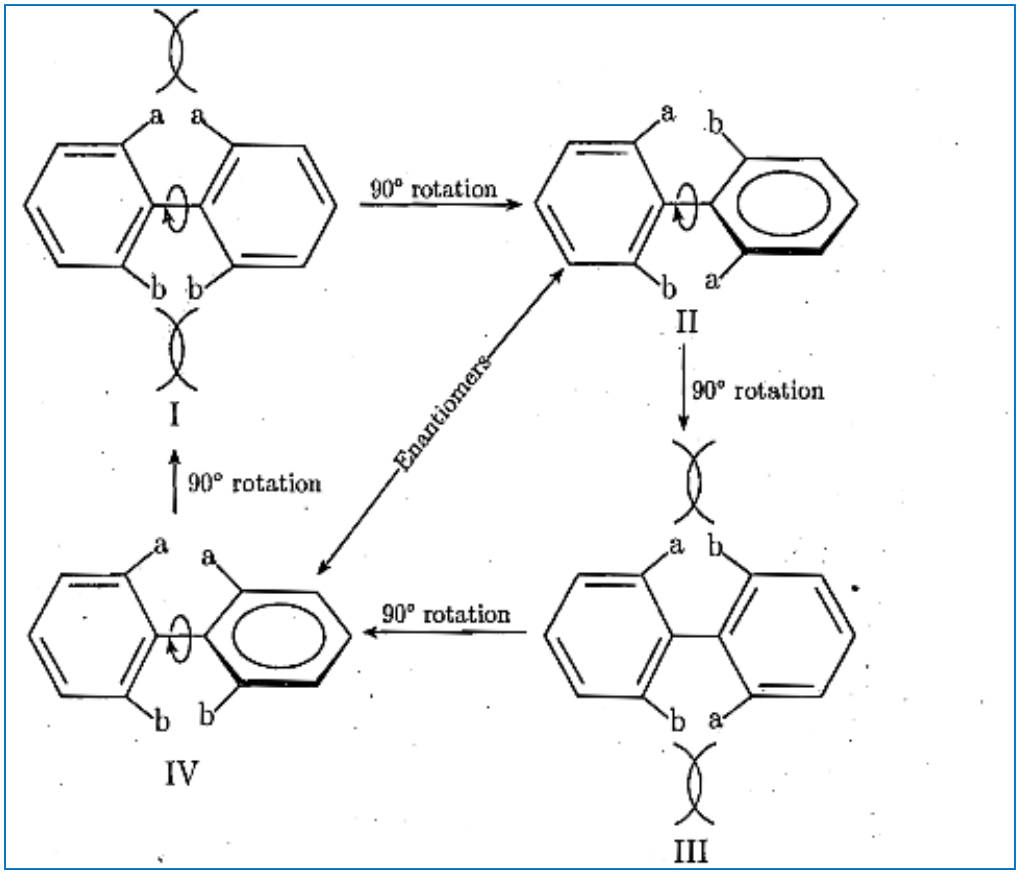
Not resolved at RT

Resolved at RT; racimizes easily

Resolved at RT; racimizes slowly

steric hindrance at 2,2'-position increase gradually

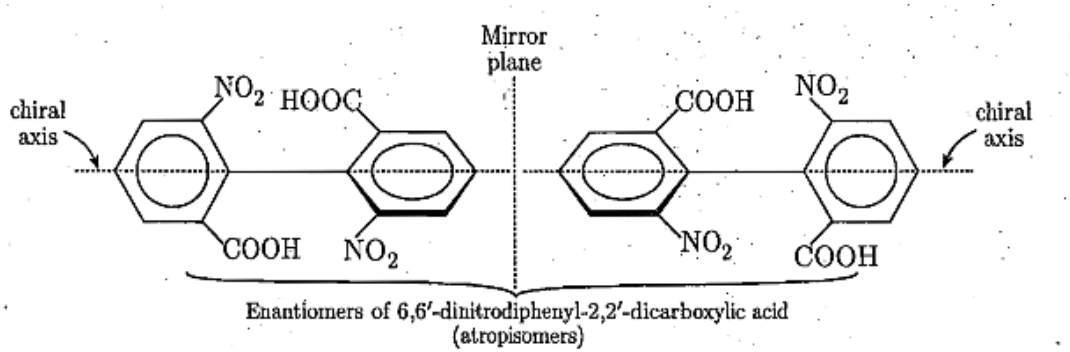
Ortho-substituted Biphenyl system: Stability of Rotamers



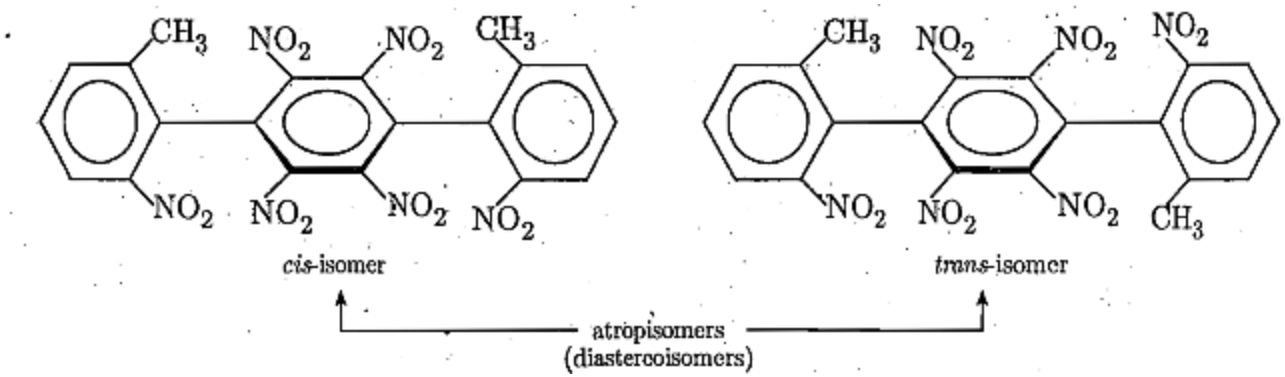
Biphenyl Systems: Atropisomerism

The biphenyls with large substituents at the ortho positions on either side of the central *σ bond experience restricted rotation along this bond due to steric hindrance.*

The stereoisomerism arising out due to the restricted roation around a single bond is known as *atropisomerism and the isomers are called atropisomers.*

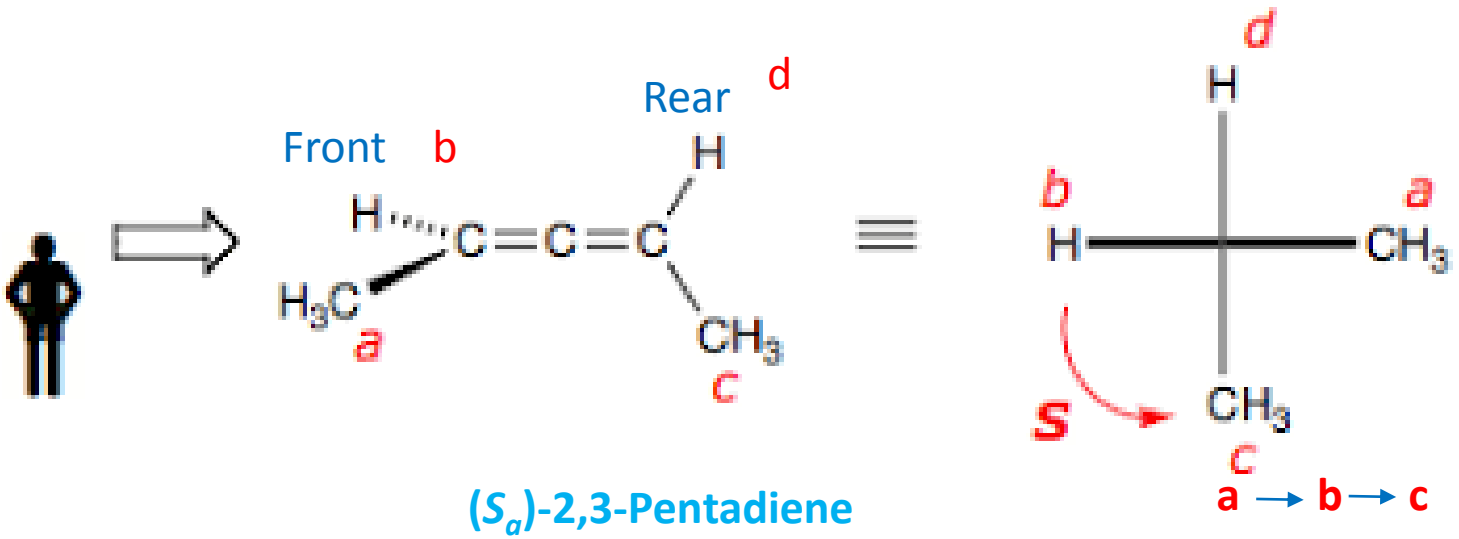


6,6’-dinitrodiphenyl-2,2’-dicarboxylic acid (optically active)



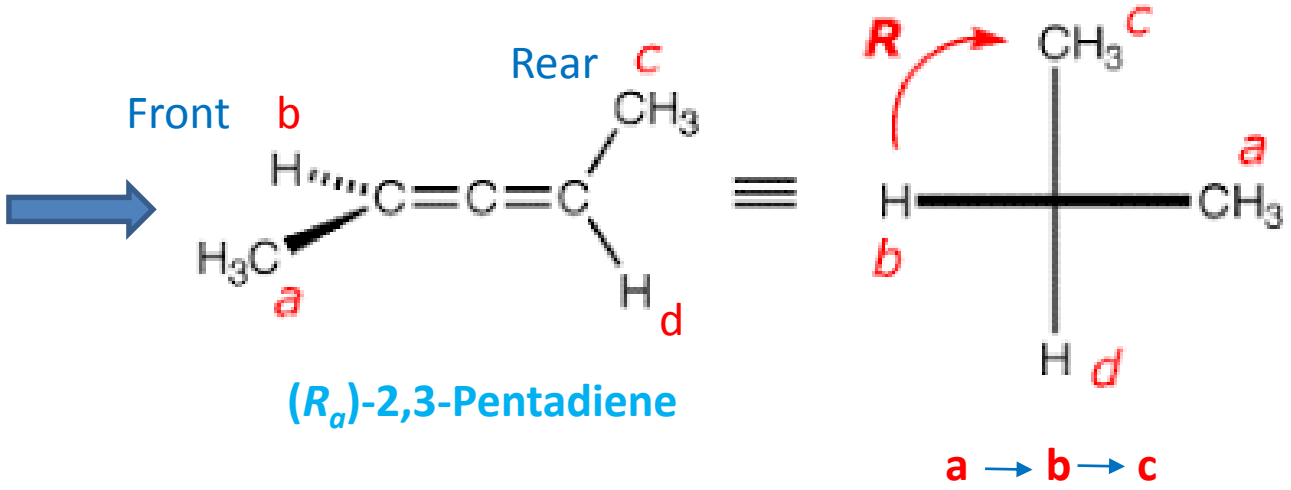
Terphenyl derivative (optically inactive, due to the presence of a sigma-plane)

Assigning R_a/S_a- Configuration: : Chiral Allene



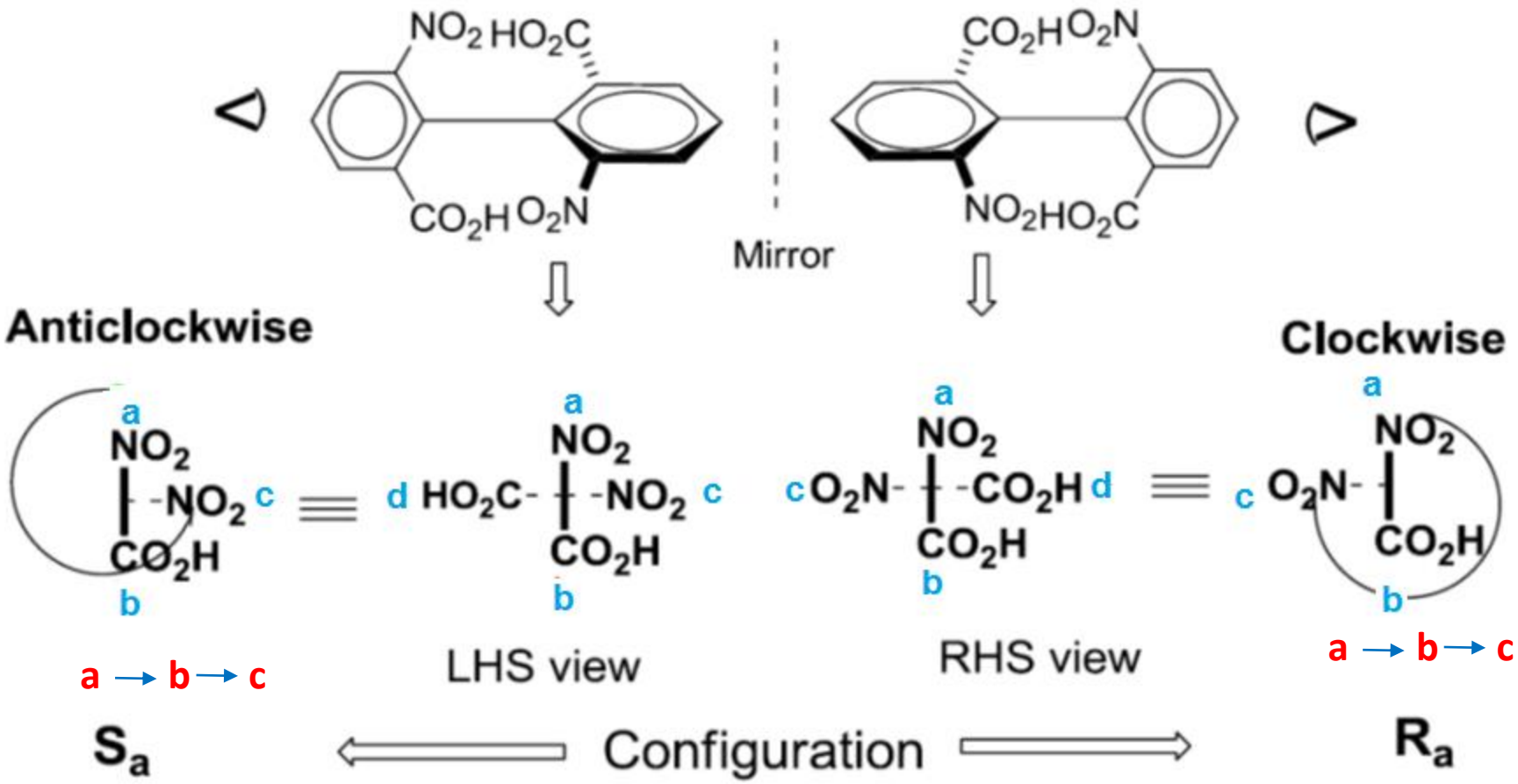
(S_a)-2,3-Pentadiene

Front group Precedes the rear group (Group at back)

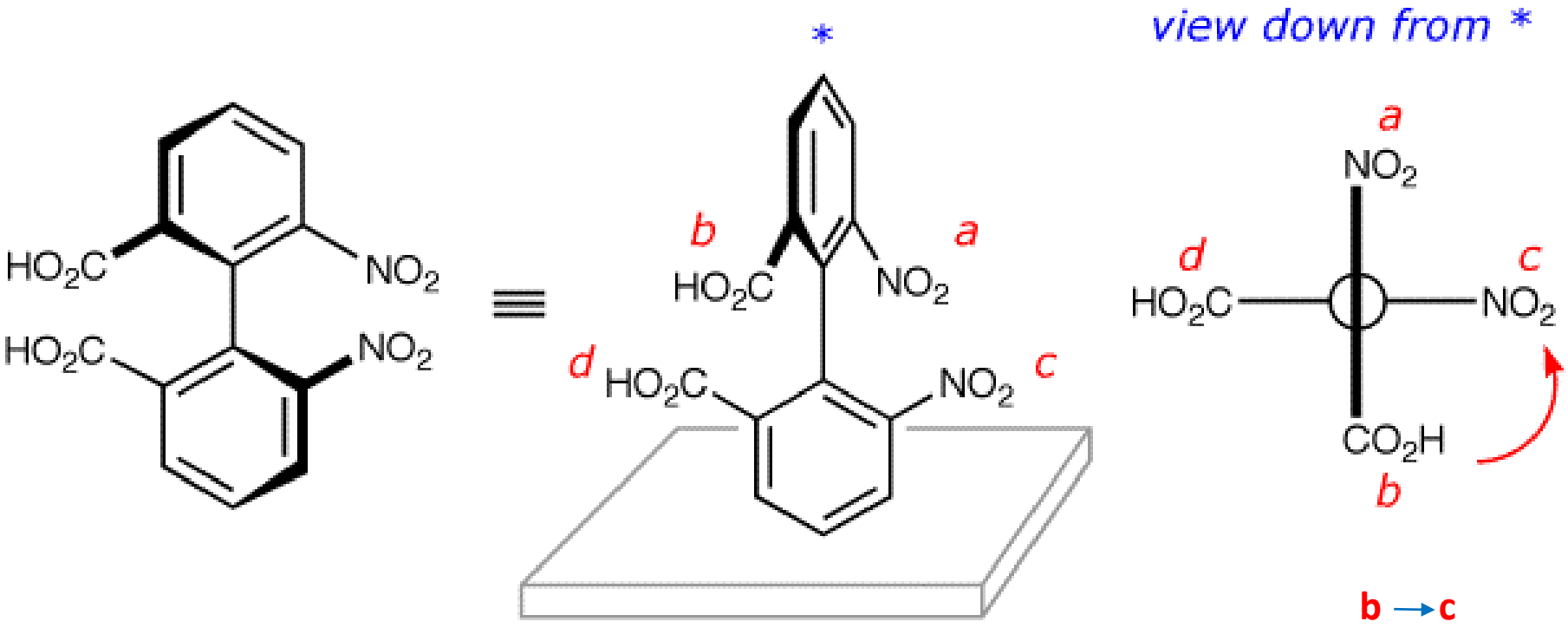


(R_a)-2,3-Pentadiene

Assigning R_a/S_a- Configuration: Biphenyl system

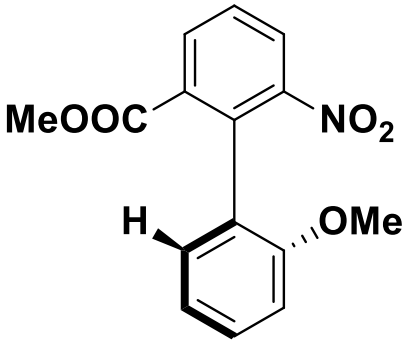


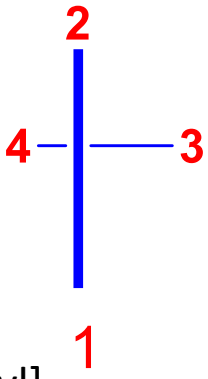
R_a/S_a- Nomenclature: Biphenyl system

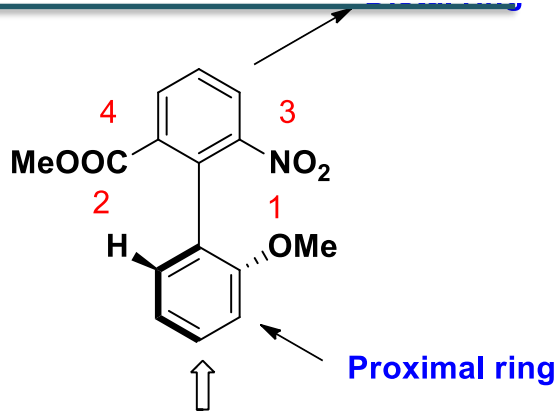


(S_a)-6,6'-dinitrobiphenyl-2,2'-dicarboxylic acid

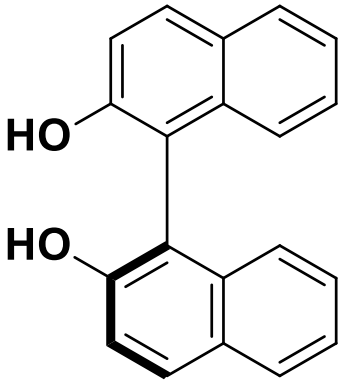
R_a/S_a- Nomenclature: Biphenyl system

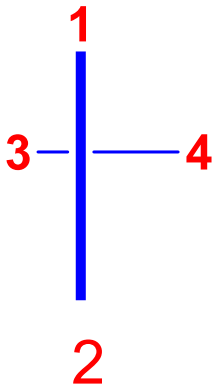


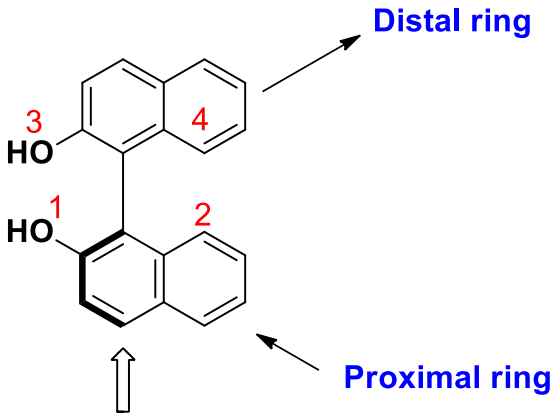




(R_a)-methyl 2'-methoxy-6-nitro-[1,1'-biphenyl]-2-carboxylate

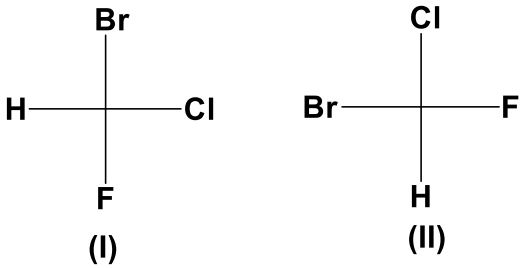






(R_a)-[1,1'-binaphthalene]-2,2'-diol

Label the following pair of structures



Rule: *Exchange among any three groups at a time in one direction keeping the fourth group fixed.*