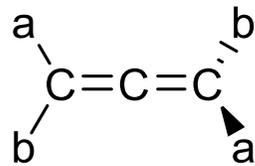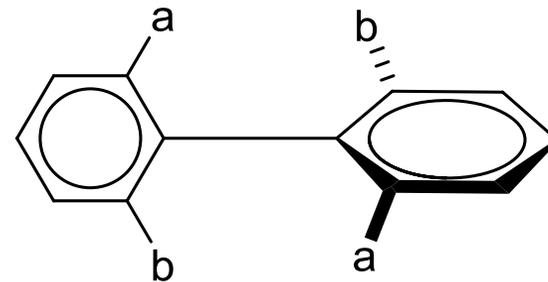# Axial Chirality in Systems Lacking Chiral Centres

Axial chirality arises from the non-planar arrangement of four groups in pairs about a *chiral axis*.

A chiral axis is a line in a chiral molecule about which a set of four groups is held in a non-planar arrangement resulting in a non-superimposable mirror image.
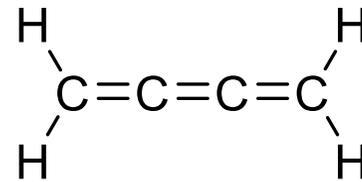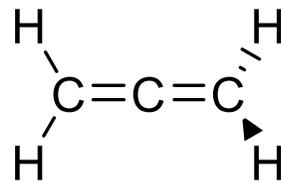

Allenes

Substituted biphenyls

Axial chirality is encountered in allenes and *ortho*-substituted biphenyls.
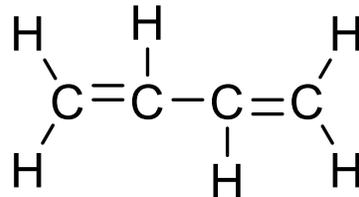
What are Allenes?
Definition

Allenes are compounds with two or more double bonds side-by-side. Such bonds are called *cumulated double bonds.*

These are distinct from the alternate double-single-double or *conjugated* bonds.

Allenes have cummulated double bonds

Some alkenes have conjugated double bonds
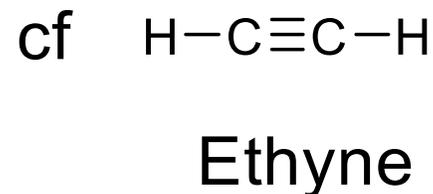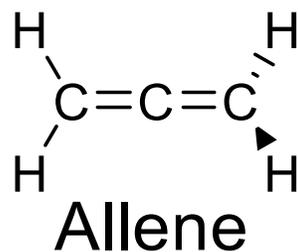
Structure of Allenes
The Facts Revisited

The central carbon of allene forms two sigma bonds and two pi bonds. The central carbon is sp-hybridized and the two terminal carbons are sp^2-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 planes.
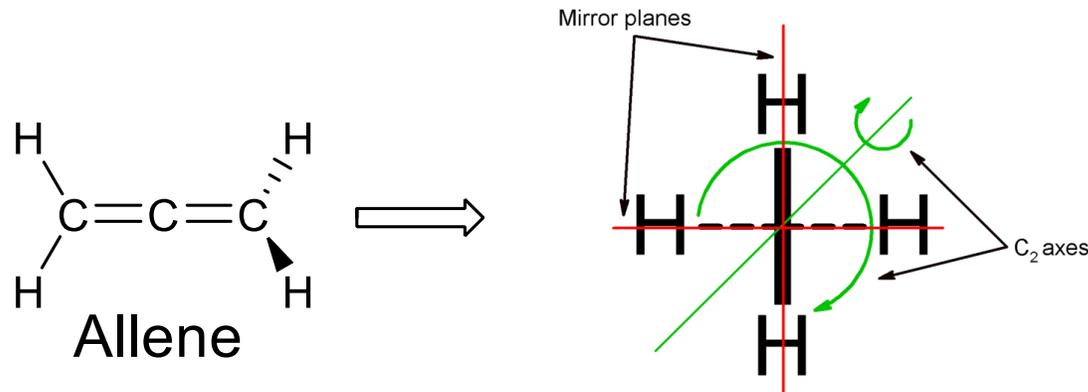
The bond angle formed by the three carbons is 180°, indicating linear geometry for the carbons of allene.

$$\underset{H}{\overset{H}{\diagdown}}C=C=C\underset{H}{\overset{H}{\diagup}}$$

Allene

cf   H−C≡C−H

Ethyne

Structure of Allene
The Geometry and Symmetry

Since the bond angle formed by the three carbons is 180°, the cummulated carbons of the allene are in a linear geometry.

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. There is a mirror plane passing through both CH_2 planes.

Axially Chiral Systems
Chirality of Allenes: The Genesis

Since the geometry of the cumulated π-bonds causes the groups at the terminal carbons to lie in perpendicular planes, allenes that are unsymmetrically substituted on both terminals are chiral.

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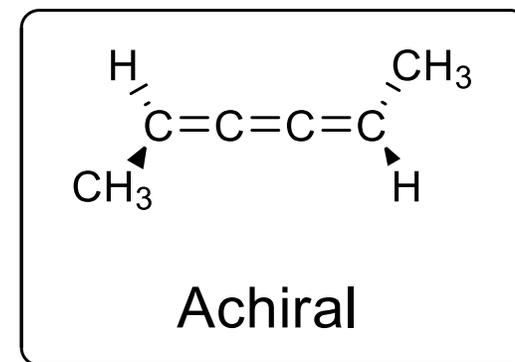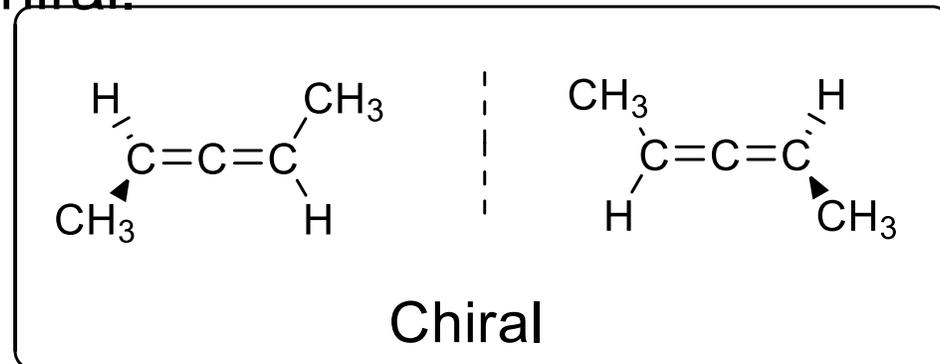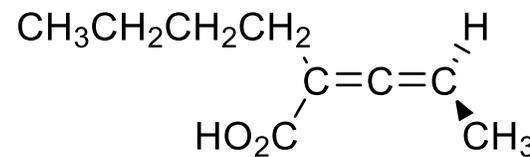

Chiral

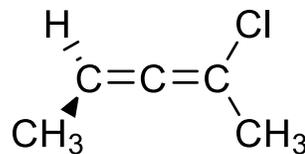Achiral

Chirality of Allenes
Specific Rotations

Since allenes with different substitutents attached to the end carbons form nonsuperimposable mirror images, they show optical activities even though they do not have a chiral carbon.
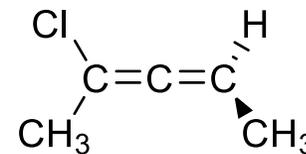

$[\alpha]^D = -30.7^o$

$[\alpha]^D = +30.7^o$

$[\alpha]^D = -21^o$

$[\alpha]^D = +21^o$
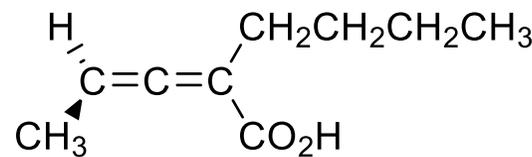
How do you assign configurations to the optically active allenes?

Chirality of Allenes
Configurations of Axially Chiral Systems

The *configurations* in axially chiral systems are specified using R_a and S_a or P (plus) and M (minus). The subscript "a" refers to "axially chiral".

Sequence Rules

The CIP rules are used to assign priority to the end groups, but with one addition: That the near groups have a higher precedence over far groups. The two "near" and two "far" groups on the chiral axis are ranked (a, b, c & d).
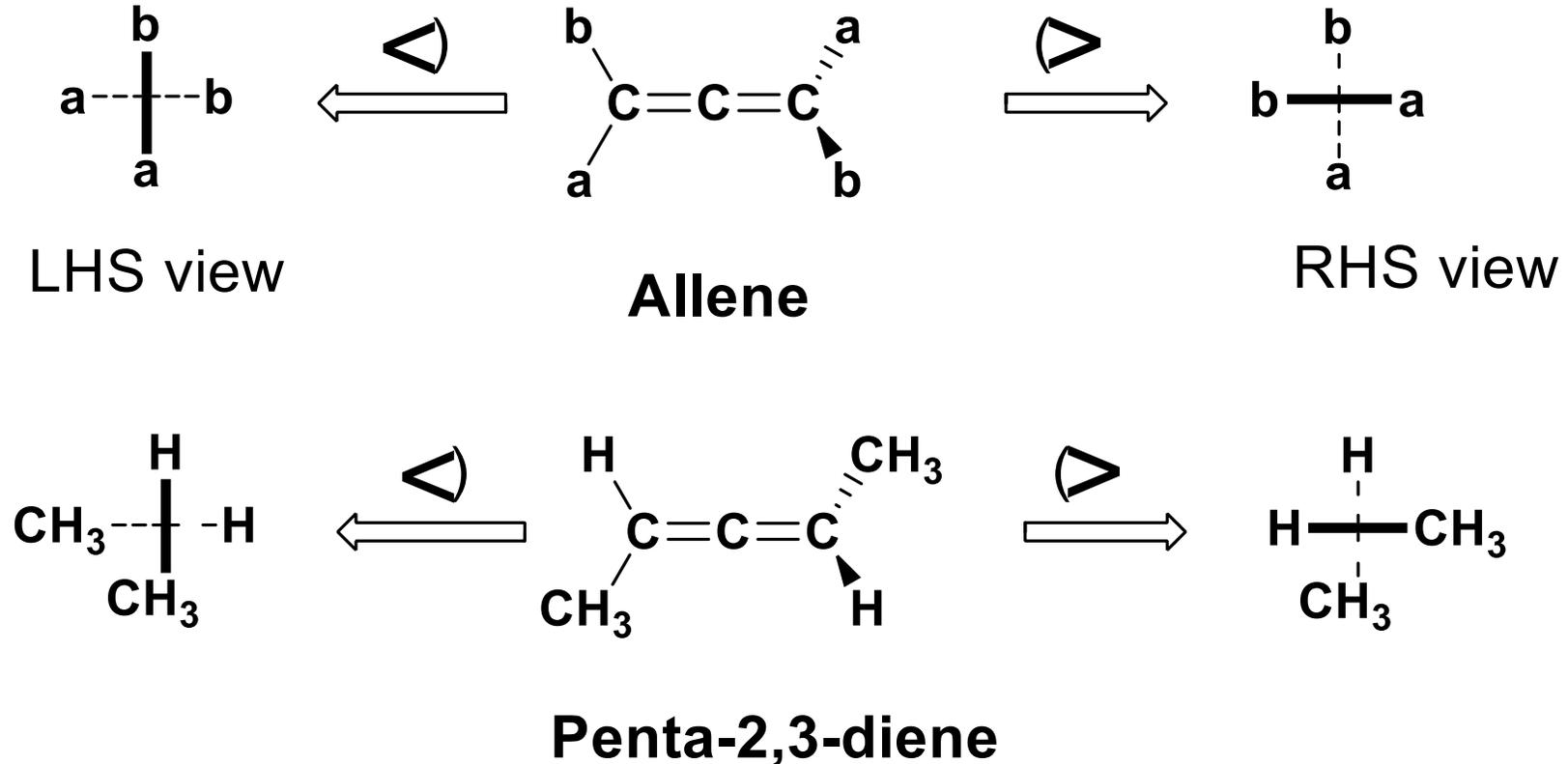
Viewing Rule

The chiral axis is viewed end-on and the sense of configuration determined .

Chirality of Allenes
## Configurations of Axially Chiral Systems

The model below shows the side views and representations of the allene along the chiral axis.

LHS view

Allene

RHS view

Penta-2,3-diene

Configurations of Chiral Allenes
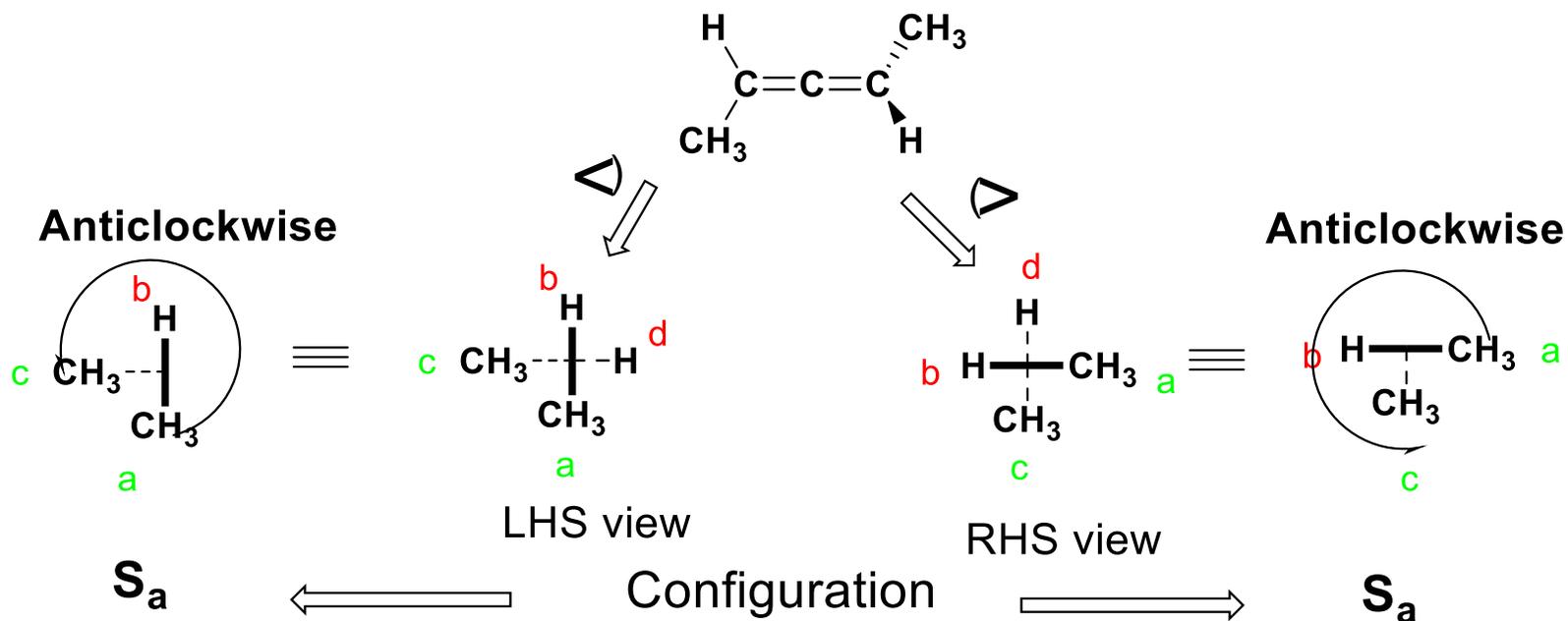## Assigning Priority to Substituents

To determine the sense of configuration, assign priority to the substituents on each of the terminal carbons of the allene system (you may use **a** (highest priority) to **d** (lowest priority).

LHS view

RHS view
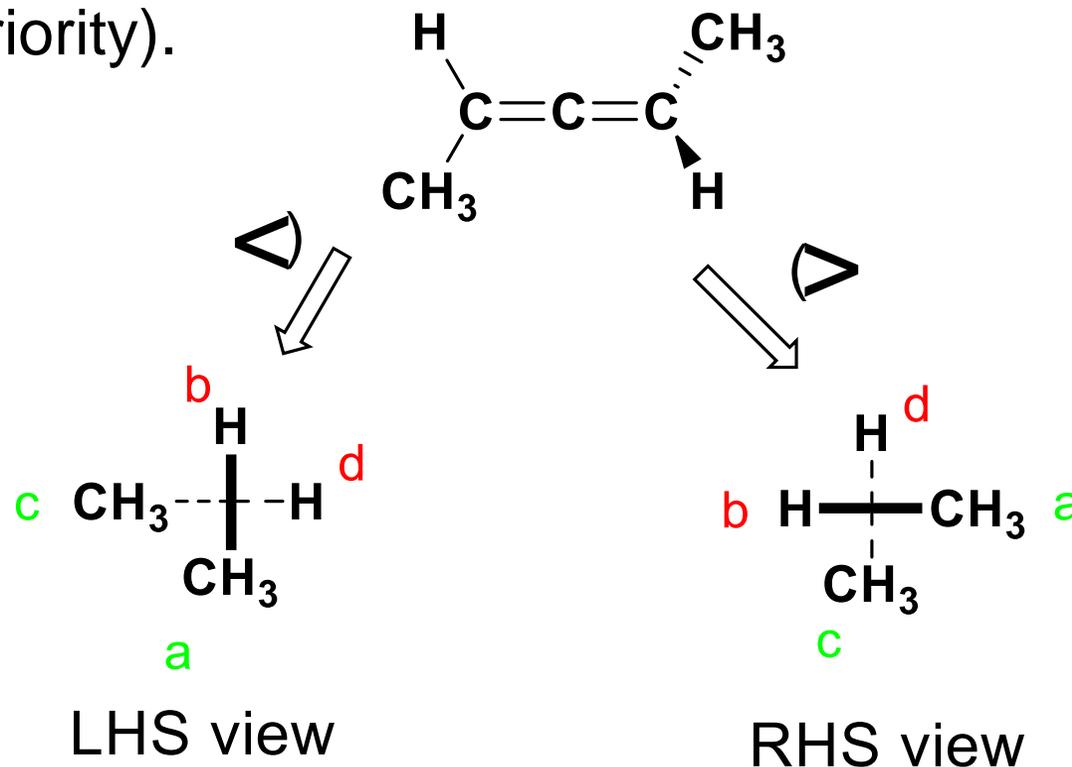
Configurations of Chiral Allenes
Determining the Sense of Rotation (R_a vs S_a)

The sense of rotation is determined starting with the end of the allene that is closest, then finishing with the end that is farthest. For the farthest end, only the group of higher priority is considered.
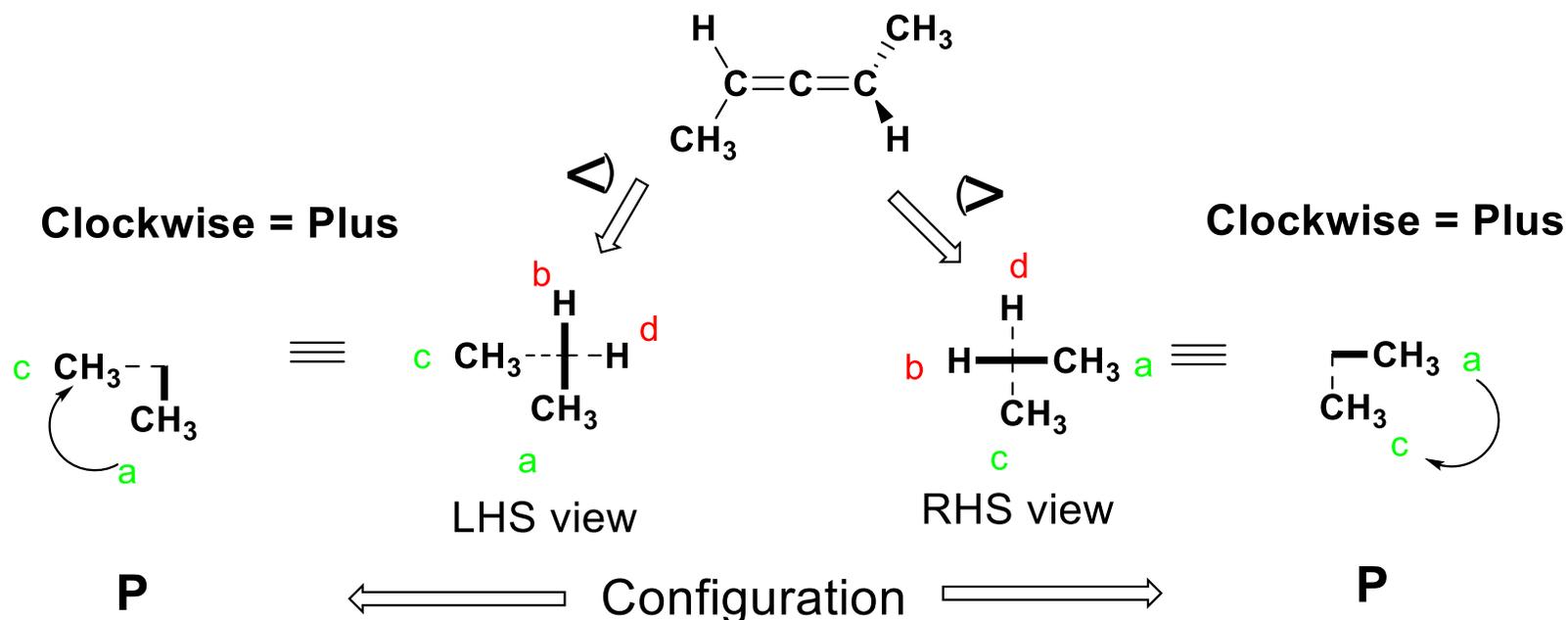
Determining the Sense of Rotation (P vs M)

The sense of rotation is determined by looking only at the high priority substituents starting with the end of the allene that is closest, then finishing with the end that is farthest.
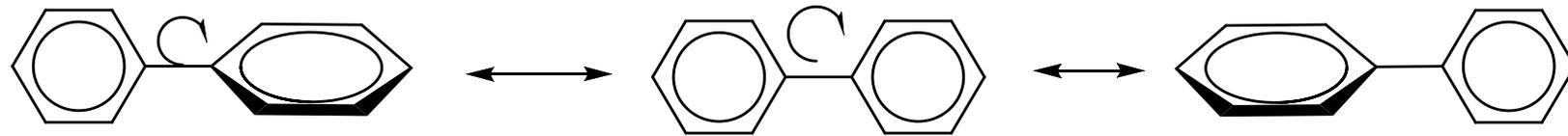
A clockwise rotation is P (plus) and an anticlockwise rotation is M (minus).

Clockwise = Plus

Clockwise = Plus

LHS view

RHS view

P

⟸ Configuration ⟹

P

Axially Chiral Systems
Biphenyl Systems

Biphenyls are compounds whereby a phenyl ring is connected to another through a central σ-bond.

In unsubstituted biphenyl, there is sufficient amount of freedom of rotation around the central single bond to allow for free interconversion between the various conformers or rotamers so that the various rotamers can not exist independently.
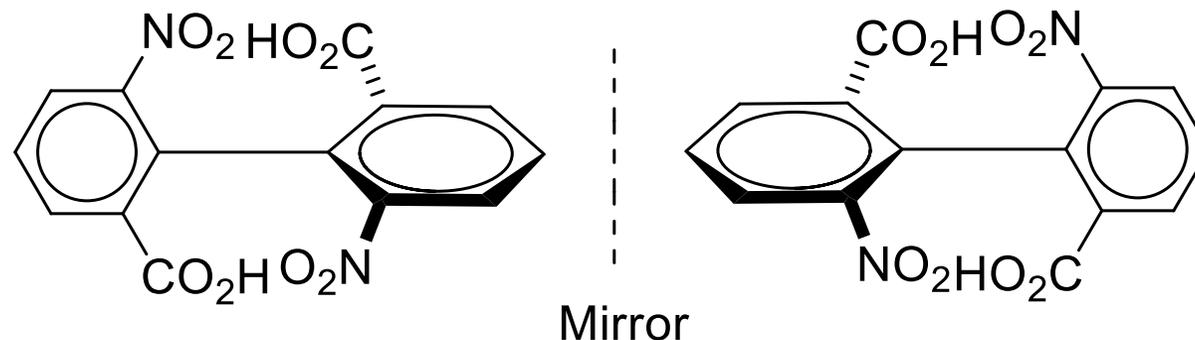
Biphenyl Systems (Atropisomerism)

However, 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.

If the substituents are different, a chiral molecule existing as a pair of enantiomers called *atropisomers* is obtained.

The enantiomers can be made racemic by heating. The free energy required is in the range of 42 - 210 kJ/mole.


Mirror

Axially Chiral Systems
Atropisomerism

Atropisomers are stereoisomers that can be interconverted by rotation about single bonds but for which the barrier to rotation is large enough that the stereoisomers do not interconvert readily at room temperature and can be separated.

Polynuclear aromatic systems such as binol also exist as enantiomers.
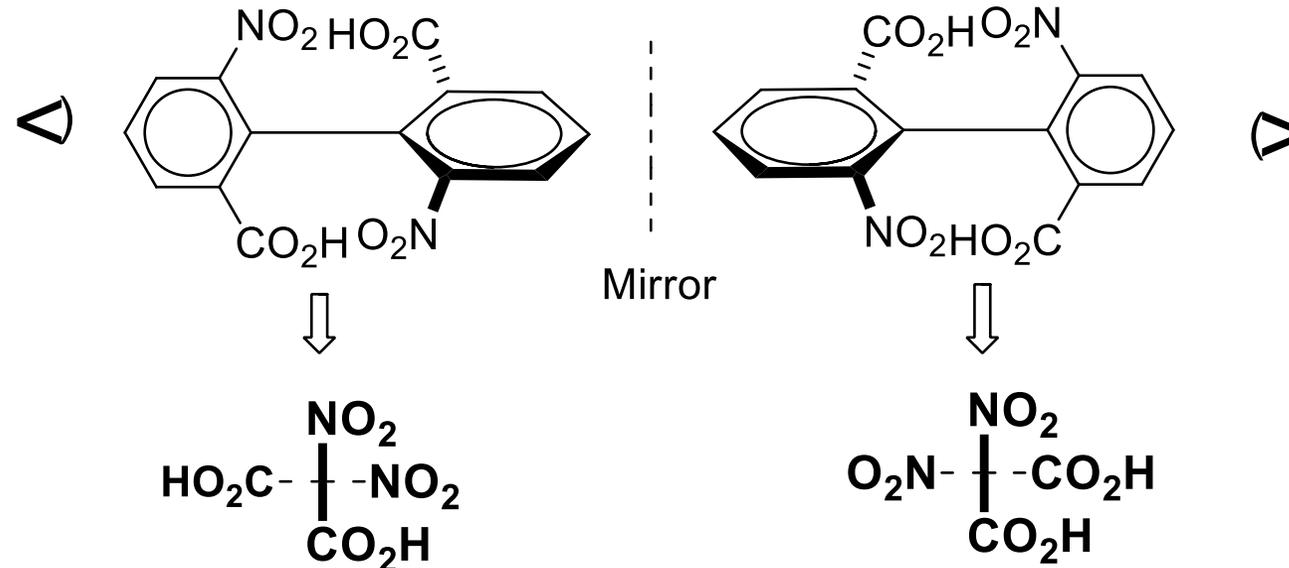

Mirror

$[\alpha]^D = +35.5^o$ $[\alpha]^D = -35.5^o$
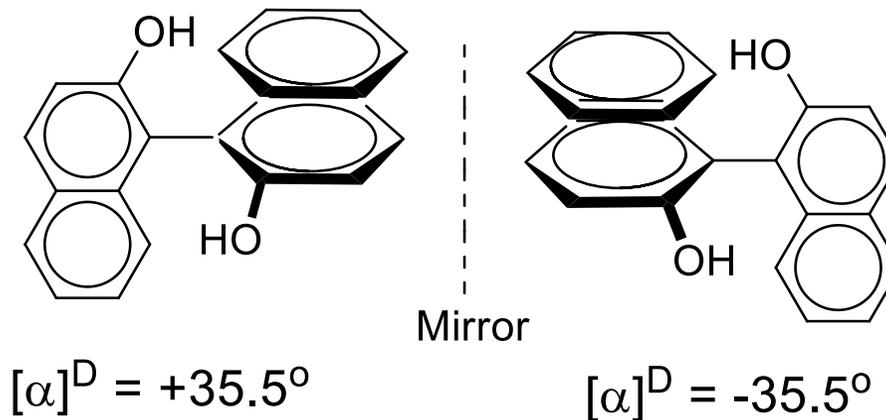
Assigning Configurations of Atropisomers

Configurations of atropisomers are assigned in a similar fashion as those of chiral allenes using R_a and S_a or P (plus) and M (minus).
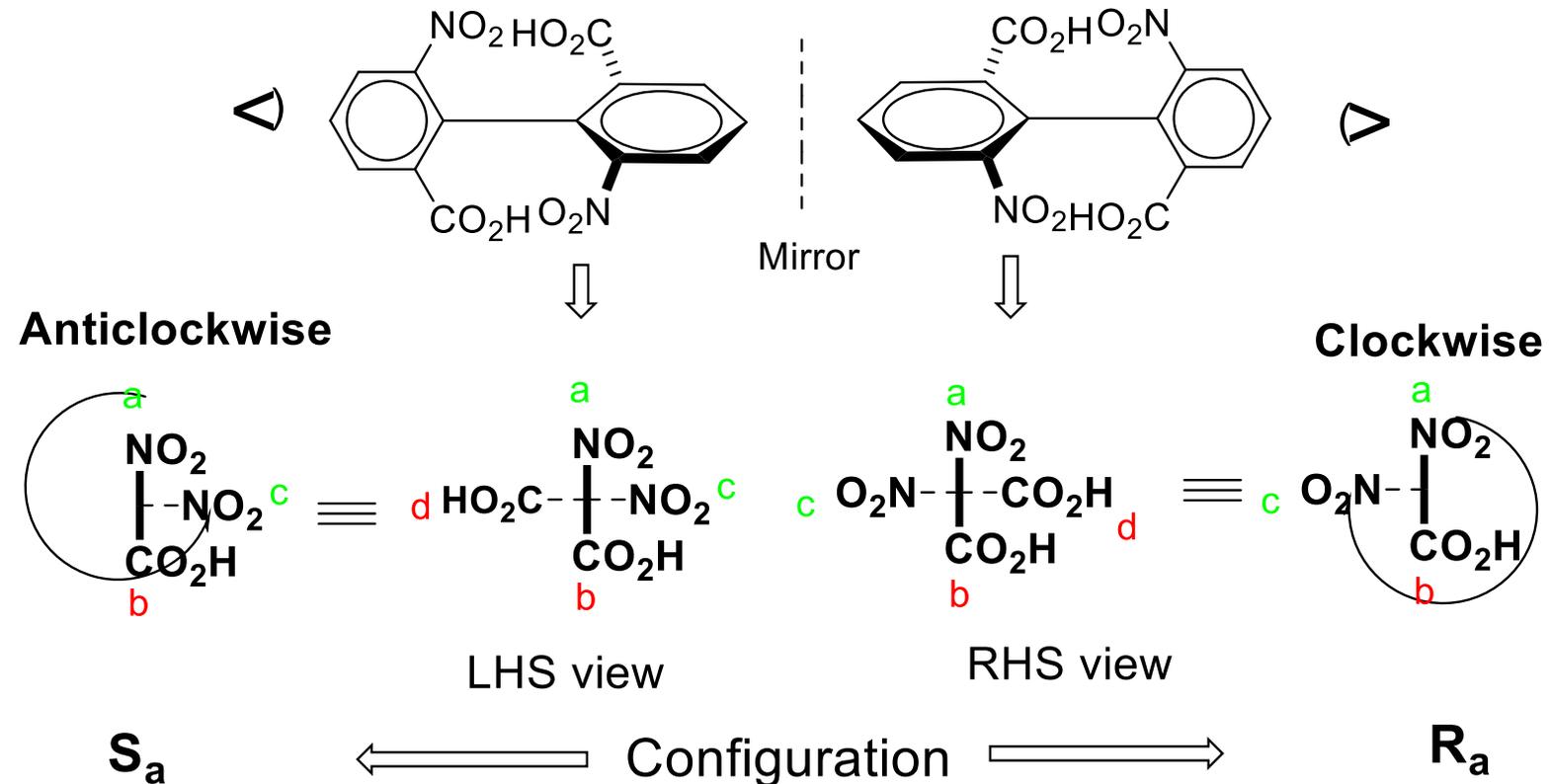
By generating appropriate models of each atropisomer, the sense of configuration can be determined.

## Assigning Configurations of Atropisomers (R_a vs S_a)

By generating appropriate models of each atropisomer, the sense of configuration can be determined.

Anticlockwise

Clockwise

LHS view

RHS view

S_a ⟸ Configuration ⟹ R_a

Assigning Configurations of Atropisomers (P vs M)

By generating appropriate models of each atropisomer, the sense of configuration can be determined.

Clockwise

Anticlockwise

LHS view

RHS view
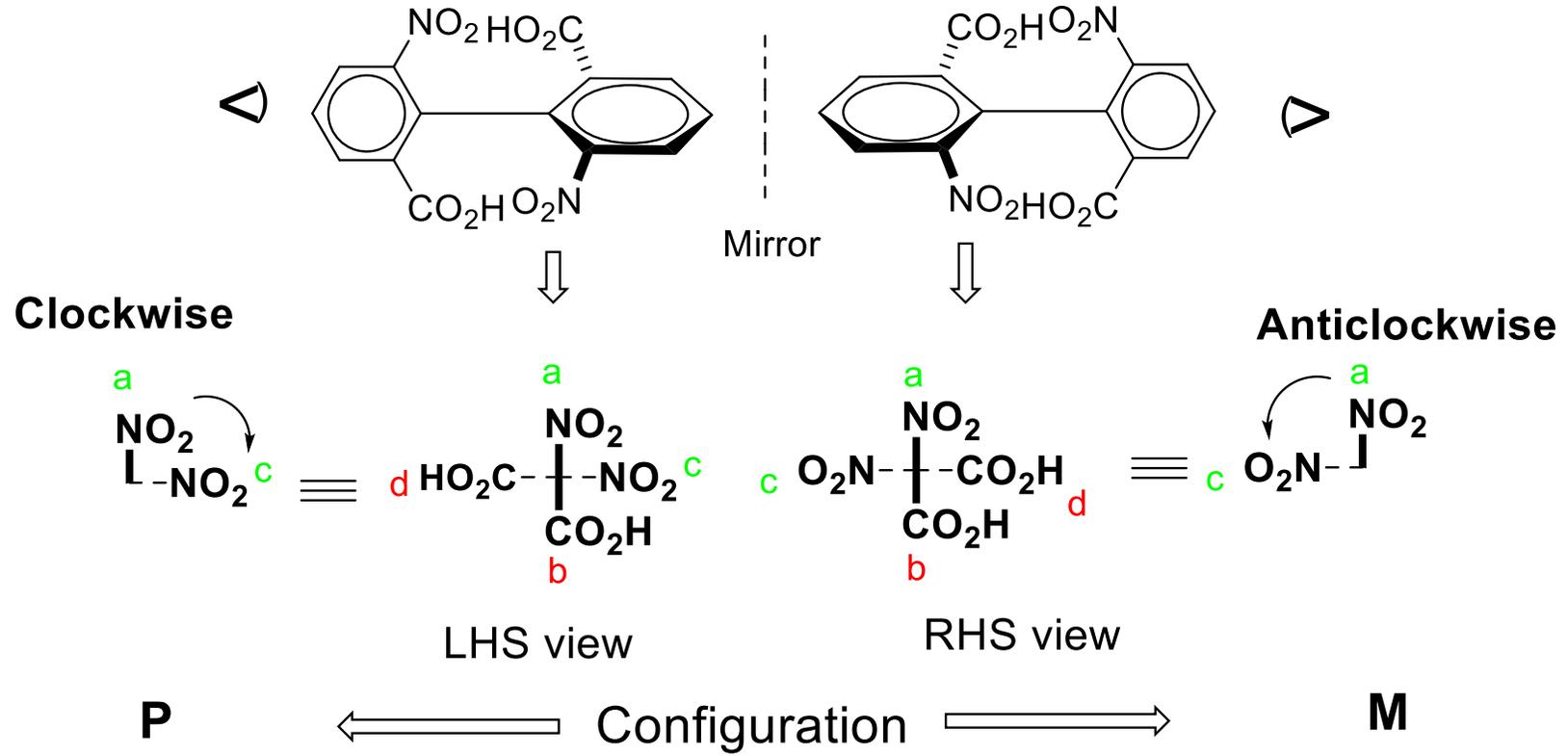
P ⟸ Configuration ⟹ **M**

Configurations of Axially Chiral Systems

Determine the configurations of the following axially chiral systems using both the R_a/S_a and P/M notations.

(i)

(ii)

(iii)

(iv)