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

Axial chirality is encountered in:

- Allenes
- 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 pi-bonds attached to the central carbon are perpendicular to each other.

The geometry of the pi-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.

\[
\text{Allene} \quad \text{cf} \quad \text{Ethylene}
\]
Structure of Allene

The Geometry and Symmetry

Since the bond angle formed by the three carbons is $180^\circ$, the cumulated 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 $45^\circ$ 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 $\pi$-bonds causes the groups at the terminal carbons to lie in perpendicular planes, allenes that are unsymmetrically substituted on both ends are chiral.

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

Chiral

Achiral
Chirality of Allenes

Specific Rotations

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

\[
\begin{align*}
\text{H} & \quad \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{H} \\
\text{C}=\text{C}=\text{C} & \quad \text{CO}_2\text{H} \\
\text{CH}_3 & \\
[\alpha]^D = -30.7^\circ \\
\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} & \quad \text{Cl}\text{C}=\text{C}=\text{C} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \\
\text{C}=\text{C}=\text{C} & \quad \text{HO}_2\text{C} \\
\text{CH}_3 & \\
[\alpha]^D = +30.7^\circ \\
\text{Cl} & \quad \text{CH}_3 \\
\text{C}=\text{C}=\text{C} & \quad \text{C}=\text{C}=\text{C} \\
\text{CH}_3 & \quad \text{CH}_3 \\
[\alpha]^D = -21^\circ \\
[\alpha]^D = +21^\circ
\end{align*}
\]

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” referring to “axially chiral”

Sequence Rules

The CIP priority 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" substituents on the axial unit are ranked.

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 (higher priority) and b (lower priority)).
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.
Configurations of Chiral Allenes
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

\[
\begin{align*}
&\text{LHS view} \\
&\text{RHS view}
\end{align*}
\]
Axially Chiral Systems

Biphenyl Systems

Biphenyls are compounds whereby a phenyl ring is connected to another through a central \( \sigma \) 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.
Axially Chiral Systems
Biphenyl Systems (Atropisomerism)

However, biphenyls with large substituents at the ortho positions on either side of the central $\sigma$ 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.
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.

\[ [\alpha]_D^D = +35.5^\circ \]

\[ [\alpha]_D^D = -35.5^\circ \]
Chirality of Biphenyl Systems
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.
Chirality of Biphenyl Systems
Assigning Configurations of Atropisomers ($R_a$ vs $S_a$)

By generating appropriate models of each atropisomer, the sense of configuration can be determined.
Chirality of Biphenyl Systems
Assigning Configurations of Atropisomers (P vs M)

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

Clockwise

Anticlockwise

P  Configuration  M
Assignment

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)  
\[
\begin{array}{c}
\text{H} \\
\text{C} = \text{C} = \text{H} \\
\text{CH}_3 \\
\end{array}
\]

(ii) 
\[
\begin{array}{c}
\text{H} \\
\text{C} = \text{C} = \text{H} \\
\text{CH}_3 \\
\end{array}
\]

(iii) 
\[
\begin{array}{c}
\text{H} \\
\text{C} = \text{C} = \text{H} \\
\text{CH}_3 \\
\end{array}
\]

(iv) 
\[
\begin{array}{c}
\text{H} \\
\text{C} = \text{C} = \text{H} \\
\text{CH}_3 \\
\end{array}
\]
Axially Chiral Systems

Summary

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

- Allenes are compounds with two or more cumulated double bonds.

- Since cumulated π-bonds of an allene lie in perpendicular planes, unsymmetrically substituted allenes are chiral.

- The configurations in axially chiral systems are specified using $R_a$ and $S_a$ or $P$ (plus) and $M$ (minus).
Axially Chiral Systems

Summary

- Biphenyls with large substituents at the ortho positions on either side of central $\sigma$ bond exist as a pair of enantiomers called *atropisomers*.

- The stereoisomerism caused by restricted rotation of a carbon-carbon single bond is called atropisomerism.
THURSDAY, 24TH OCTOBER 2013
8-9 AM
CHEM LAB 1