CYI101
Common CHEMISTRY(Organic)

Stereochemistry: Pericyclic reactions

Definitions, Classifications, Electrocyclic Reactions

10th January 2022/Sec G & H

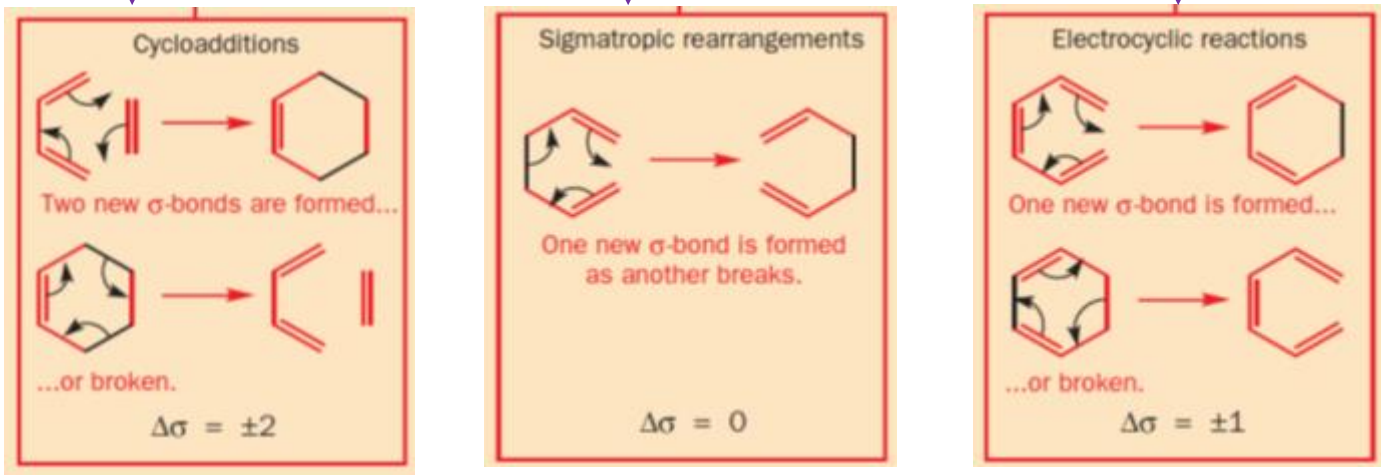
Pericyclic Reactions: Definitions, Classifications

Pericyclic reaction involves a cyclic redistribution of bonding electrons through a concerted proces.

A **pericyclic reaction** is a type of organic reaction wherein the transition state of the molecule has a *cyclic geometry*, the reaction progresses in a *concerted fashion*, and the *bond orbitals involved in the reaction overlap* in a continuous cycle at the transition state.

The three principle classes of pericyclic reactions are termed: **Cycloaddition**, **Electrocyclic**, and **Sigmatropic**

Types of Pericyclic Reactions: are distinguished by the number of σ-bonds made or broken



Pericyclic Reactions: *Electrocyclic Reaction*

an electrocyclic reaction

1,3,5-hexatriene

1,3-cyclohexadiene
the product has one fewer
π bond than the reactant

An intramolecular reaction in which a new σ bond is formed between the ends of a conjugated π system

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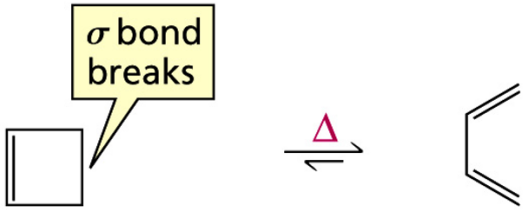


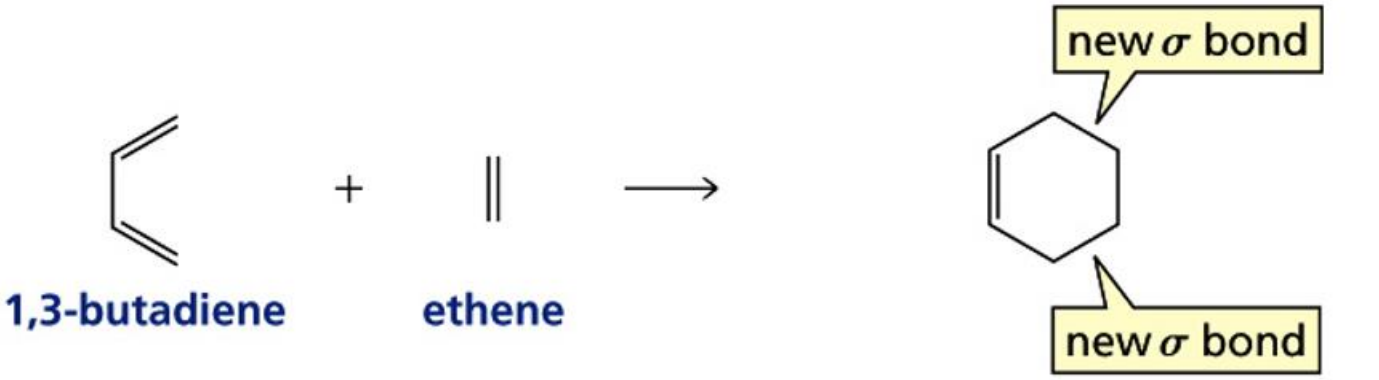
cyclobutene

1,3-butadiene
the product has one more
π bond than the reactant

Electrocyclic Reactions Are Reversible

Pericyclic Reactions: *Cycloaddition Reaction*

a cycloaddition reaction



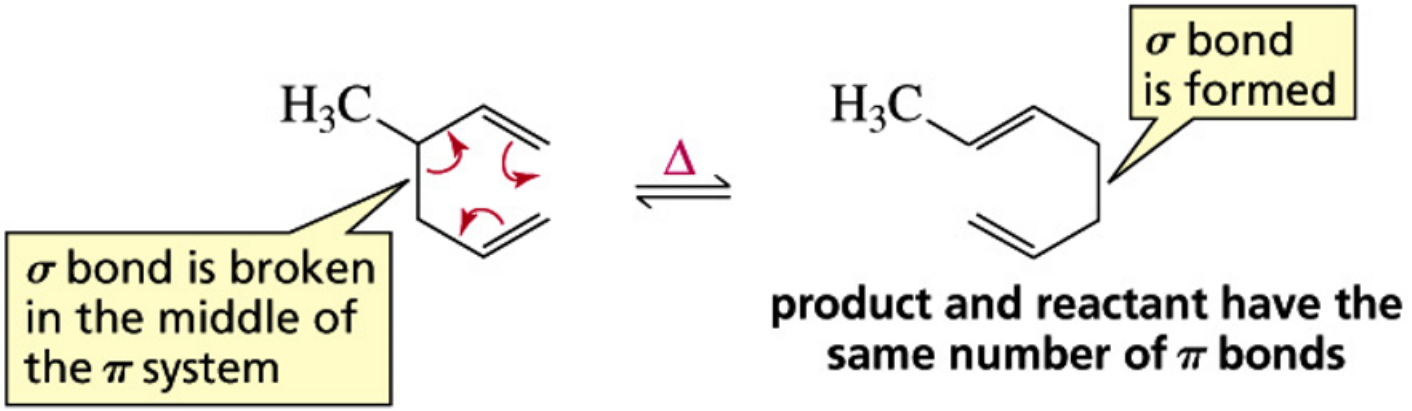
1,3-butadiene + ethene → cyclohexene

the product has two fewer π bonds than the sum of the π bonds in the reactants

Two different π bond-containing molecules react to form a cyclic compound

Pericyclic Reactions: *Sigmatropic Reaction*

sigmatropic rearrangements



A σ bond is broken in the reactant, a new σ bond is formed in the product, and the π bonds rearrange

Pericyclic Reactions: *Important Facts*

- The electrocyclic reactions and sigmatropic rearrangements are intramolecular reactions
- The cycloaddition reactions are usually intermolecular reactions

Common features among the three pericyclic reactions

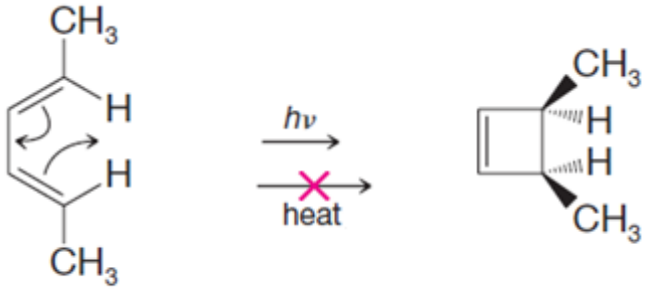
- Concerted reactions
- Highly stereoselective
- Not affected by catalysts

Electrocyclic Reaction: *Characteristic Features*

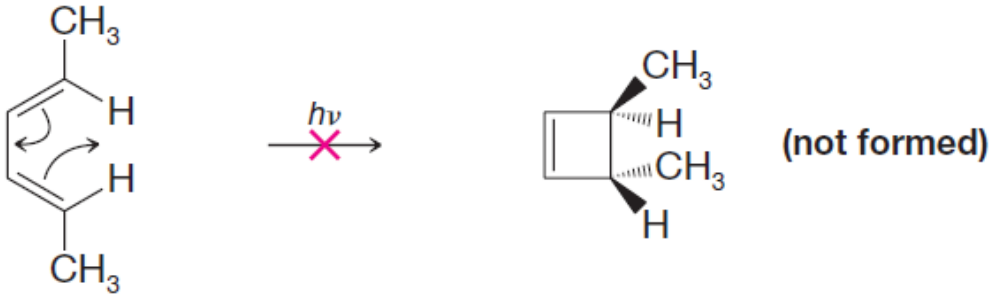
Electrocyclic reactions have several characteristic features:

1. They require only heat or light for initiation.
2. Their mechanisms do not involve radical or ionic intermediates.
3. Bonds are made and broken in *a single concerted step involving a cyclic transition state*.
4. The reactions are *stereospecific*.

Electrocyclic Reaction: *Stereospecific*

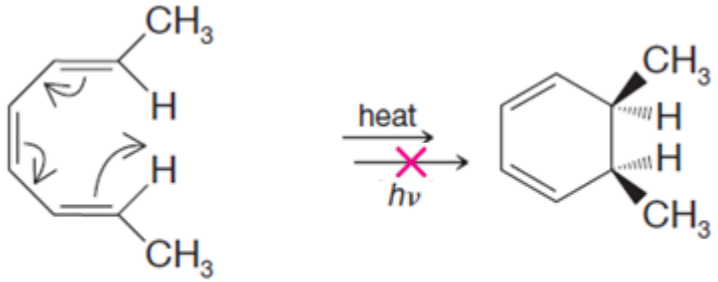


trans,trans-2,4-Hexadiene *cis*-3,4-Dimethylcyclobutene



(not formed)

trans,trans-2,4-Hexadiene *trans*-3,4-Dimethylcyclobutene



trans,cis,trans-2,4,6-Octatriene *cis*-5,6-Dimethyl-1,3-cyclohexadiene

Mechanism: *Frontier Molecular Orbitals (FMO) Approach*

- Mechanism of ECR can be understood in terms of FMO theory and the outcome can be predicted using the Woodward-Hoffman rules. The pathway of such reactions is determined by the symmetry properties of the orbitals that are directly involved. **The orbital symmetry must be same during overall mechanism**.

- In *electrocyclic* reactions, **only one reactant is involved and thus only the highest occupied molecular orbital (HOMO) needs to be considered**. Thus, the **stereochemistry of the reaction is controlled by the symmetry properties of the HOMO** of the reacting system.

- These reactions take place **thermally** or **photochemically**.

- In **thermal condition**, the **ground state HOMO is involved in the reaction**, but in **photochemical condition**, the **excited state HOMO involved**.

Guidelines of Electrocyclic Reaction: *W-H Rules*

Woodward-Hoffmann Rule:

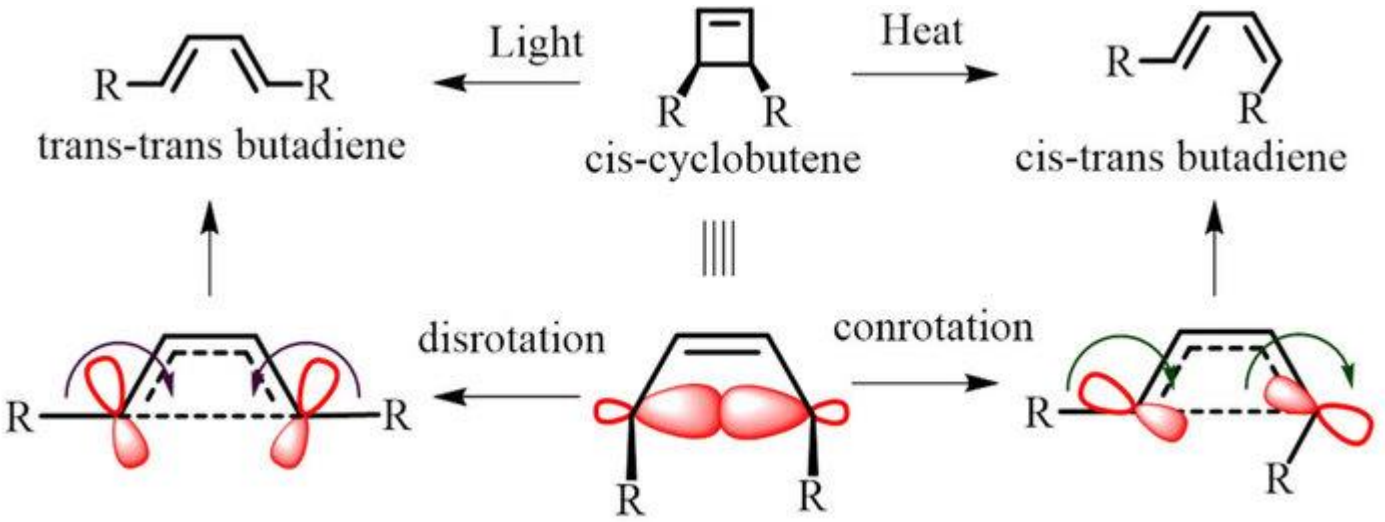
- A *thermal electrocyclic* reaction involving *4n π electrons* (where *n* = 1, 2, 3, . . .) proceeds with *conrotatory motion*; the *photochemical* reaction proceeds with *disrotatory motion.*
- A *thermal electrocyclic* reaction involving *(4n + 2) π electrons* (where *n* = 0, 1, 2, . . .) proceeds with *disrotatory motion*; the *photochemical* reaction proceeds with *conrotatory motion*.

TABLE D.1 WOODWARD–HOFFMANN RULES FOR ELECTROCYCLIC REACTIONS

Number of π Electrons	Motion	Rule
$4n$	Conrotatory	Thermally allowed, photochemically forbidden
$4n$	Disrotatory	Photochemically allowed, thermally forbidden
$4n + 2$	Disrotatory	Thermally allowed, photochemically forbidden
$4n + 2$	Conrotatory	Photochemically allowed, thermally forbidden

Simple Single Rule: **"4-Con-Tha"**

Mode of Rotation: *Conrotatory vs Disrotatory*

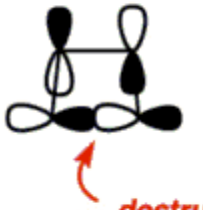


What if both lobes rotate in the opposite direction?

If both lobes rotate in the opposite direction, there will not be constructive orbital overlap and no bond can form.

clockwise rotation

counter-clockwise rotation



destructive overlap

no bond forms

Frontier Molecular Orbitals (FMO): *4πe -Systems*

ψ = **LCAO** (Linear combination of Atomic orbitals)

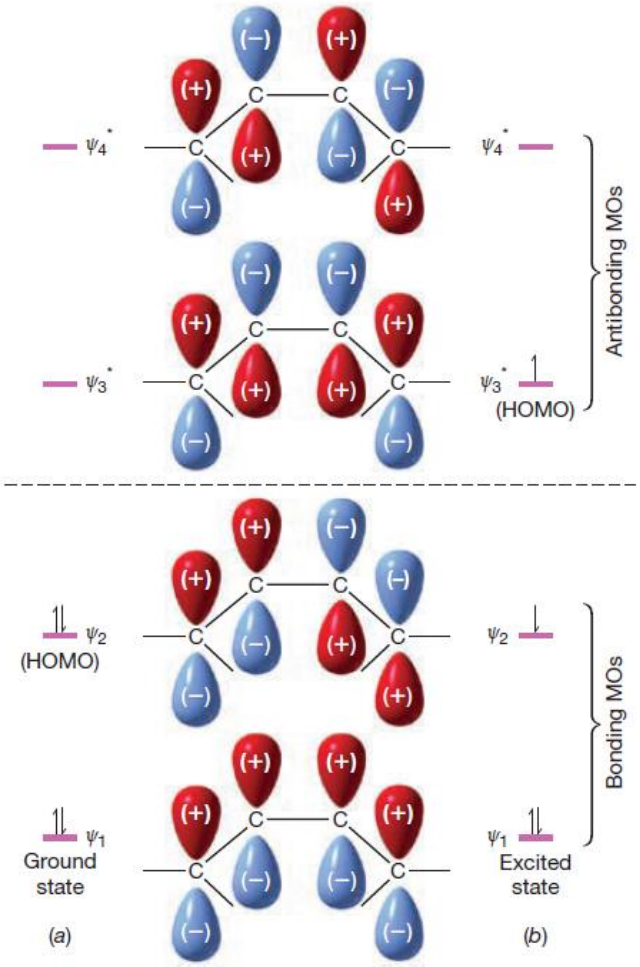
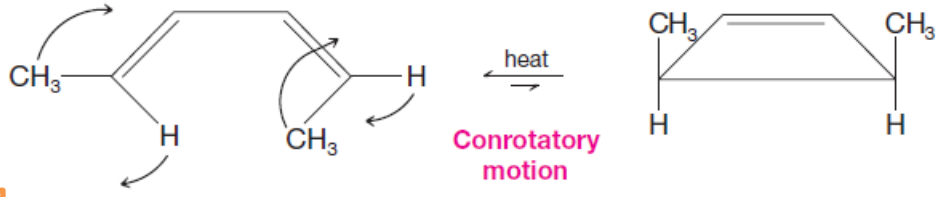


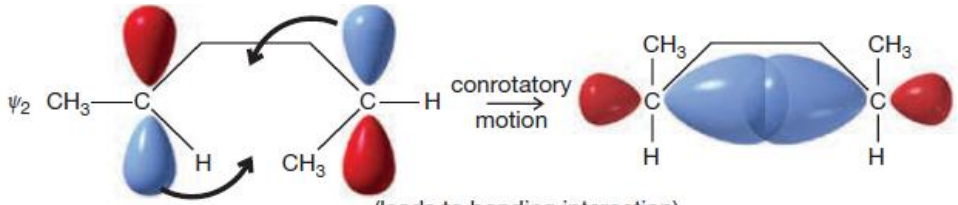
FIGURE D.1 The π molecular orbitals of a 2,4-hexadiene (other parts of the formula omitted for clarity). (*a*) The electron distribution of the ground state. (*b*) The electron distribution of the first excited state. (The first excited state is formed when the molecule absorbs a photon of light of the proper wavelength.) Notice that the orbitals of a 2,4-hexadiene are like those of 1,3-butadiene shown in Fig. 13.4.

Electrocyclic Reaction: *4πe -Systems*

Thermal

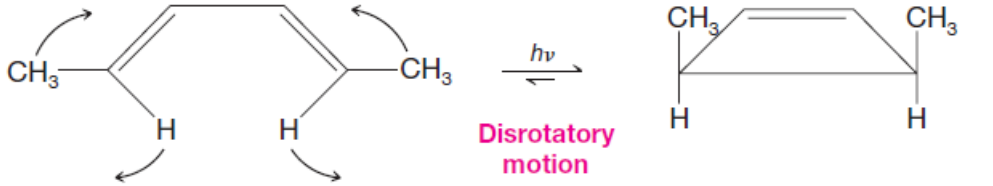


cis,trans-2,4-Hexadiene — *cis*-3,4-Dimethylcyclobutene

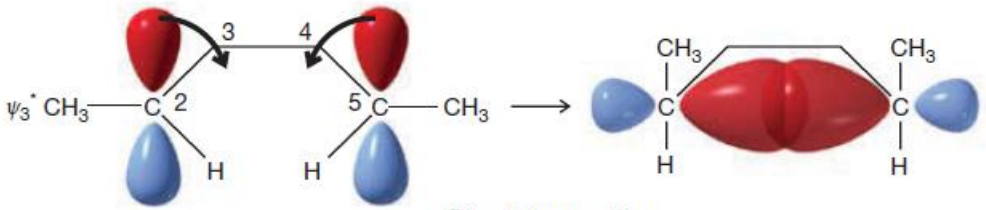


(leads to bonding interaction)

Photochemical

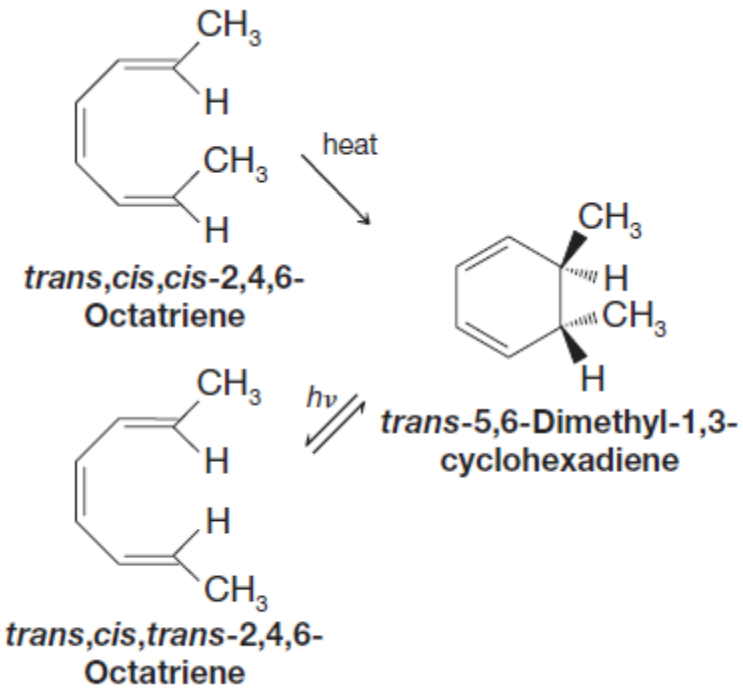


trans,trans-2,4-Hexadiene — *cis*-3,4-Dimethylcyclobutene

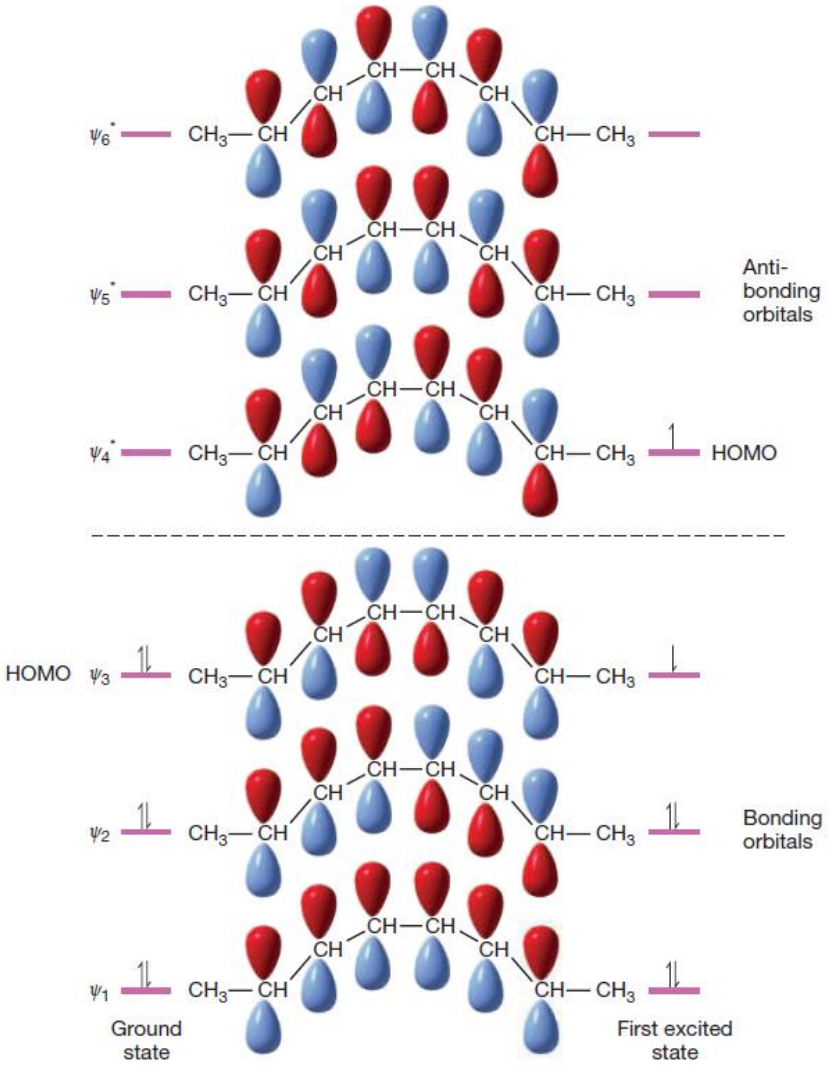


Disrotatory motion (leads to bonding interaction between C2 and C5)

Electrocyclic Reaction: *6πe -Systems*

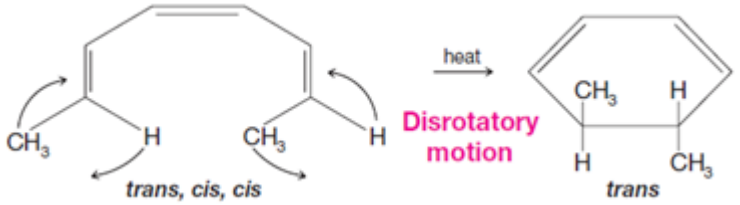


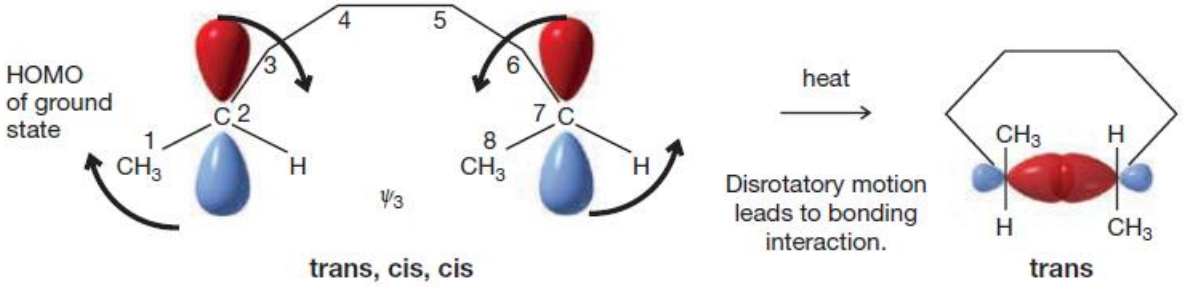
Frontier Molecular Orbitals: *6πe -System*



Electrocyclic Reaction: *6πe -Systems*

Thermal





Photochemical