Chapter 6

Pericyclic Reactions

周环反应

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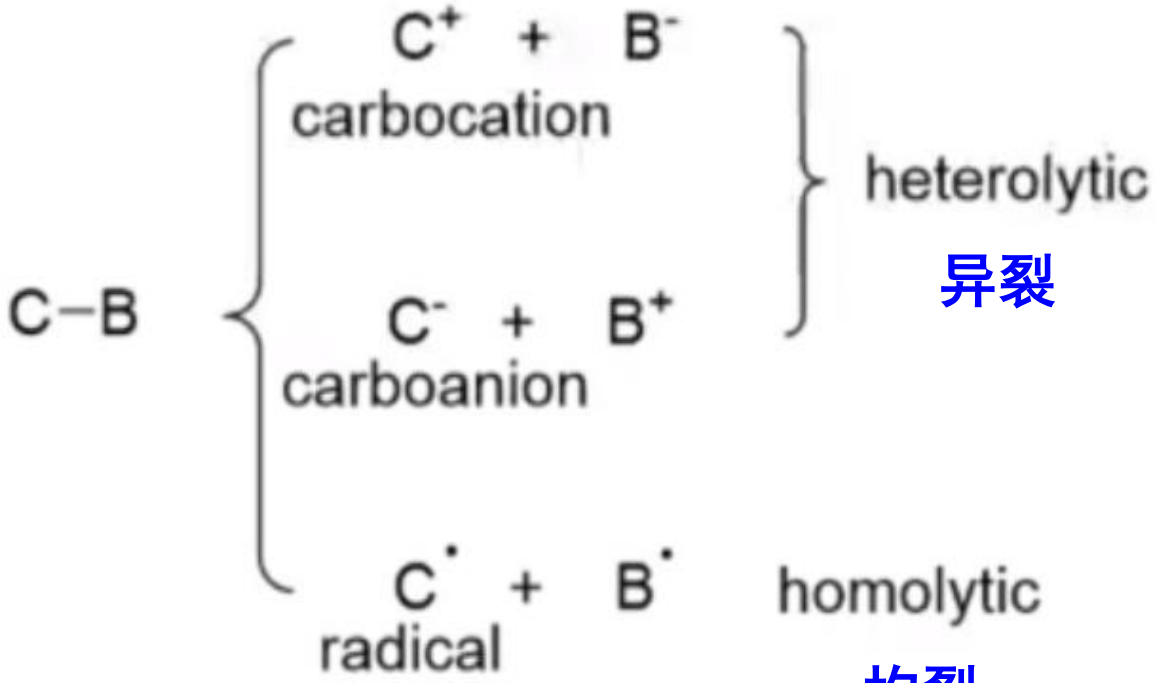
Pericyclic Reactions

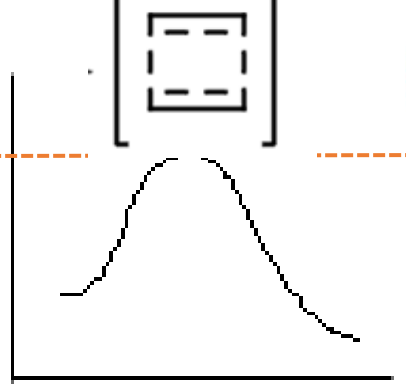
Content

6.1 Introduction to pericyclic reactions

6.1.1 Characteristics of pericyclic reactions

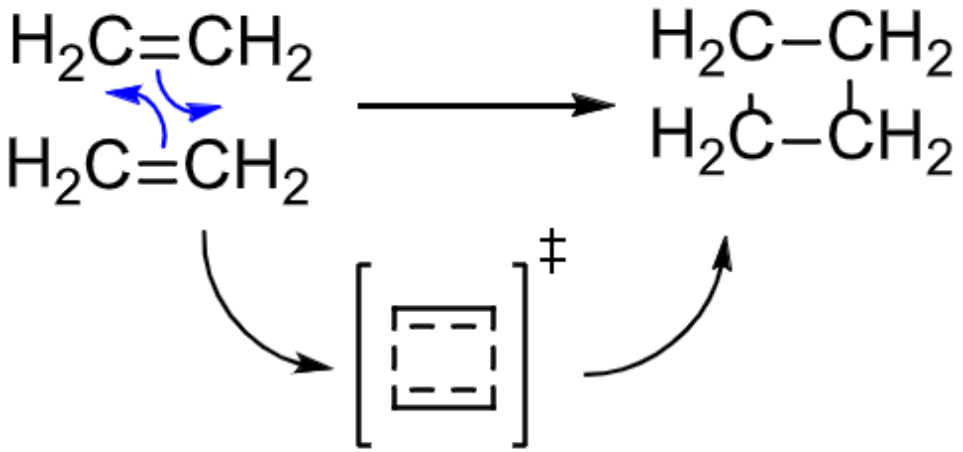
共价键不同的断裂方式，产生不同的中间体，对应不同的反应类型。





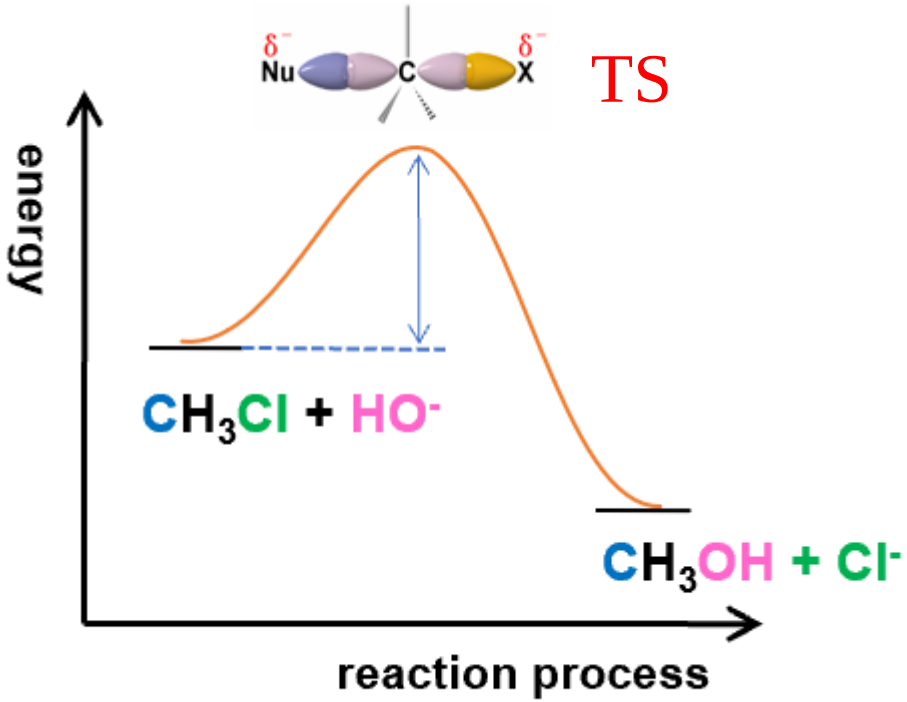
Pericyclic Reactions

不经过中间体，一步完成

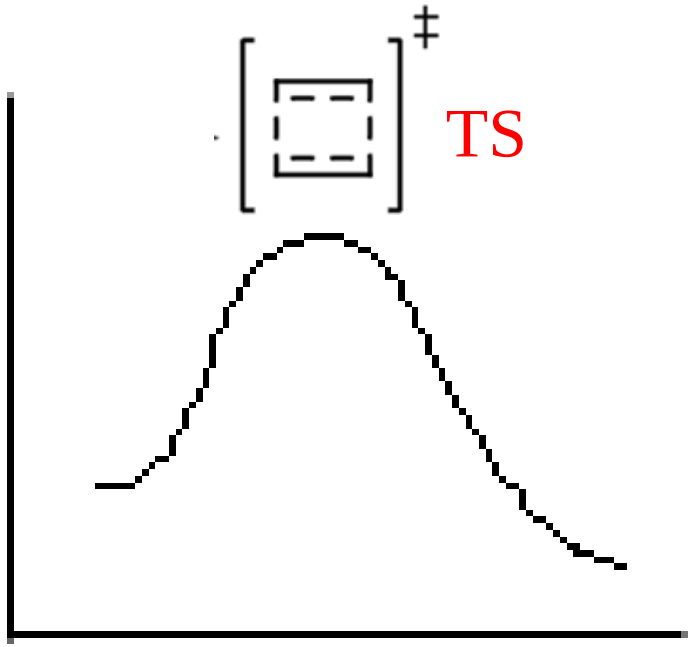


6.1 Introduction to pericyclic reactions

S_N2



Pericyclic Reaction



6.1 Introduction to pericyclic reactions

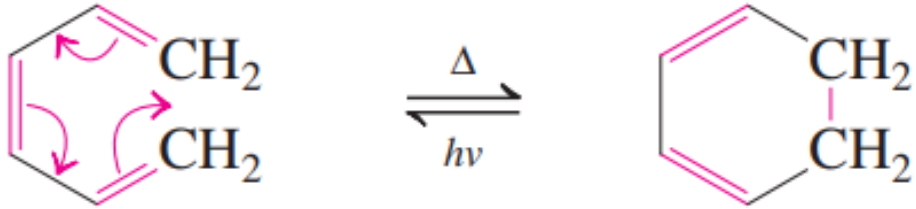
Classification of pericyclic reactions

Cycloaddition

环加成反应

Electrocyclic Reactions

电环化反应



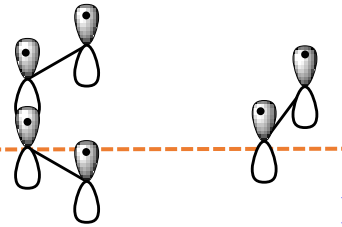
Sigmatropic Rearrangement

σ-迁移反应

Ene Reactions

烯反应

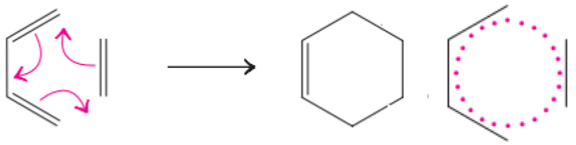
6.1 Introduction to pericyclic reactions



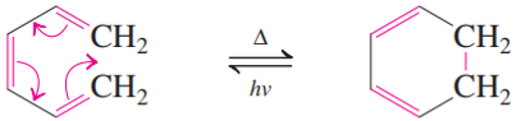
Characteristics of pericyclic reactions-1

1. No active intermediate involved
2. Complete in a single step, reversible
3. Cyclic transition state, aromatic

Cycloaddition
环加成反应



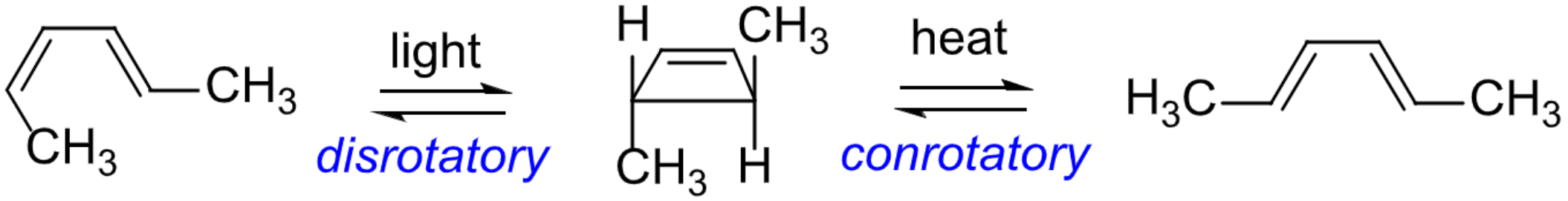
Electrocyclic Reactions
电环化反应



Sigmatropic Rearrangement
σ-迁移反应

Ene Reactions
烯反应

Characteristics of pericyclic reactions-2 Stereospecific



6.1 Introduction to pericyclic reactions

Stereospecific of electrocyclic Reactions

↓

Woodward-Hoffmann rule

↓

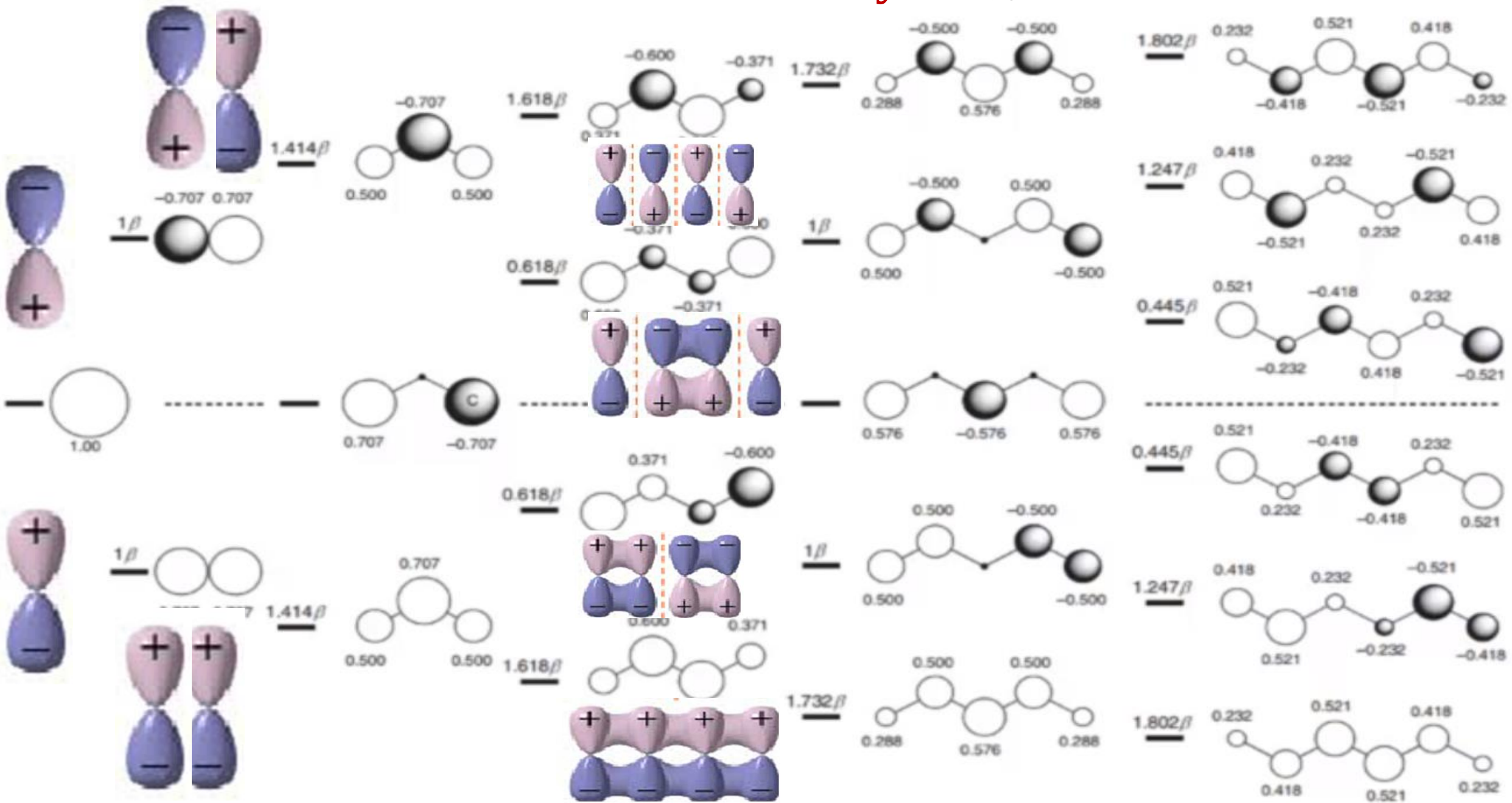
6.1.2 Frontier Molecular Orbital Theory

前线分子轨道理论

6.1.3 Principle of conservation of molecular orbital symmetry

分子轨道对称守恒原理

6.1.2 Frontier Molecular Orbital Theory 前线分子轨道理论



6.1 Introduction to pericyclic reactions

- 电子由低到高依次填充
  (HOMO轨道和LUMO轨道)

- 两端相位由相同/不同/相同。。。。。。依次变化
  （与立体选择性相关）

- 每个分子轨道中轨道系数不一样。
  （与区域选择性相关）

6.1 Introduction to pericyclic reactions

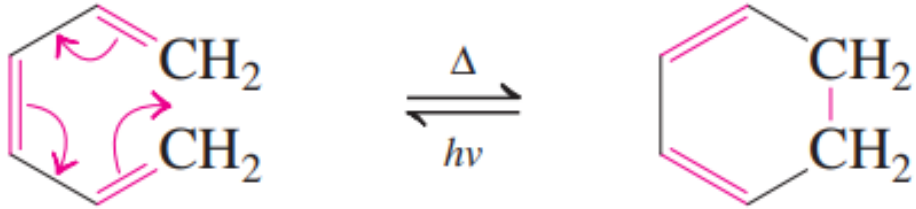
Classification of pericyclic reactions

Cycloaddition

环加成反应

Electrocyclic Reactions

电环化反应



Sigmatropic Rearrangement

σ-迁移反应

Ene Reactions

烯反应

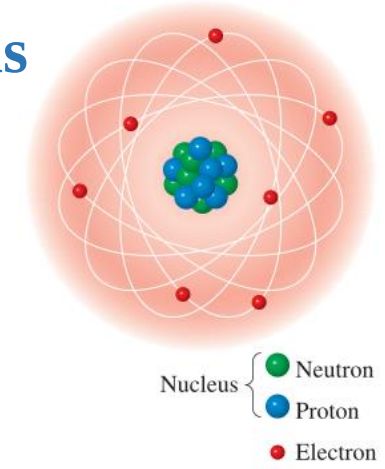
1.5 Molecular Orbital theory

LCAO(Linear Combination of Atomic Orbital)

1. **Bonding is considered to arise from the overlap of atomic orbitals.**

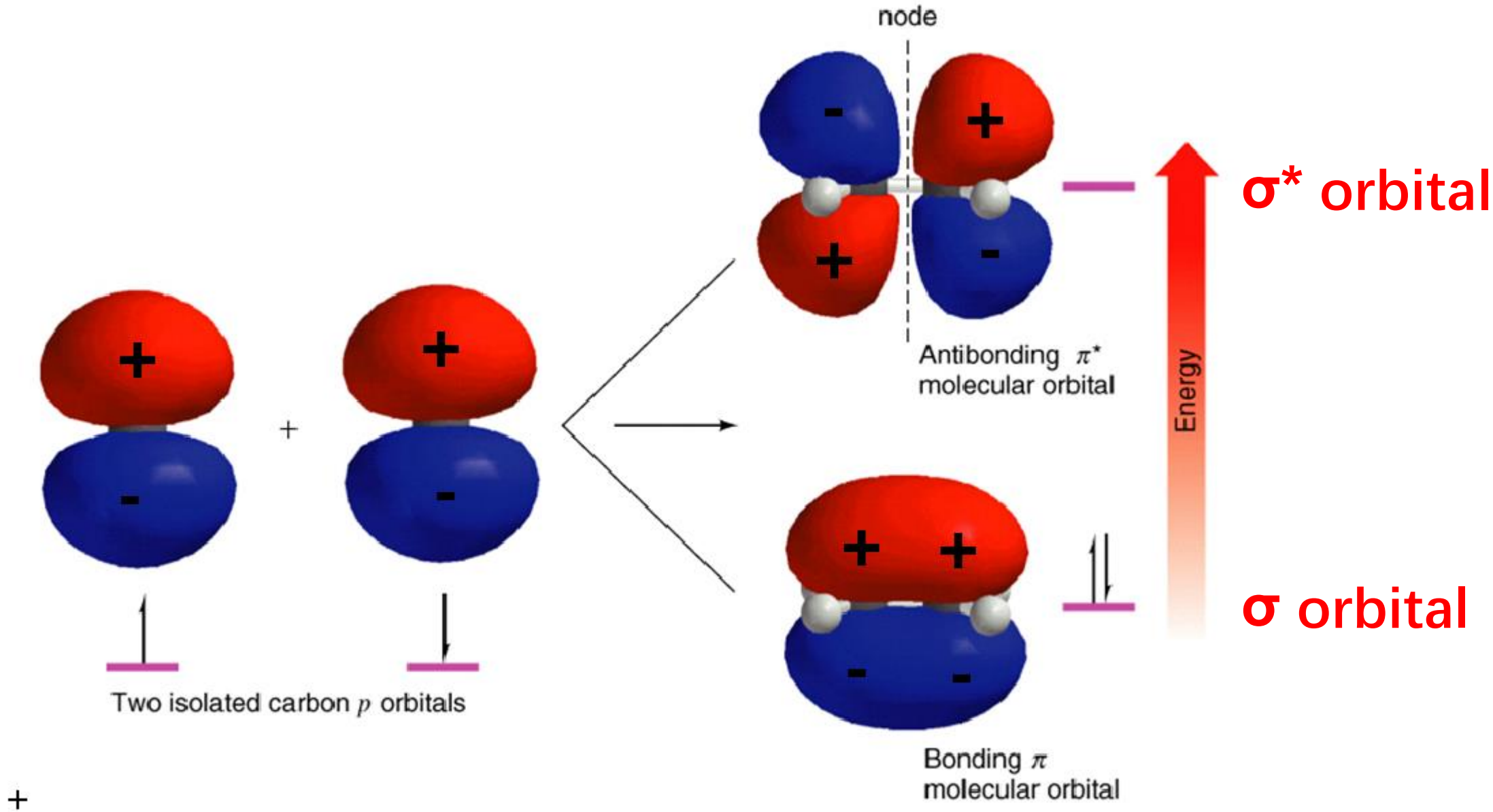
2. **When any number of atomic orbitals overlap, they combine to form equal number of new orbitals, called molecular orbitals.**

3. **In localized bonding for single covalent bond, the number of atomic orbitals that overlap is two(each containing one electron), so that two molecular orbitals are generated. One called *bonding orbital*, has lower energy than the original atomic orbitals, and the other , called *antibonding orbital*, has higher energy.**

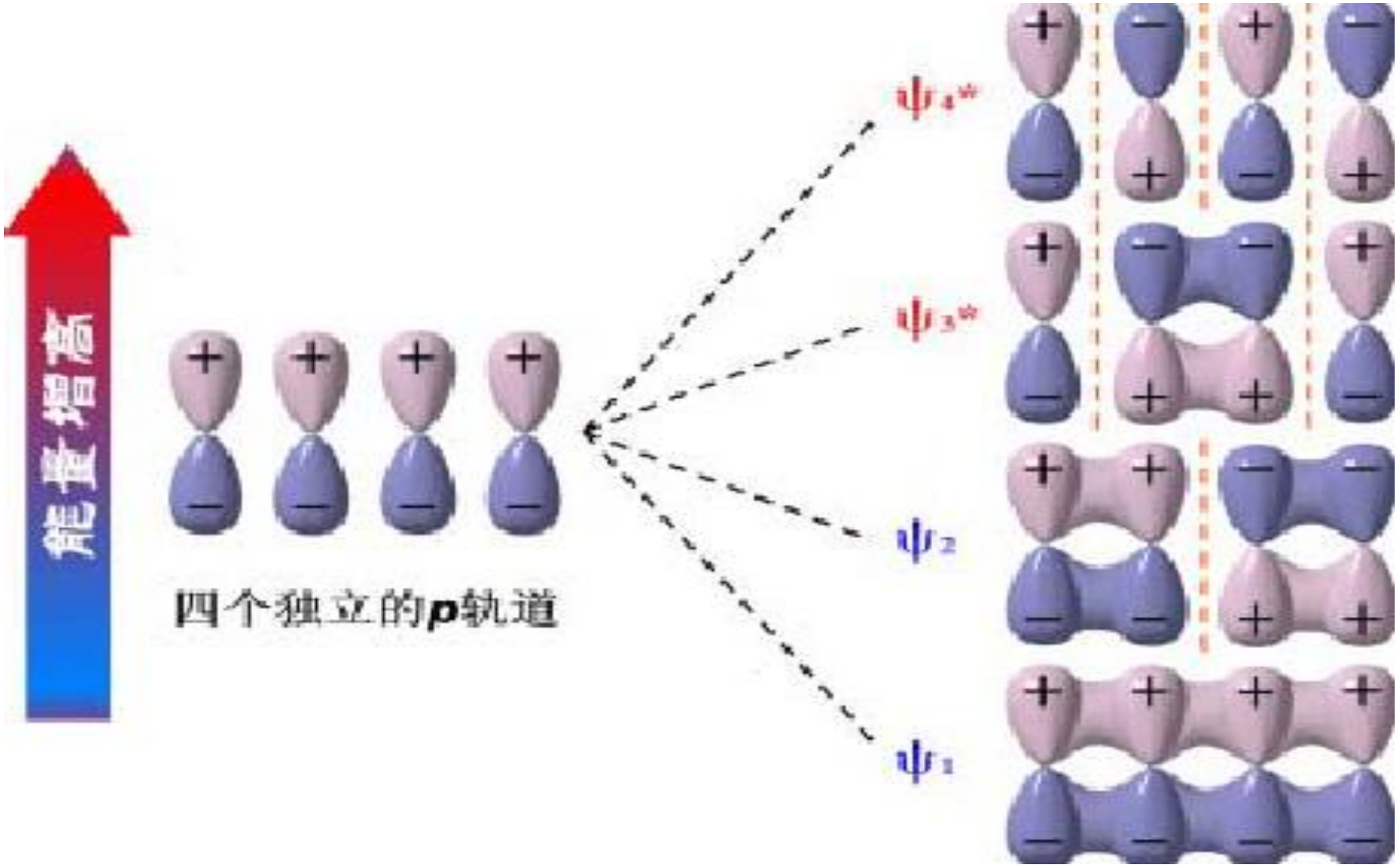


Classical atom: electrons in "orbit" around the nucleus

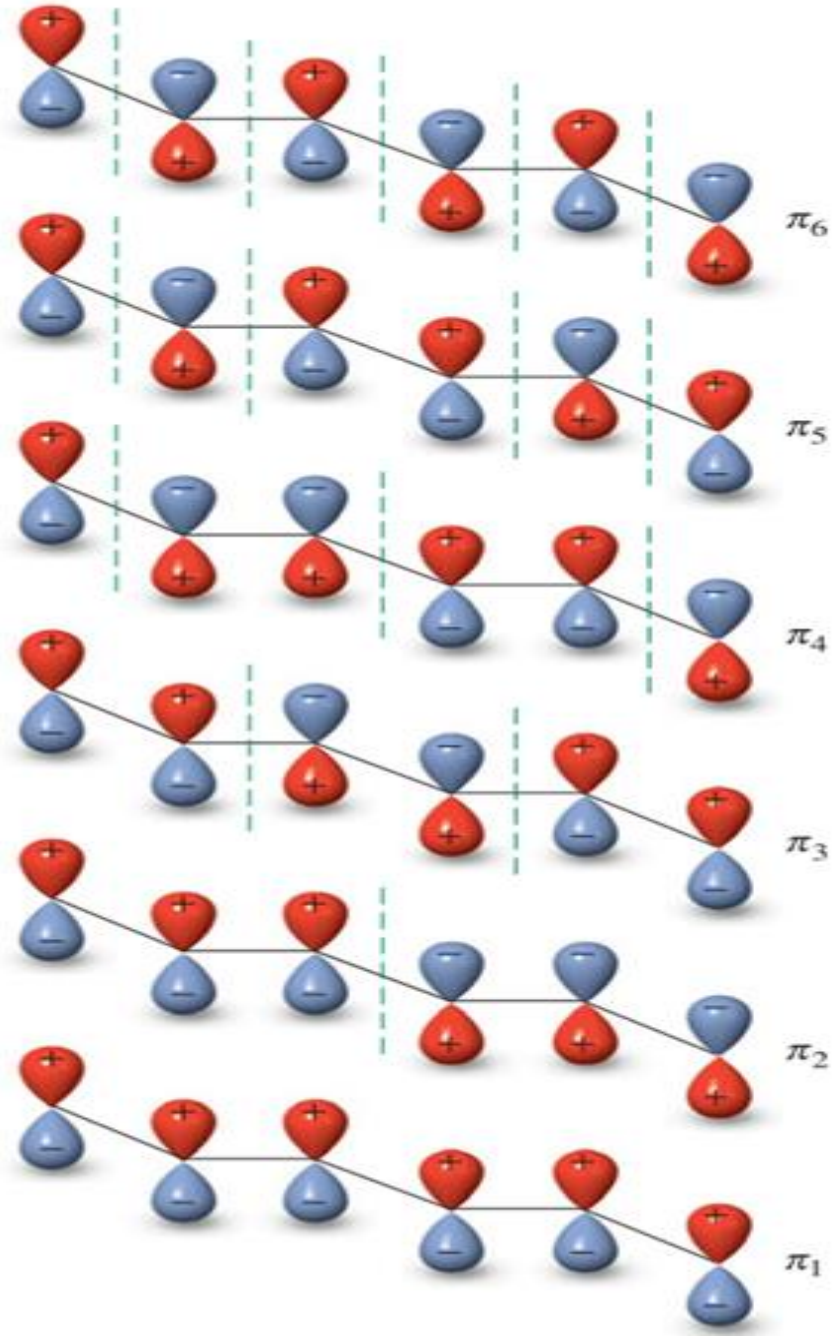
6.1 Introduction to pericyclic reactions



6.1 Introduction to pericyclic reactions

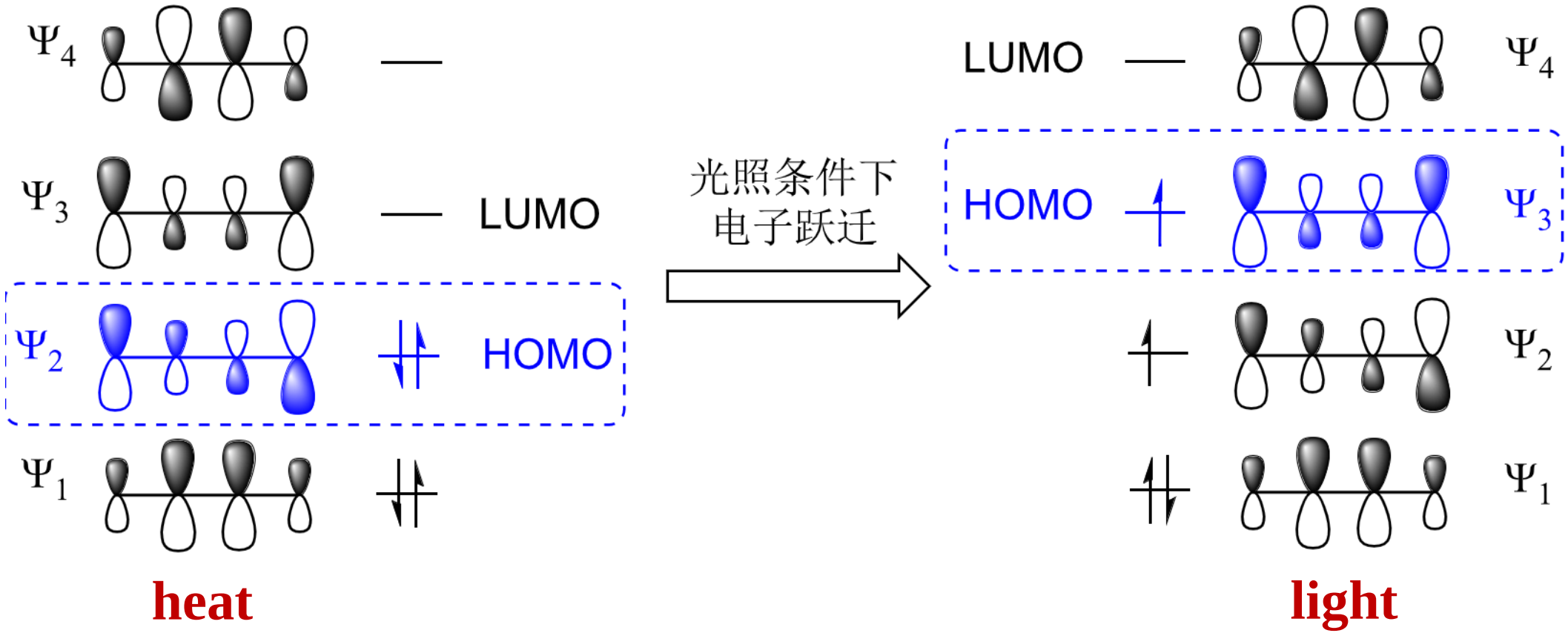


6.1 Introduction to pericyc



6.1 Introduction to pericyclic reactions

MO of buta-1, 3-diene



前线分子轨道理论：反应立体专一性由HOMO轨道的对称性决定

加热条件下由π 2决定

光照条件下由π 3决定

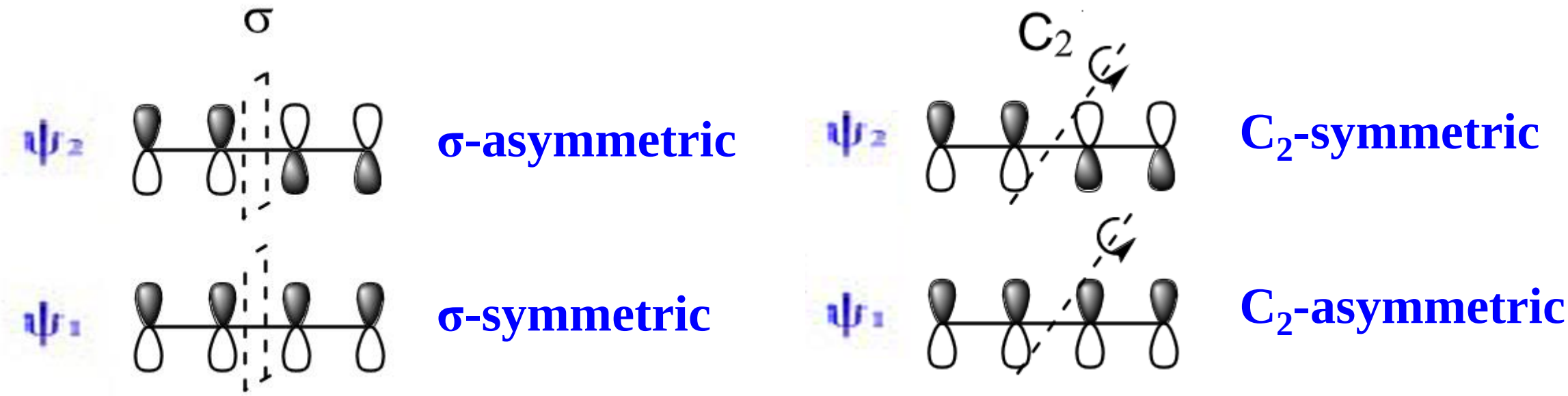
6.1 Introduction to pericyclic reactions

6.1.3 Principle of conservation of molecular orbital symmetry

分子轨道对称守恒原理

Symmetry　　σ （面对称性）　　C_2（轴对称性）

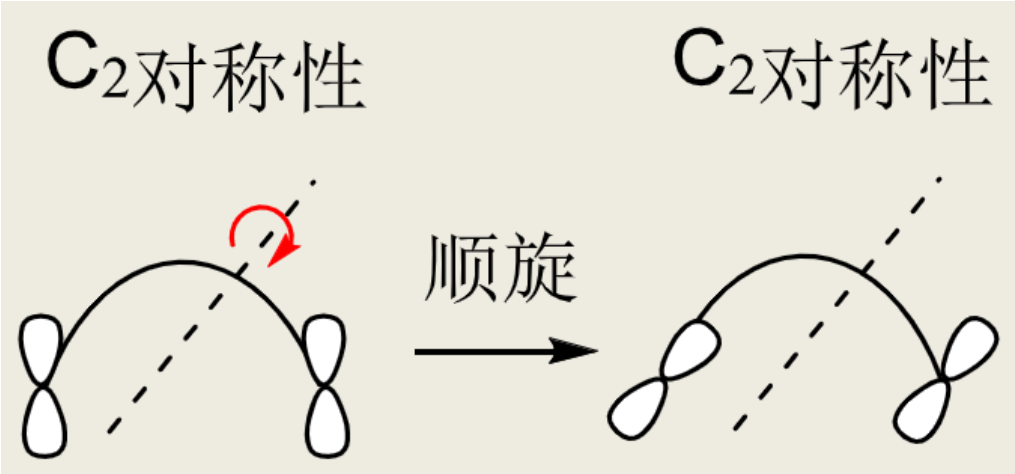
Orbital symmetry of reactant and product



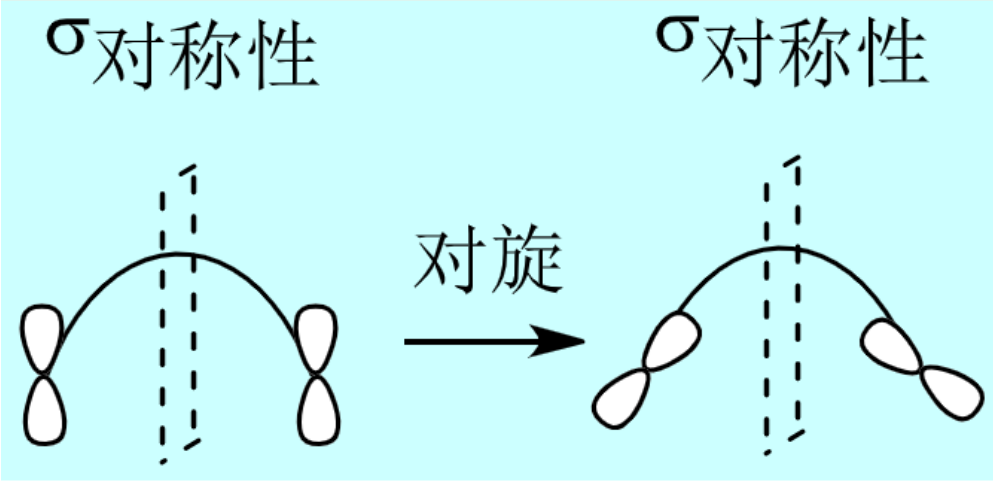
6.1 Introduction to pericyclic reactions

操作对称性

conrotatory（顺旋） → **C_2（轴对称性）**



disrotatory（对旋） → **σ（面对称性）**



轨道对称守恒原理：
反应立体专一性由原料/产物的分子轨道对称性以及对称性操作决定
在原料/产物对称守恒前提下，采用能量有利的途经。

6.1 Introduction to pericyclic reactions

前线分子轨道理论：反应立体专一性由HOMO轨道的对称性决定

加热条件下由π 2(4π e)决定

光照条件下由π 3 (4π e)决定

轨道对称守恒原理：

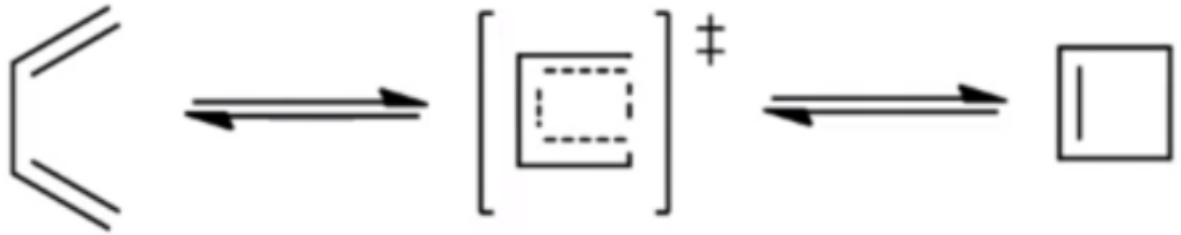
反应立体专一性由原料/产物的分子轨道对称性以及对称性操作决定

在原料/产物对称守恒前提下，采用能量有利的途经。

6.2 Electrocyclic Reactions

Classification of electrocyclization reactions

The number of π-electrons of substrates



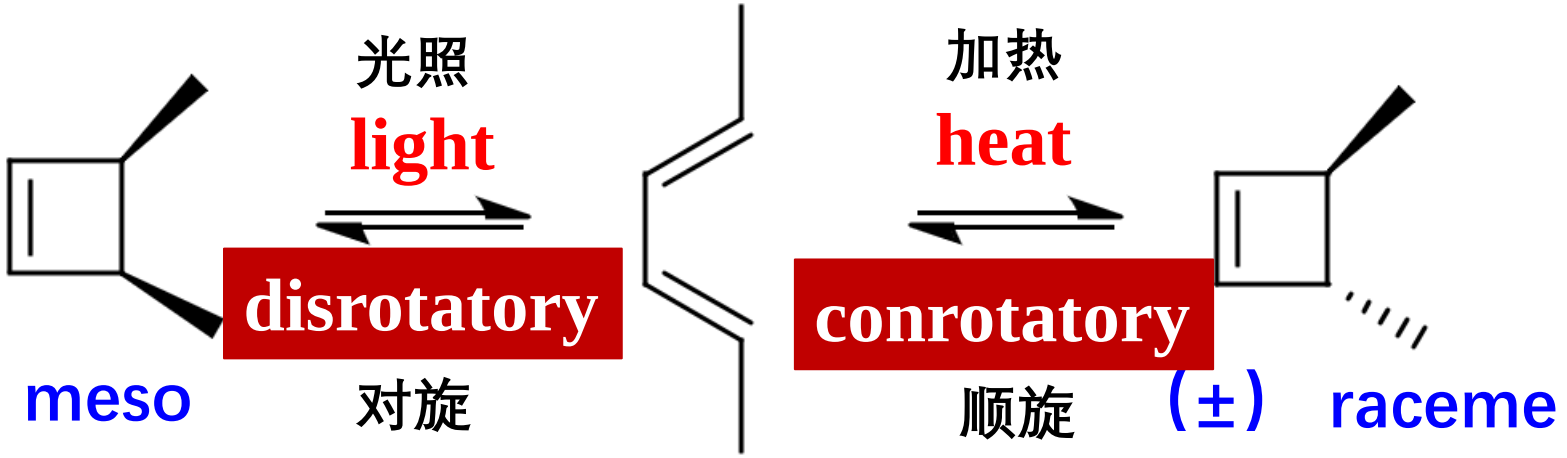
4π electrocyclic → **1. 4n π electrocyclic**

6π electrocyclic → **2. 4n+2 π electrocyclic**

6.2 Electrocyclic Reactions

6.2.1 4n π electrocyclic reaction

Electrocyclic transformations are driven by heat or light



Electrocyclic reactions are concerted and stereospecific

One-step reaction, reversible

Heat conrotatory (加热顺旋), light disrotatory (光照对旋)

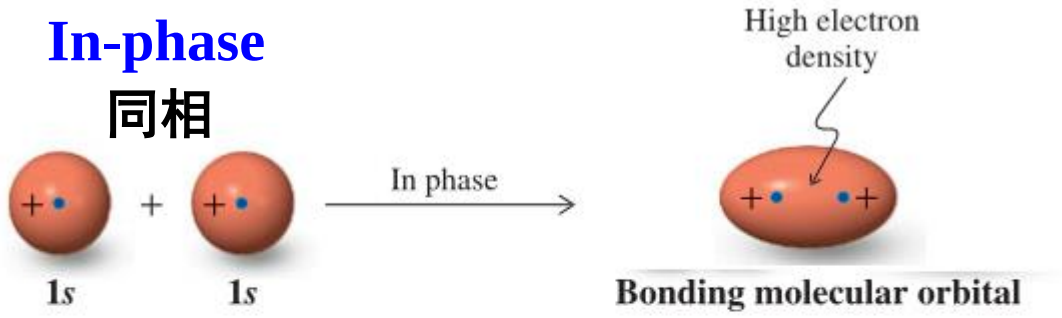
1.5 Molecular Orbital theory

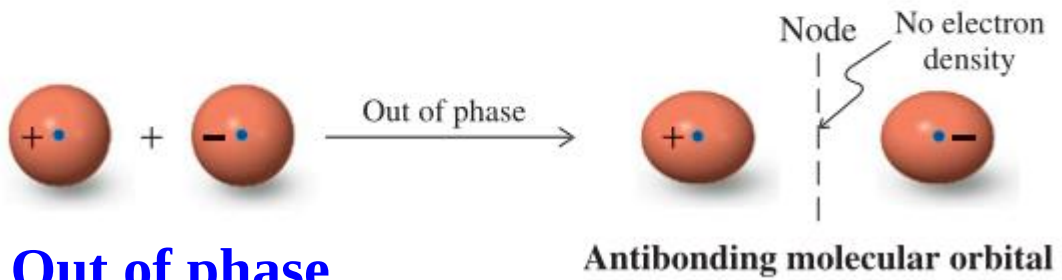
Molecular Orbitals and Covalent Bonding

Pauling: Bonds are made by the in-phase overlap of atomic orbitals.

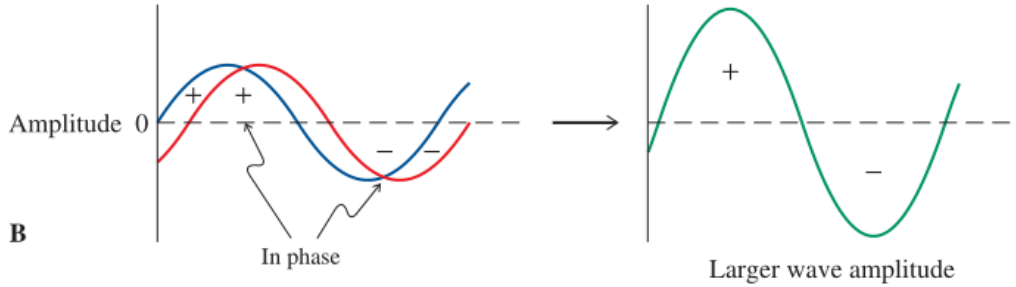
H · · H

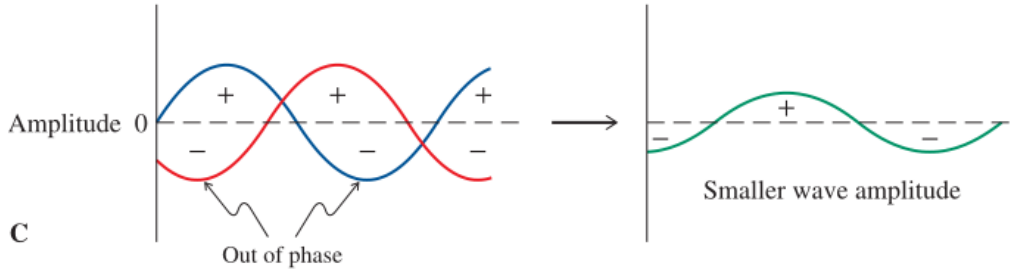
In-phase
同相





Out of phase
异相

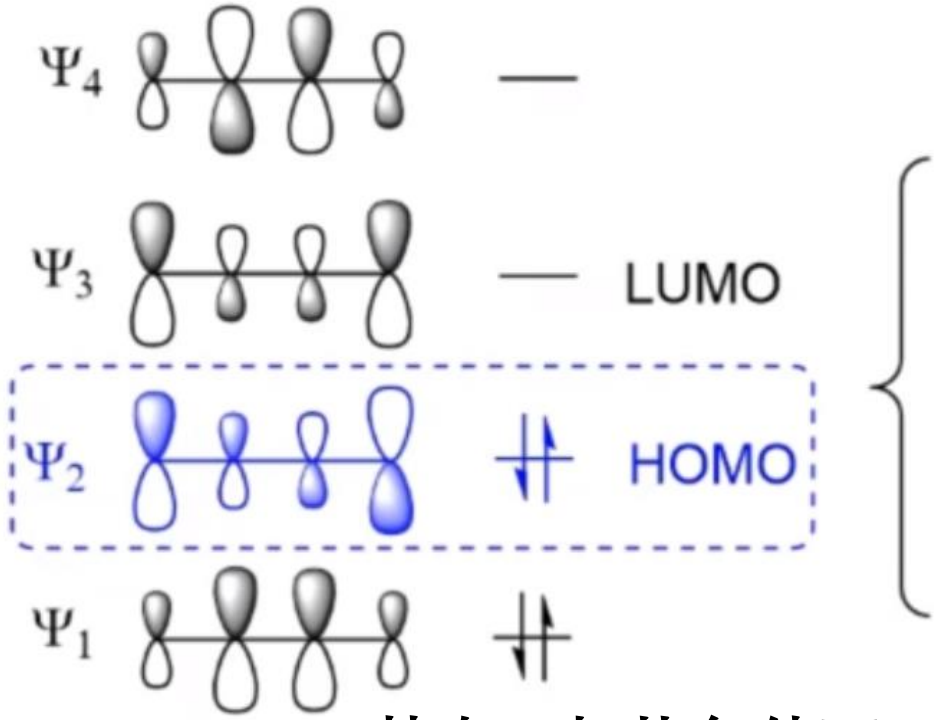




6.2 Electrocyclic Reactions

Frontier Molecular Orbital Theory　4n π

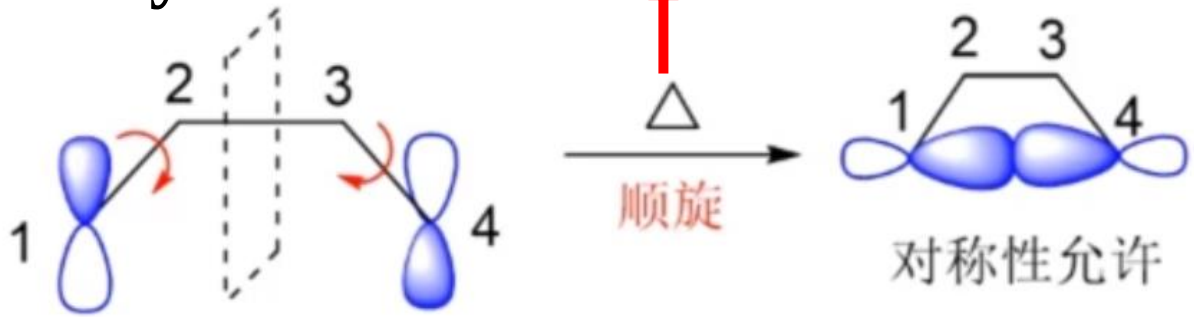
Heat



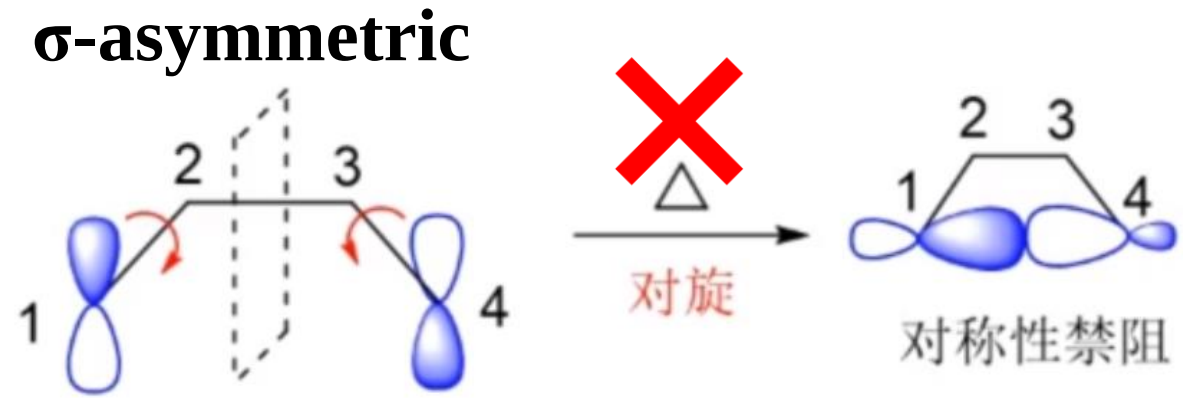
ground state(基态，加热条件下)

满足同相重叠，可以成键

σ-asymmetric

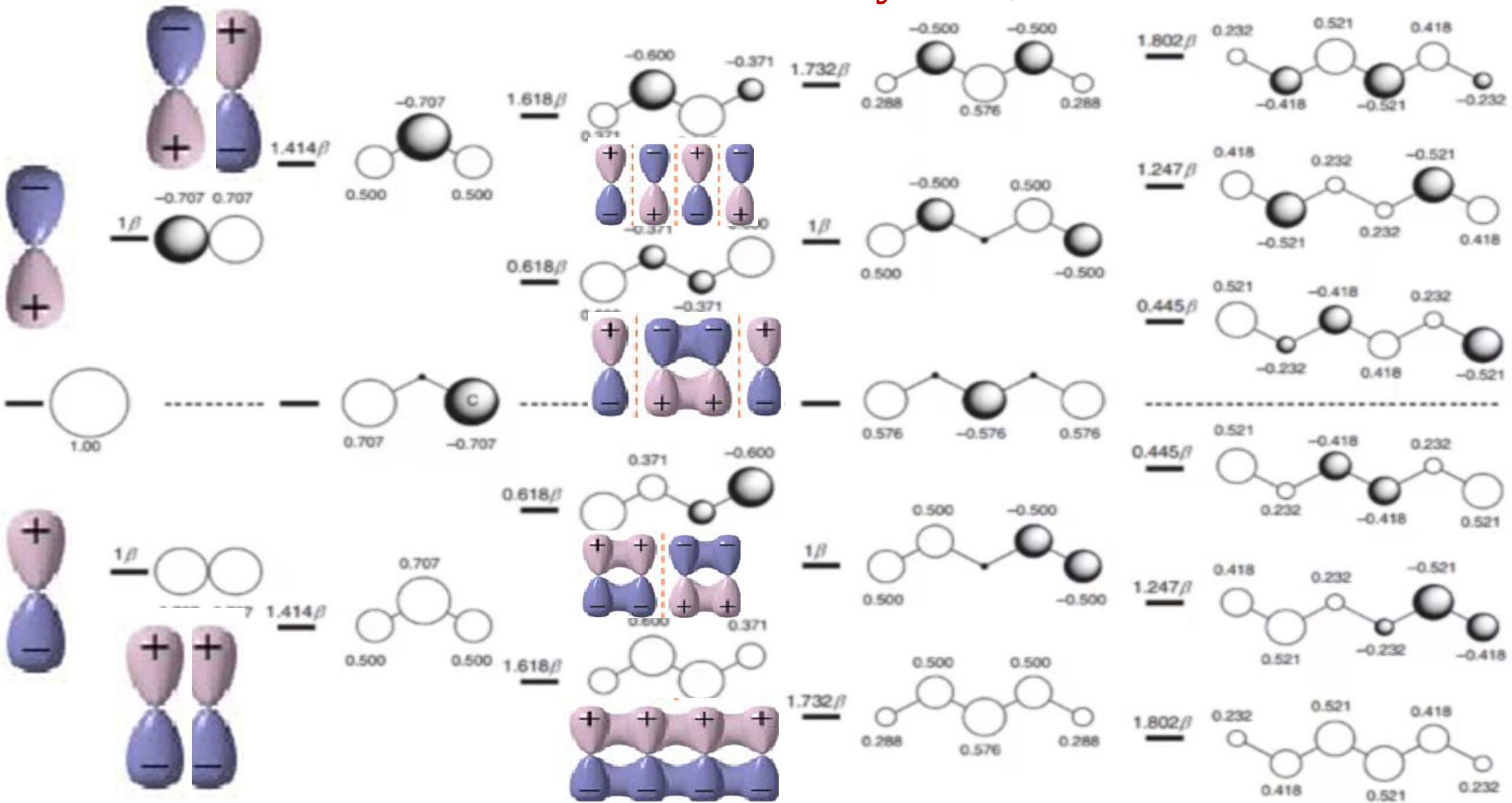


σ-asymmetric



4n π electrons, heat, conrotatory, bonding

6.1.2 Frontier Molecular Orbital Theory 前线分子轨道理论

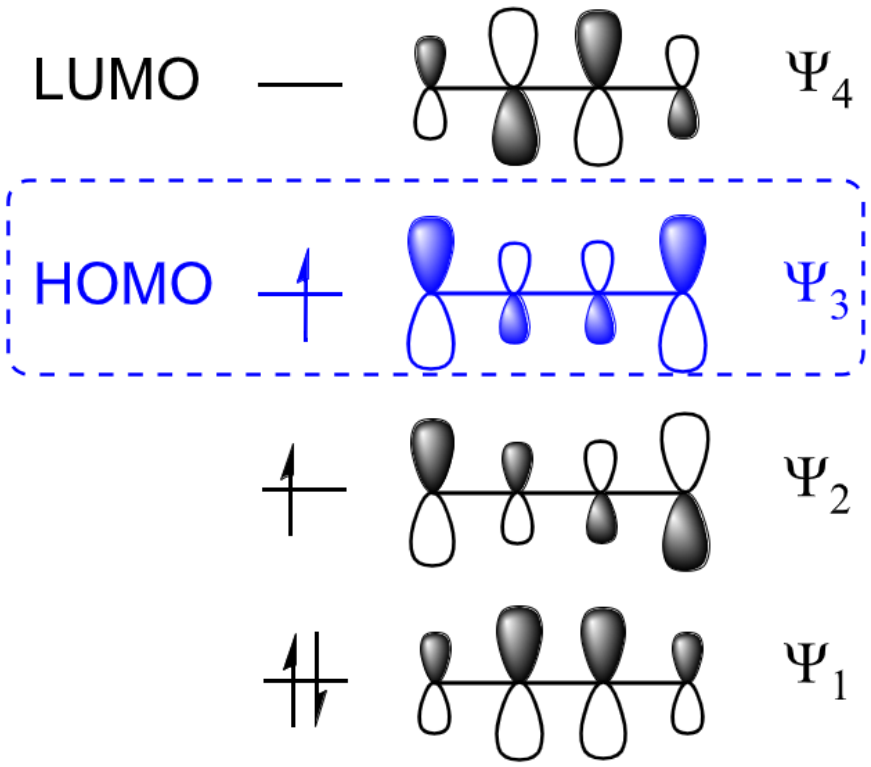


6.1 Introduction to pericyclic reactions

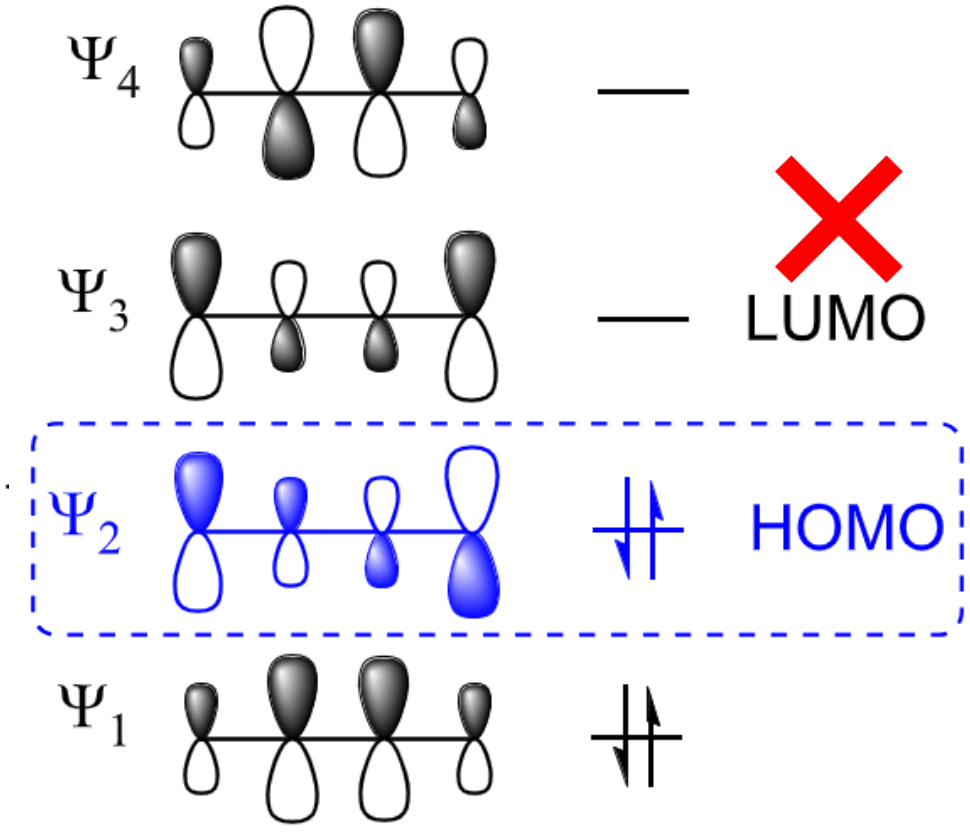
- **电子由低到高依次填充**
  (HOMO轨道和LUMO轨道)
- **两端相位由相同/不同/相同。。。。。。依次变化**
  （与立体选择性相关）
- **每个分子轨道中轨道系数不一样。**
  （与区域选择性相关）

6.2 Electrocyclic Reactions

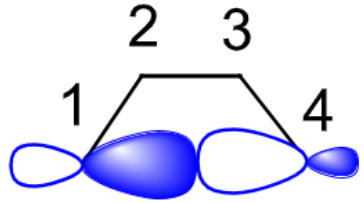
light



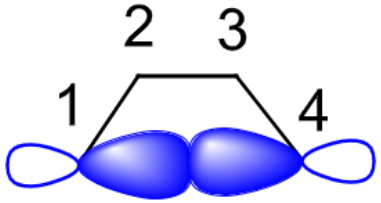
excited state (激发态，光照条件)



基态（加热）



对称性禁阻



对称性允许

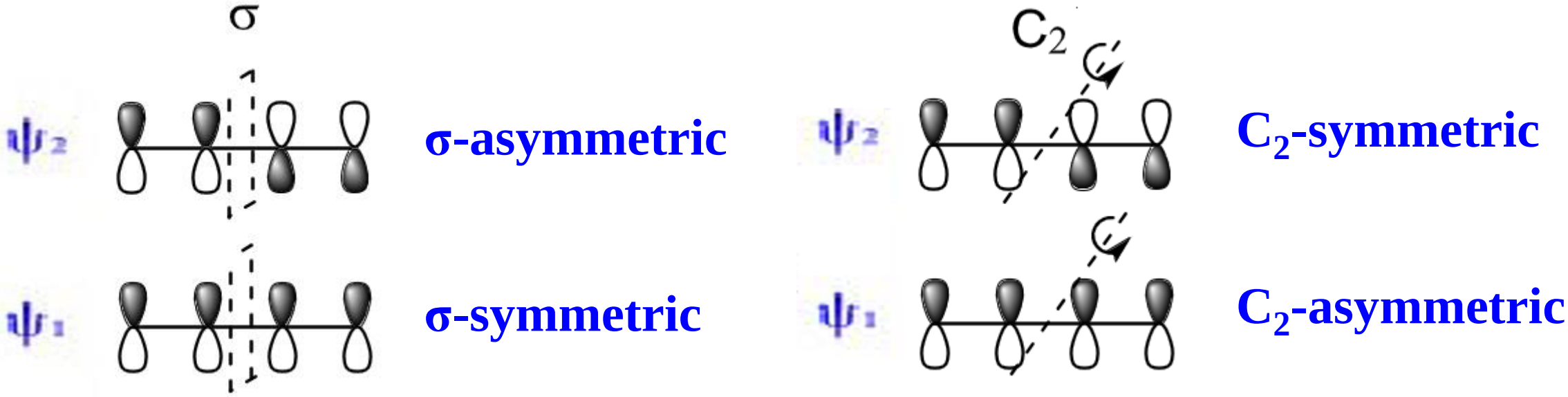
4n π electrons, light, disrotatory, bonding

6.1 Introduction to pericyclic reactions

Principle of conservation of molecular orbital symmetry 分子轨道对称守恒原理

Symmetry　　σ （面对称性）　　C_2（轴对称性）

Orbital symmetry of reactant and product



6.2 Electrocyclic Reactions

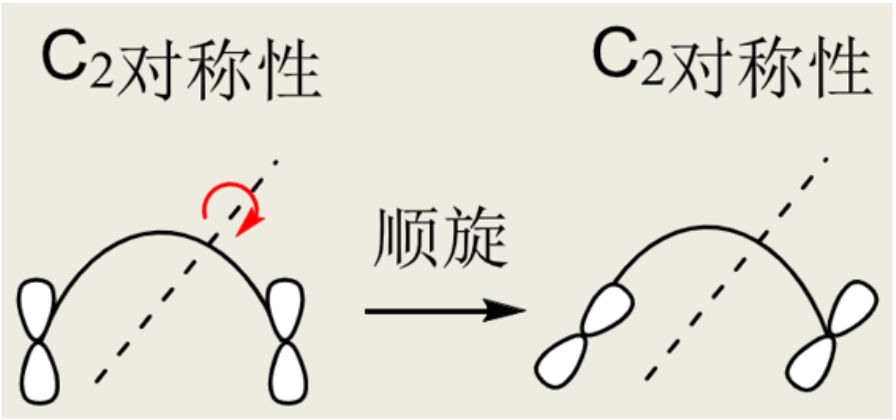
Principle of conservation of molecular orbital symmetry 分子轨道对称守恒原理

操作对称性

conrotatory（顺旋）

↓

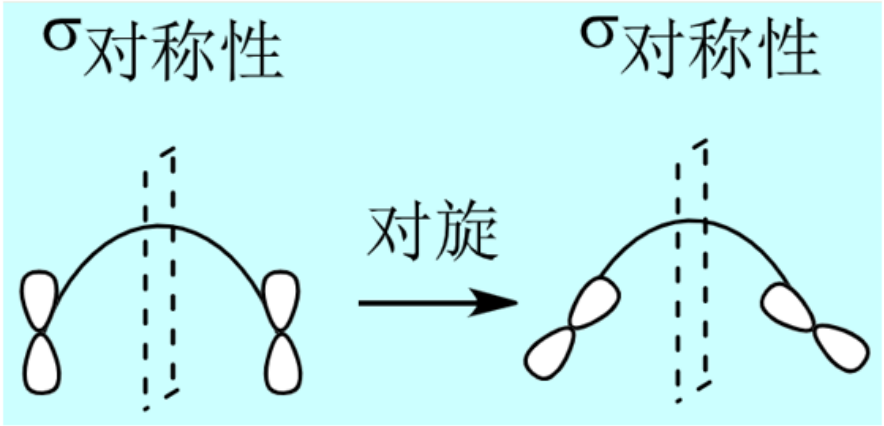
C_2（轴对称性）



disrotatory（对旋）

↓

σ（面对称性）



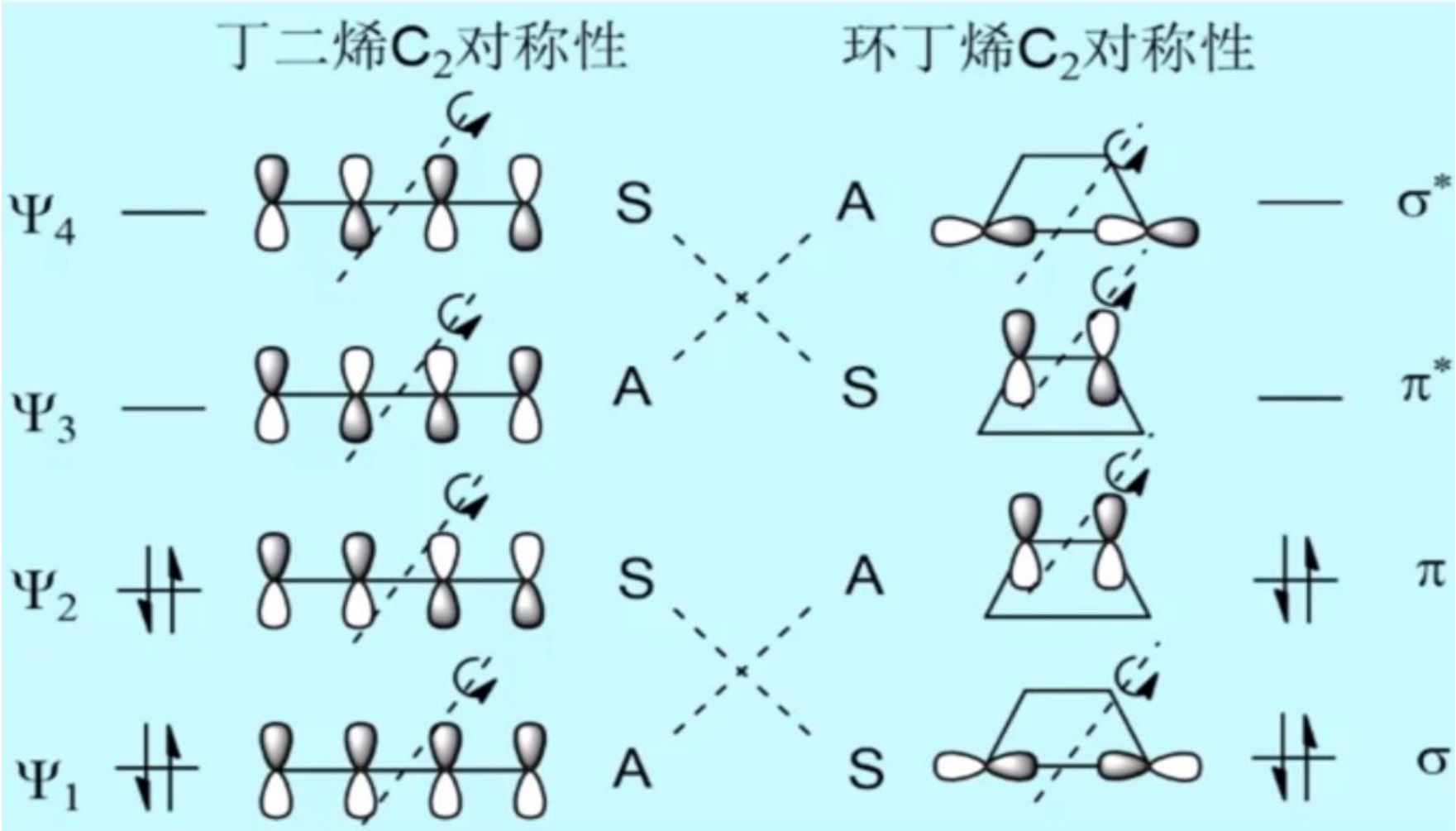
轨道对称守恒原理：

反应立体专一性由原料/产物的分子轨道对称性以及对称性操作决定

在原料/产物对称守恒前提下，采用能量有利的途经。

6.2 Electrocyclic Reactions

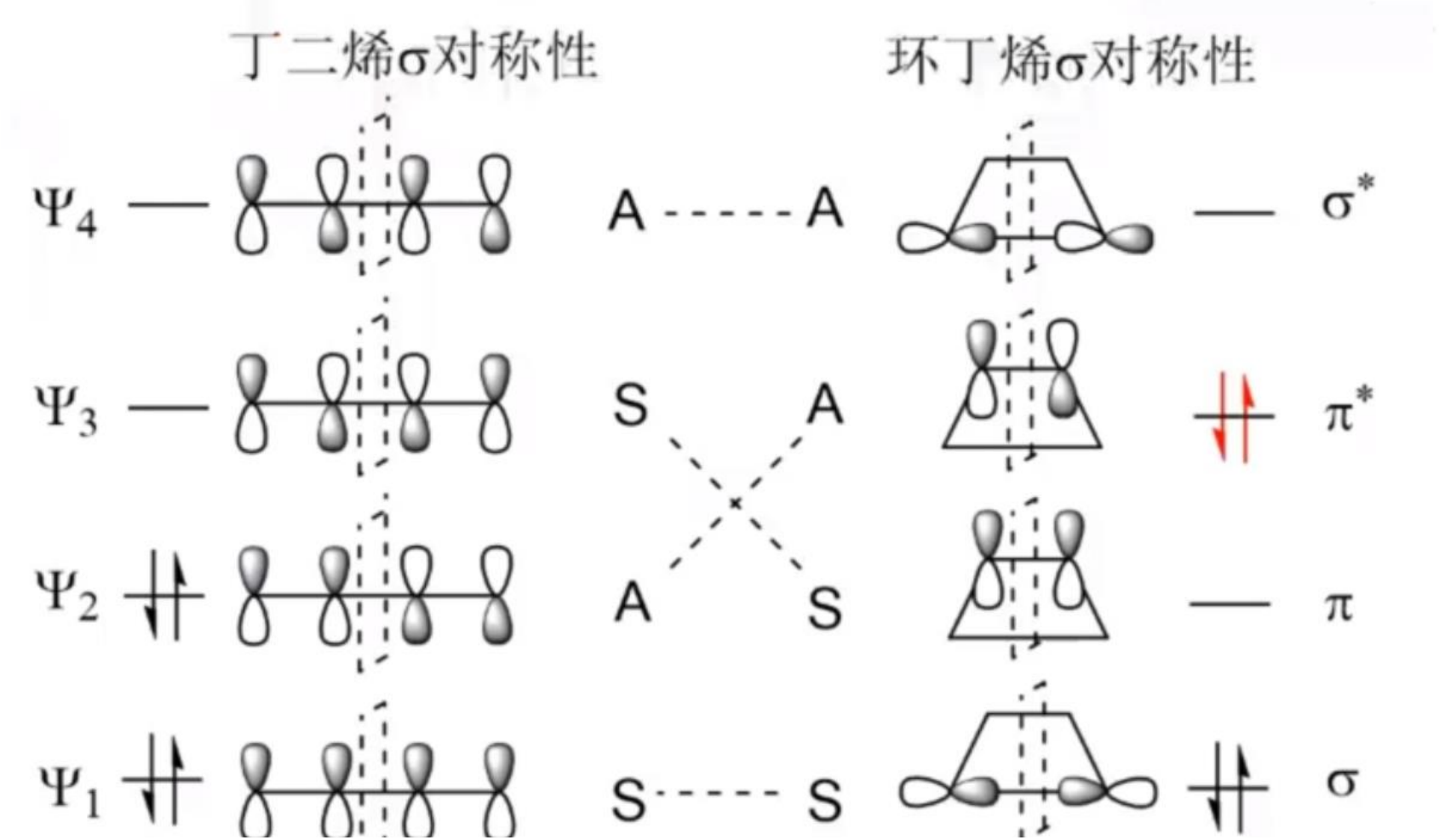
顺旋操作（轴对称操作）下的丁二烯和环丁烯分子轨道能级相关图



4n电子——加热——顺旋——保持轨道对称性守恒，能量有利！

6.2 Electrocyclic Reactions

对旋操作（面对称操作）下的丁二烯和环丁烯分子轨道能级相关图

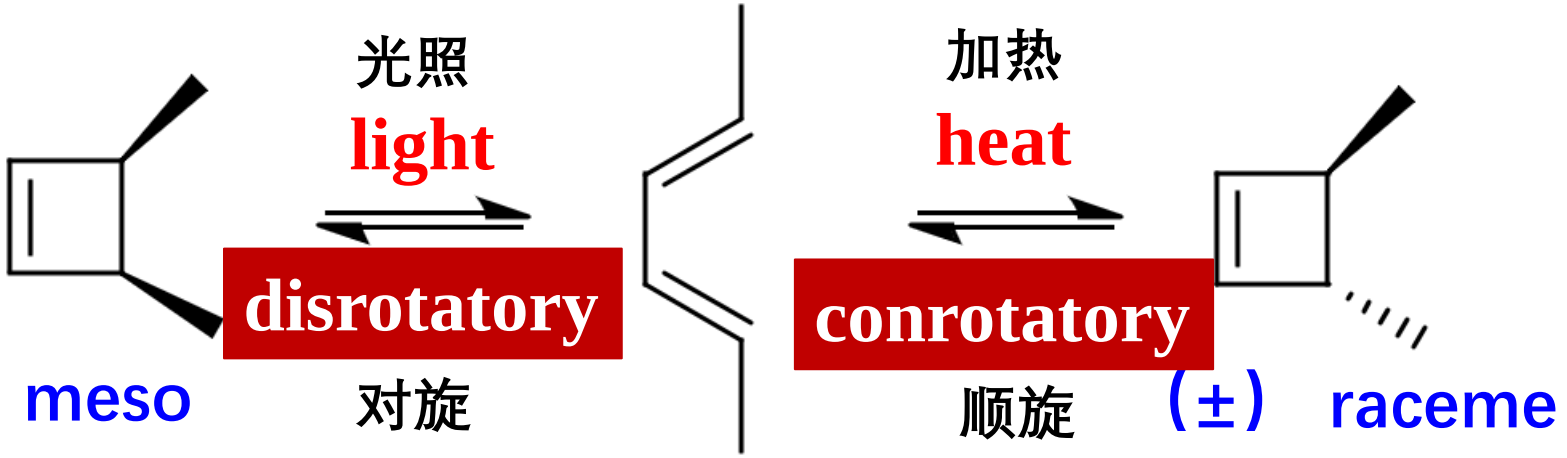


4n电子——加热——对旋——保持轨道对称性守恒，能量不利！

6.2 Electrocyclic Reactions

6.2.1 4n π electrocyclic reaction

Electrocyclic transformations are driven by heat or light



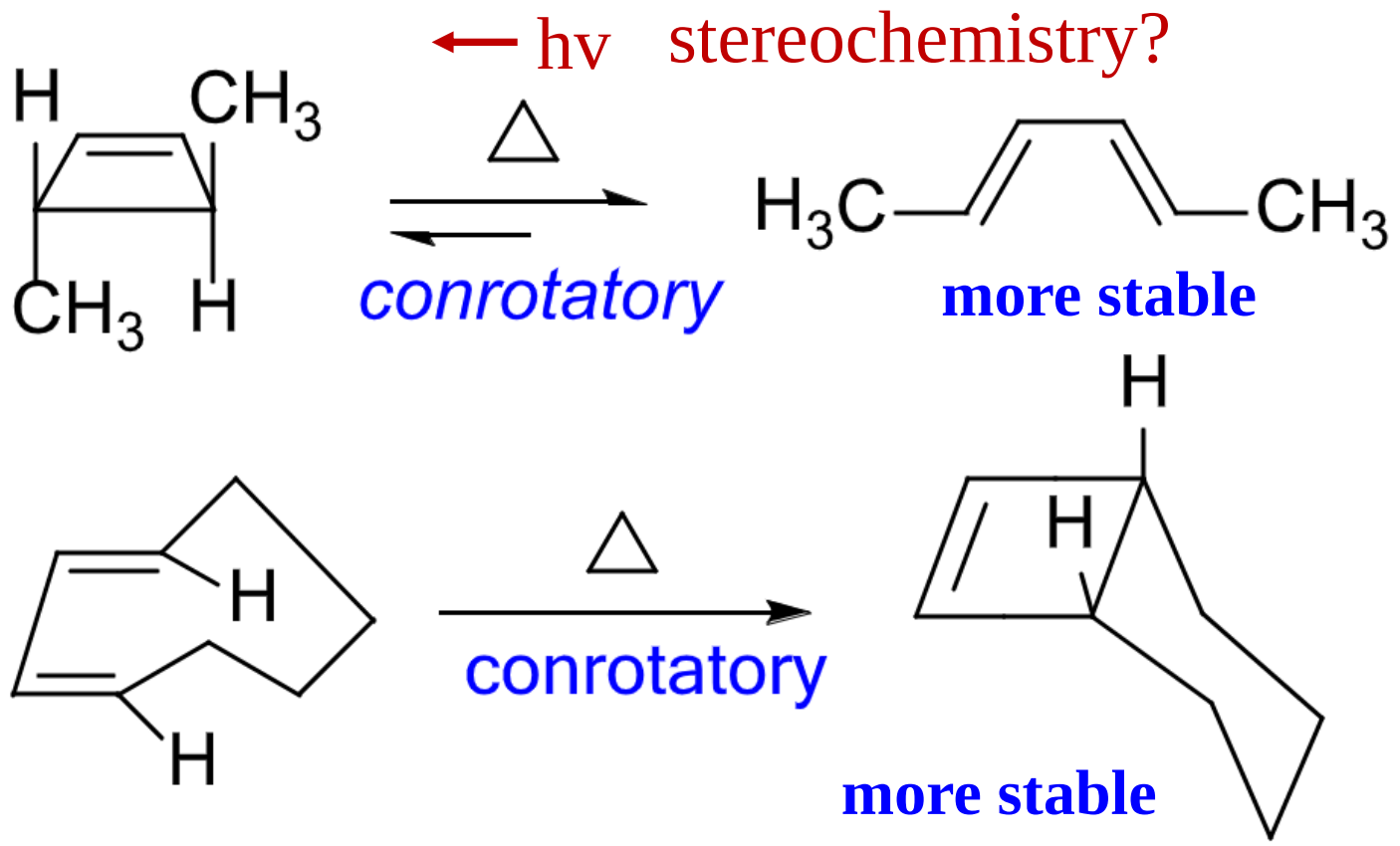
Electrocyclic reactions are concerted and stereospecific

One-step reaction, reversible

Heat conrotatory (加热顺旋), light disrotatory (光照对旋)

6.2 Electrocyclic Reactions

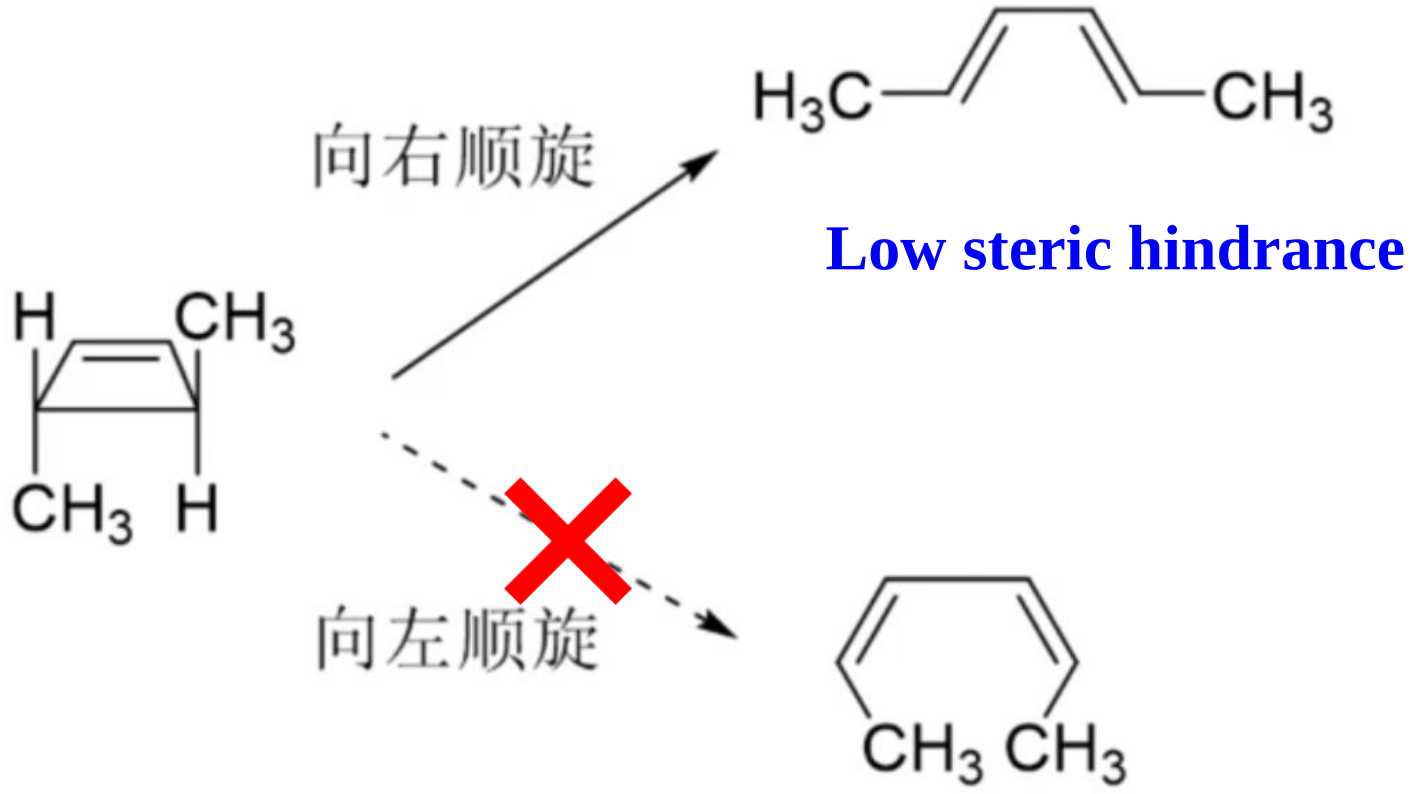
根据微观可逆性原则，正反应和你反应所经过的途径是相同的



Depends on which one is more stable

6.2 Electrocyclic Reactions

Torquoselectivity 扭转选择性



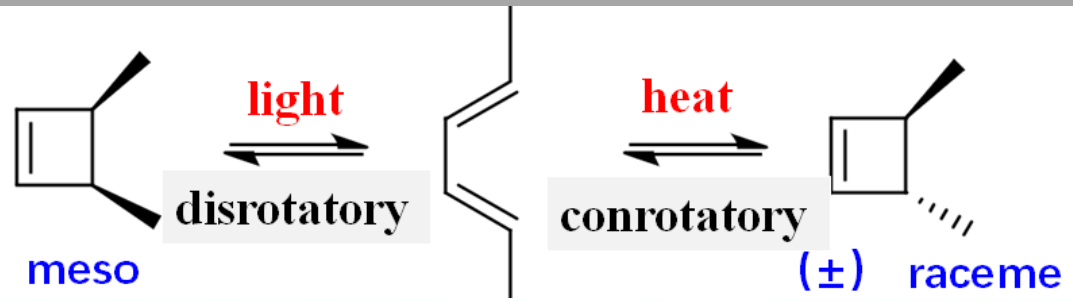
Low steric hindrance

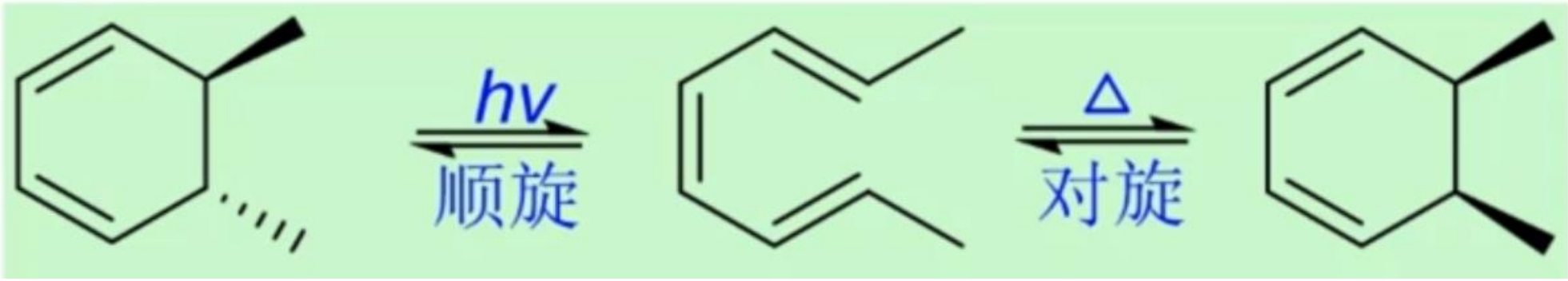
Depends on which one has less steric hindrance

6.2 Electrocyclic Reactions

6.2.2 4n+2 π electrocyclic reaction

Electrocyclic transformations are driven by heat or light





(±) raceme

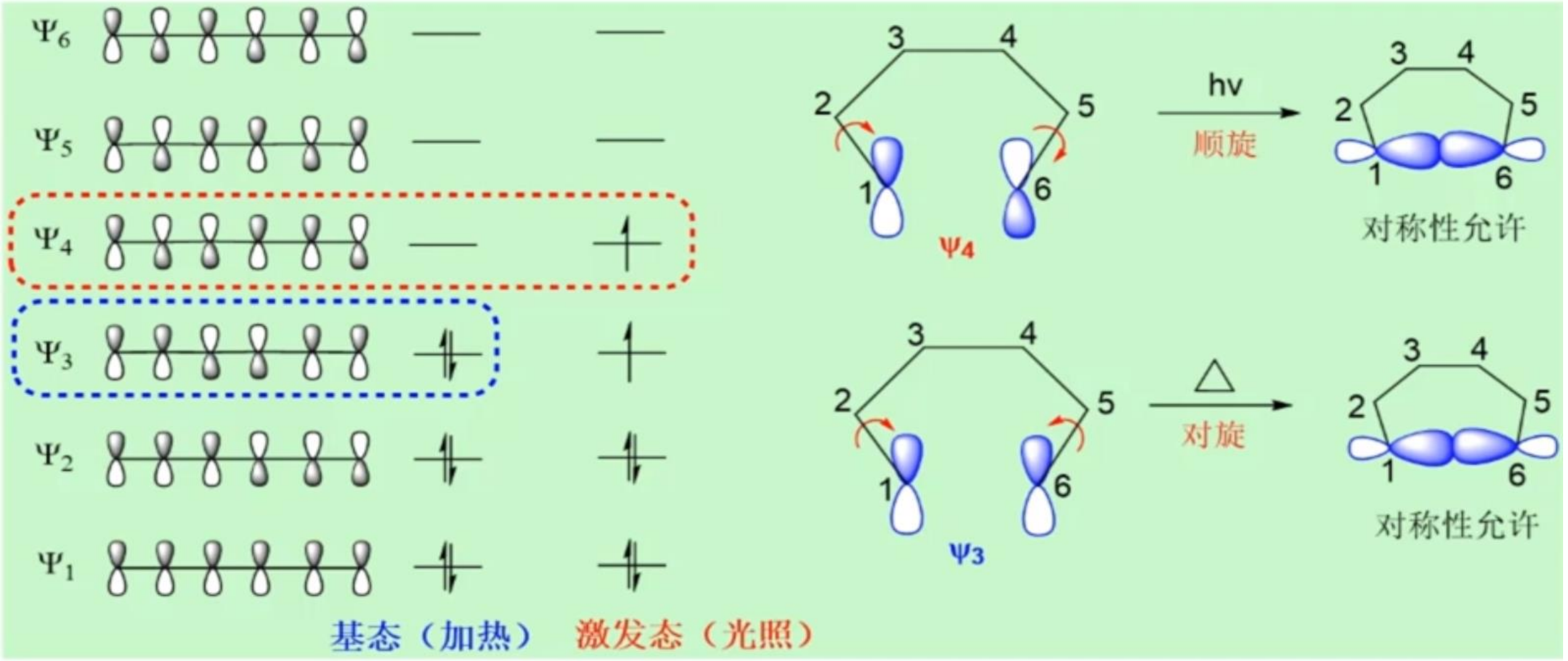
meso

Electrocyclic reactions are concerted and stereospecific

One-step reaction, reversible

Heat conrotatory (加热对旋), light disrotatory (光照顺旋)

Frontier Molecular Orbital Theory 4n+2 π



4n+2 π electrons, heat, disrotatory, bonding

4n+2 π electrons, light, conrotatory, bonding

6.2 Electrocyclic Reactions

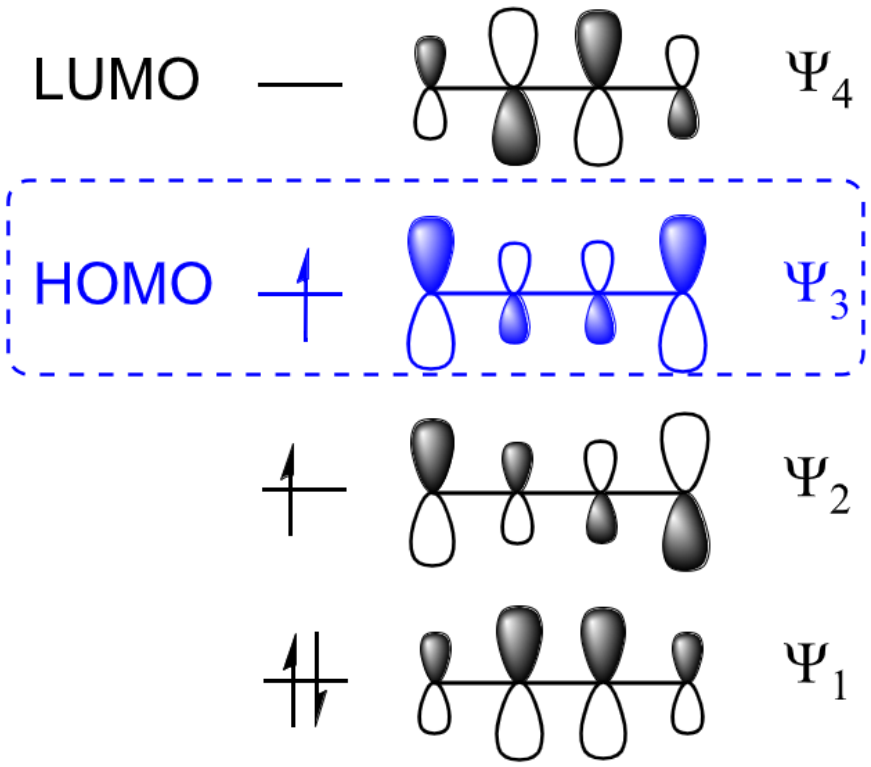
Woodward-Hoffman Rule (Electrocyclic reactions)

Table 14-2	Stereochemical Course of Electrocyclic Reactions (Woodward-Hoffmann Rules)	
Number of pairs of participating electrons	**Thermal process**	**Photochemical process**
Even	Conrotatory	Disrotatory
Odd	Disrotatory	Conrotatory

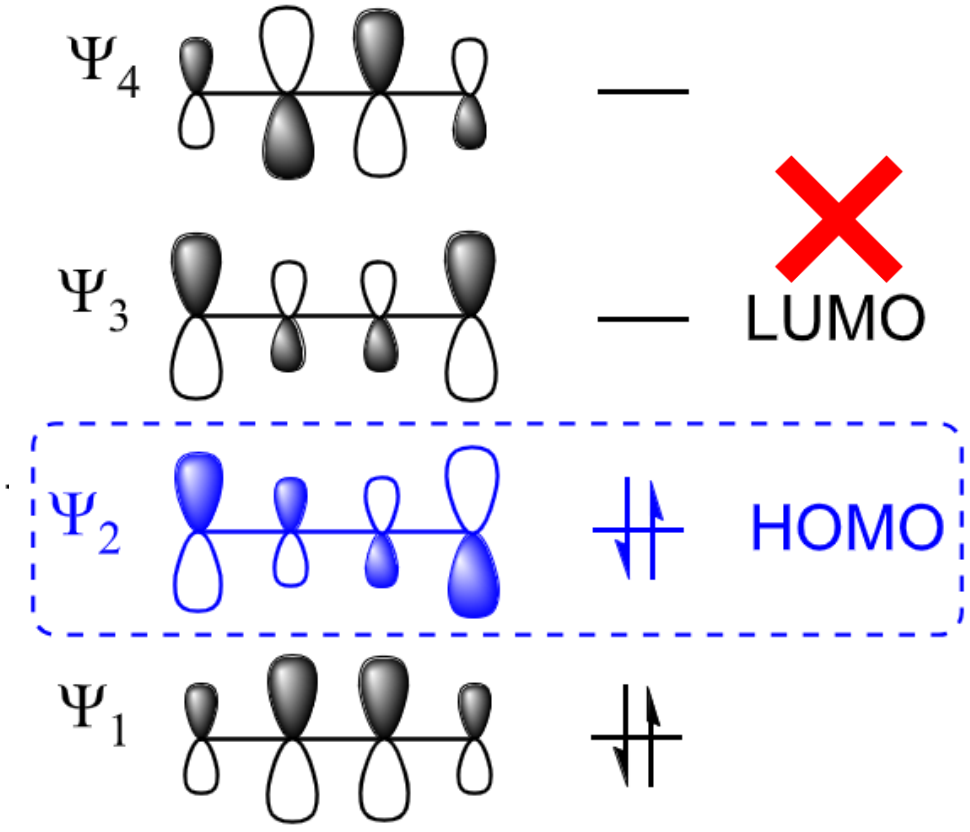
π electrons	heat	light
4n	顺旋 conrotatory	对旋 disrotatory
4n+2	对旋 disrotatory	顺旋 conrotatory

6.2 Electrocyclic Reactions

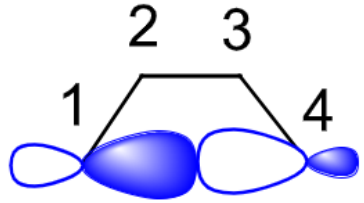
light



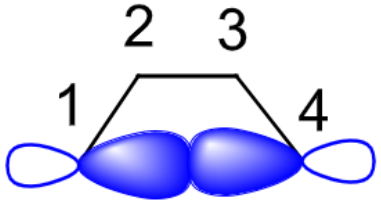
excited state (激发态，光照条件)



基态（加热）



对称性禁阻



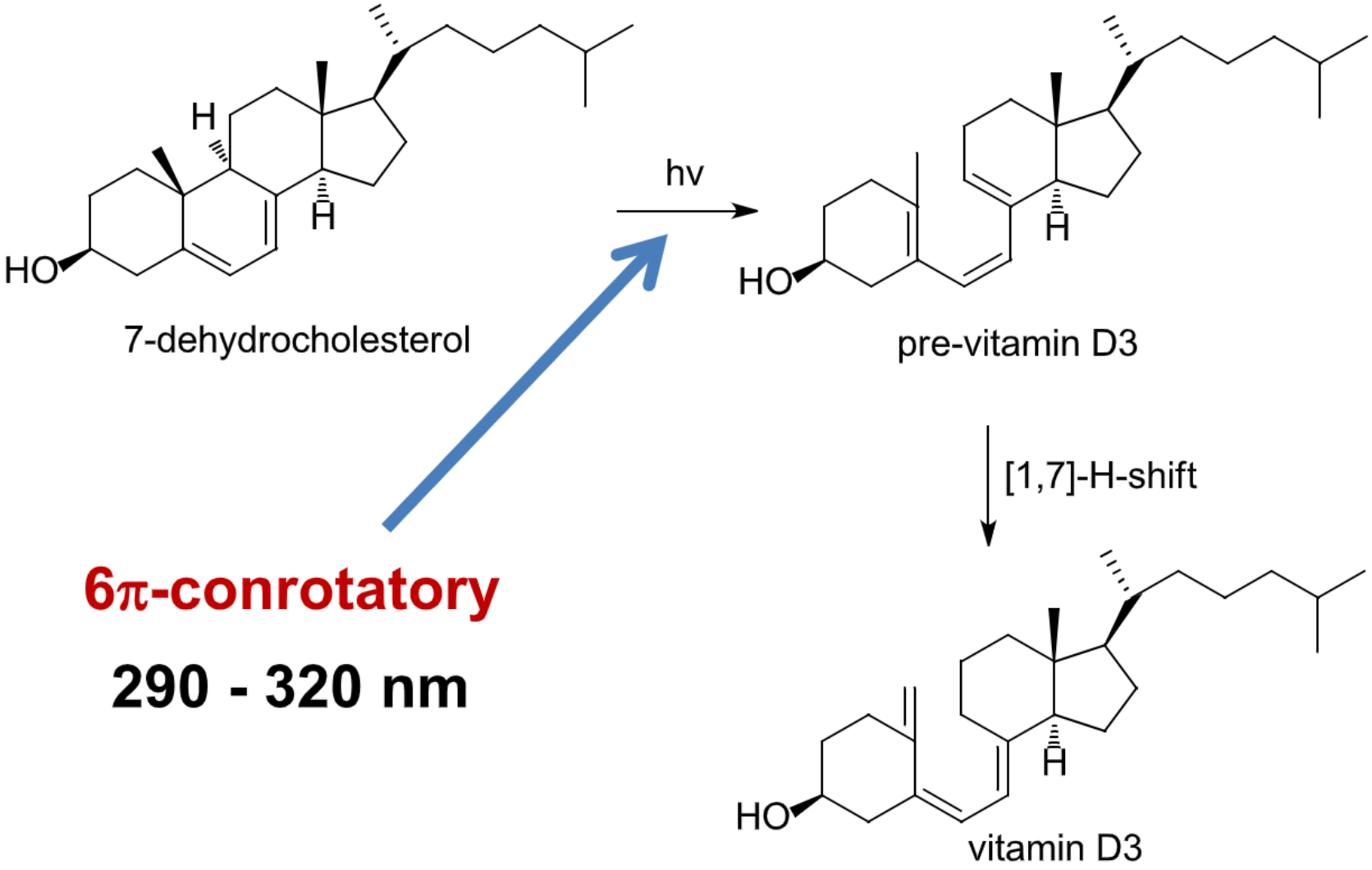
对称性允许

4n π electrons, light, disrotatory, bonding

6.2 Electrocyclic Reactions

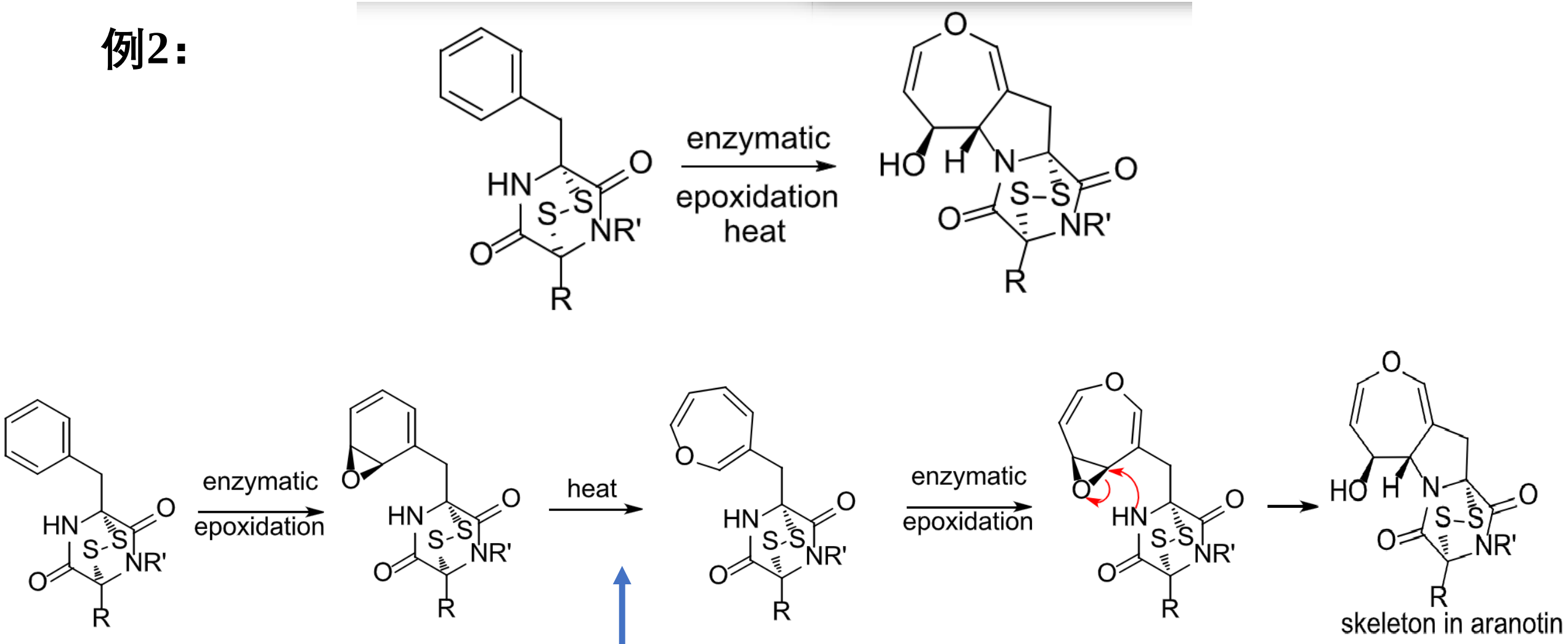
例1：

自然界中的电环化反应（维他命D3的合成）



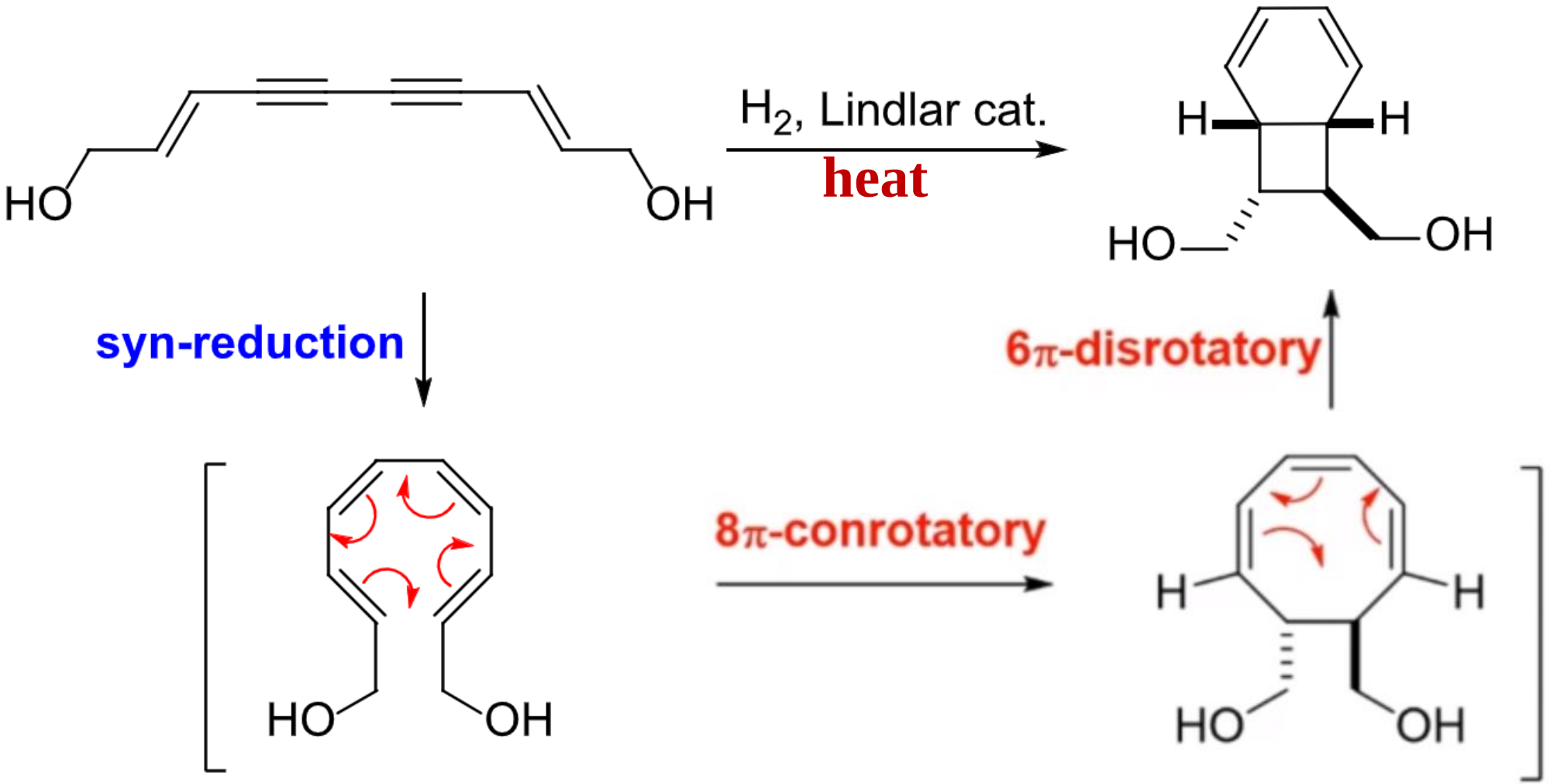
6.2 Electrocyclic Reactions

例2：

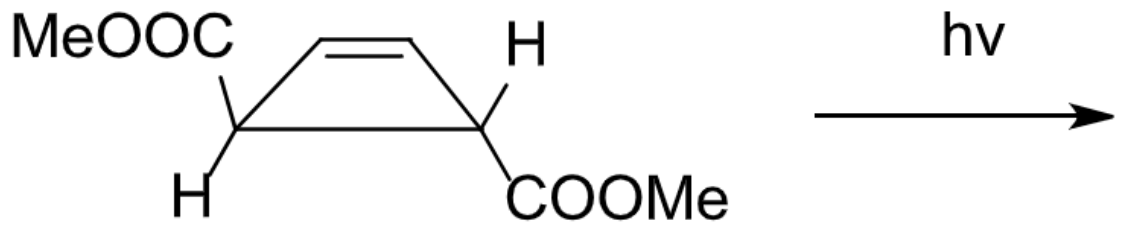


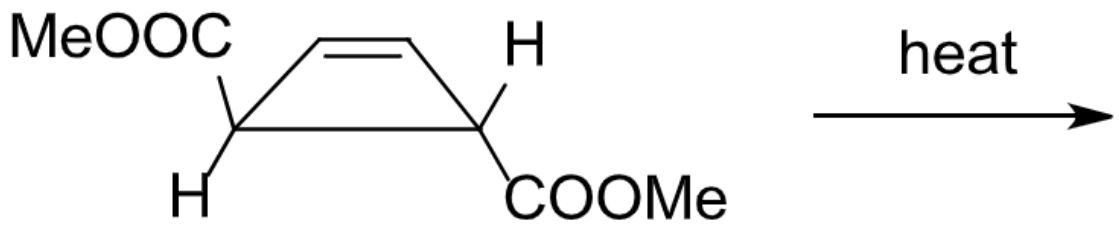
6.2 Electrocyclic Reactions

例3：

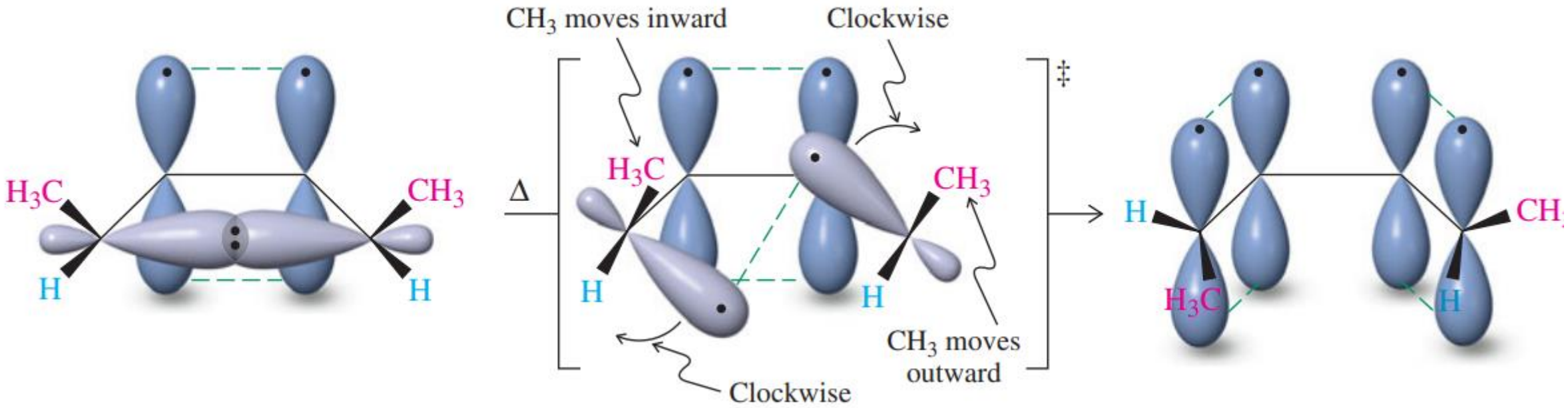


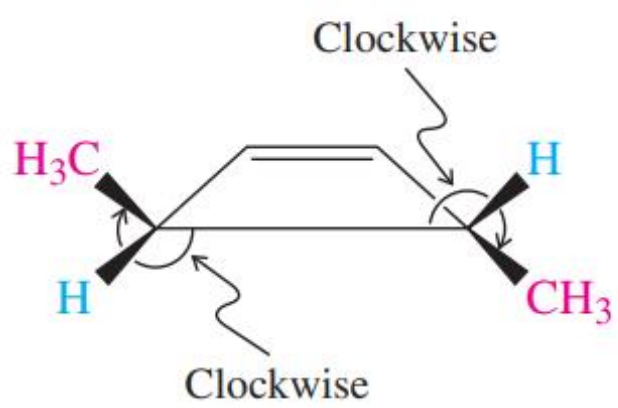
Exercise 1

1. 

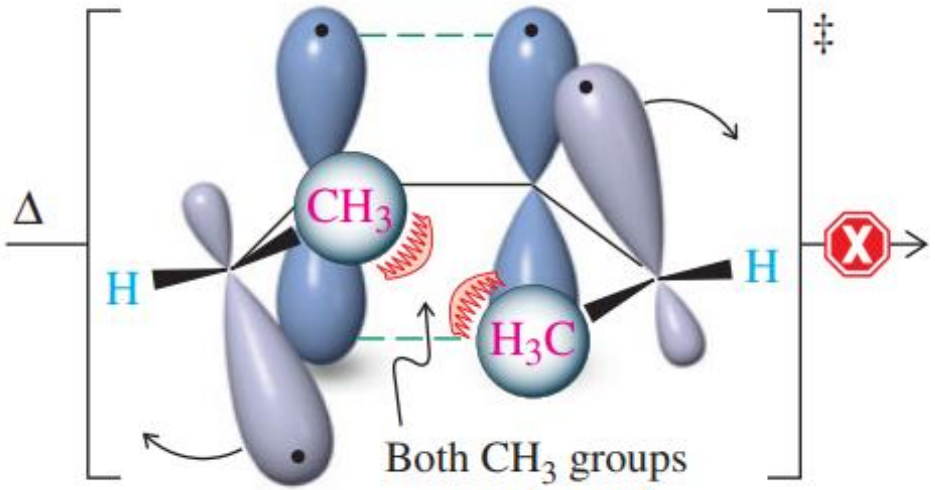
2. 

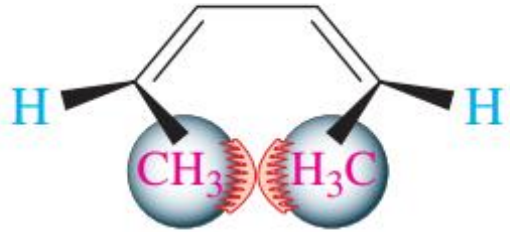
6.2 Electrocyclic Reactions





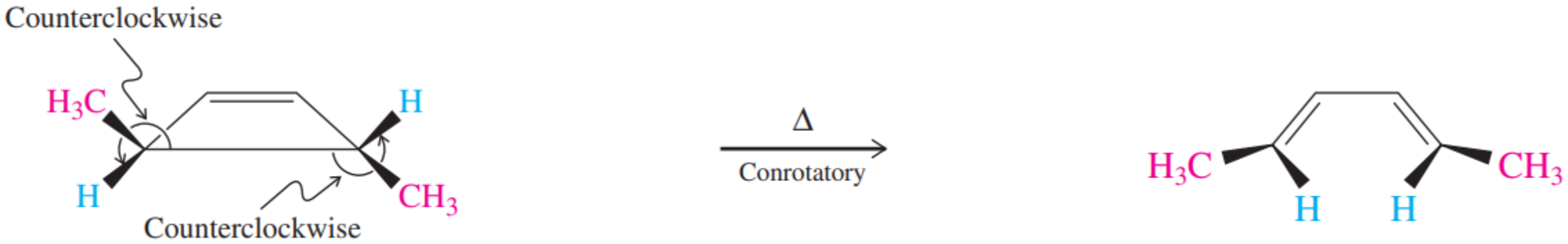
***trans*-3,4-Dimethylcyclobutene**





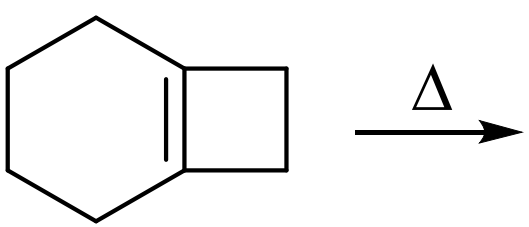
***trans,trans*-2,4-Hexadiene**

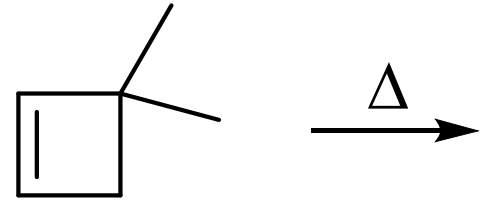
6.2 Electrocyclic Reactions

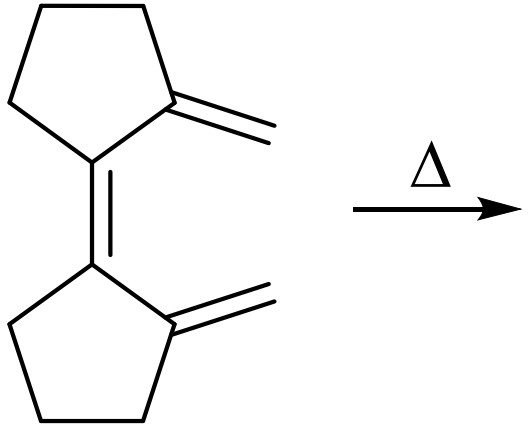


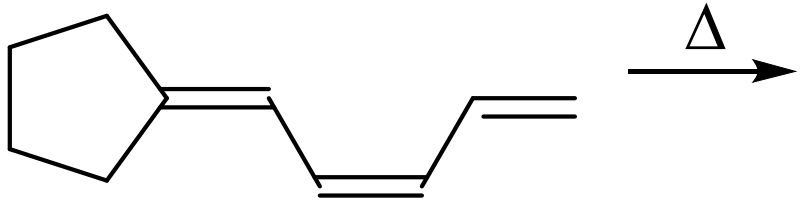
Exercise 2

Give the products obtained on heating the following compounds.



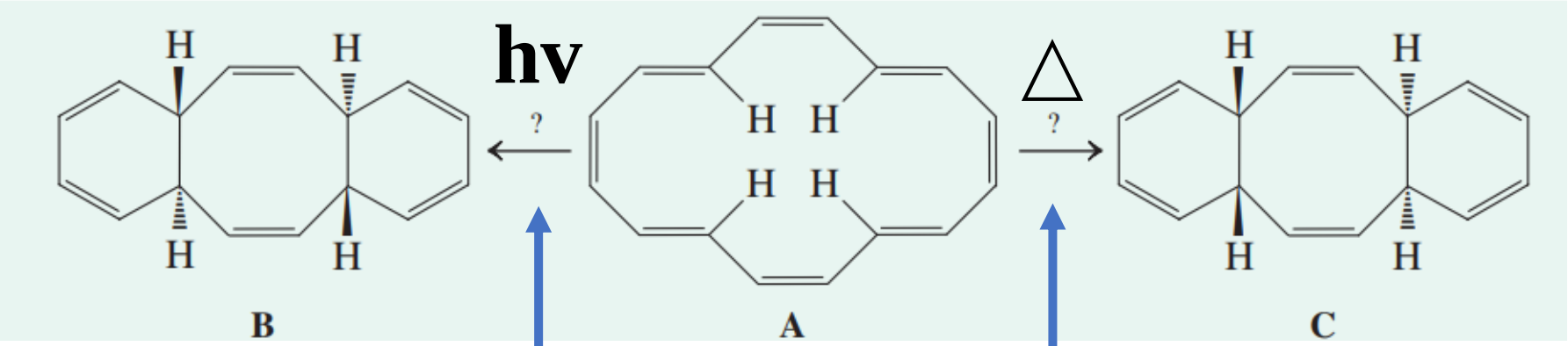






Exercise 3

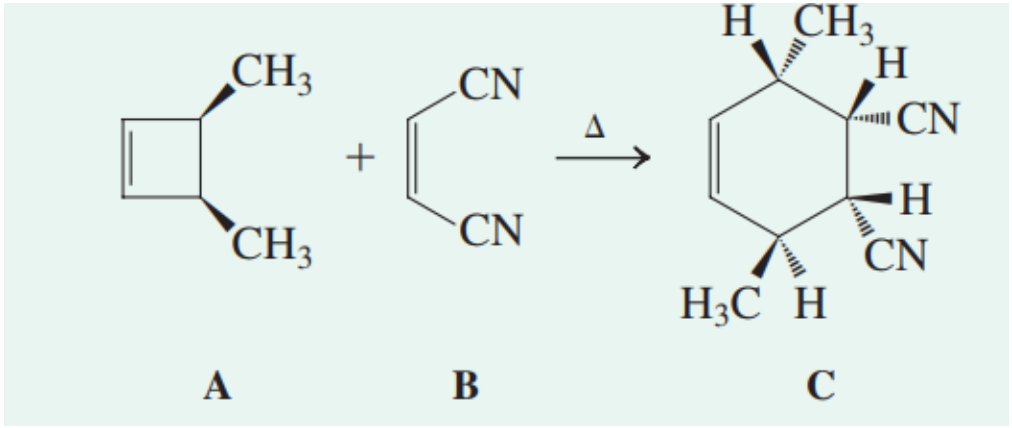
The cyclic polyene **A** can be converted to either **B** or **C** by a sequence of electrocyclic ring closures, depending on whether light or heat are used. Identify the conditions necessary to effect either transformation and identify each step as either con- or disrotatory.

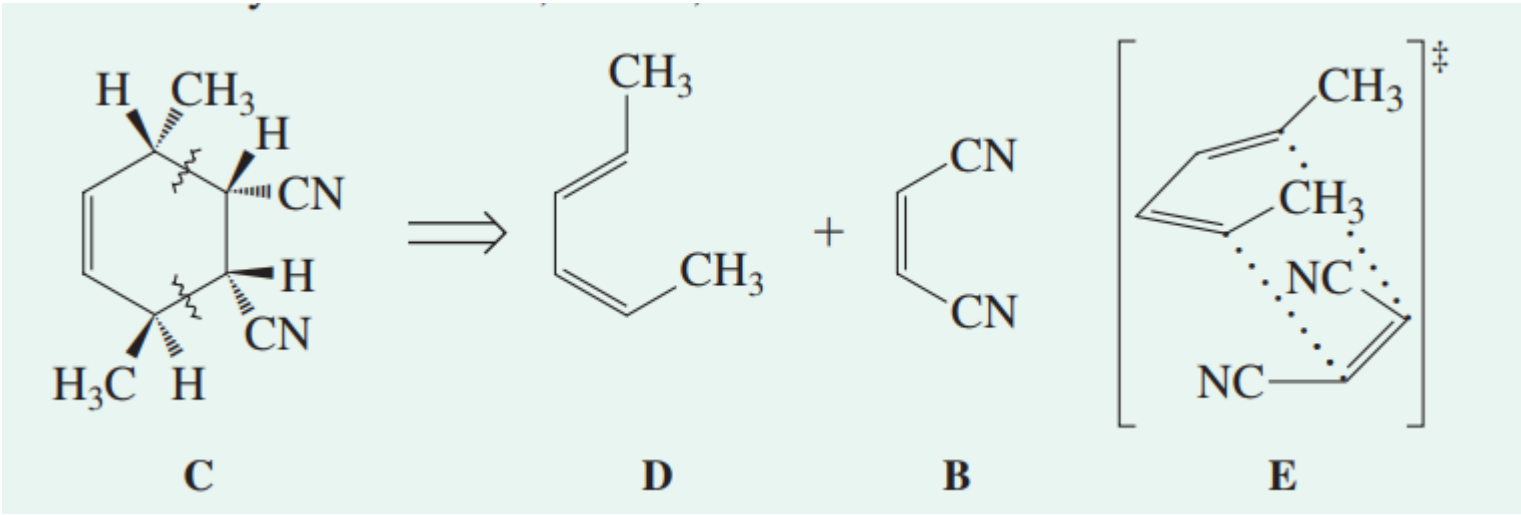


两个顺旋闭环　　两个对旋闭环

Exercise 4

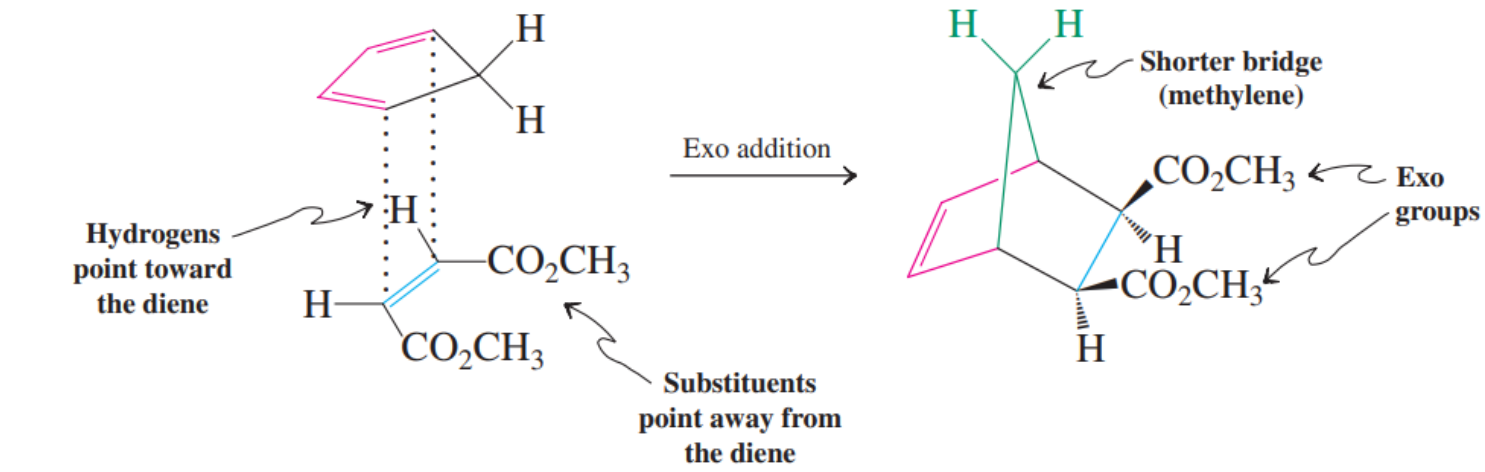
Heating cis-3,4-dimethylcyclobutene, A, in the presence of dienophile B gave exclusively the diastereomer C. Explain by a mechanism.





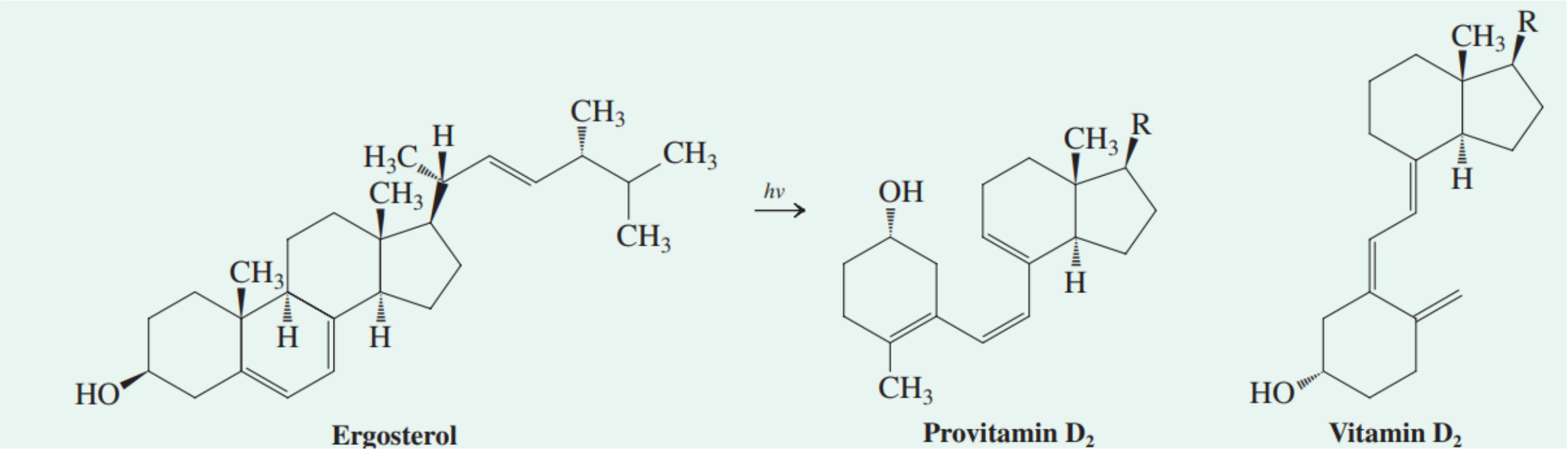
Exercise 4

Diels-Alder cycloadditions follow the endo rule



Exercise 5

Irradiation of ergosterol gives provitamin D2, a precursor of vitamin D2 (a deficiency of which causes softening of the bones, especiallyin children). Is the ring opening conrotatory or disrotatory?



Ergosterol **Provitamin D_2** **Vitamin D_2**