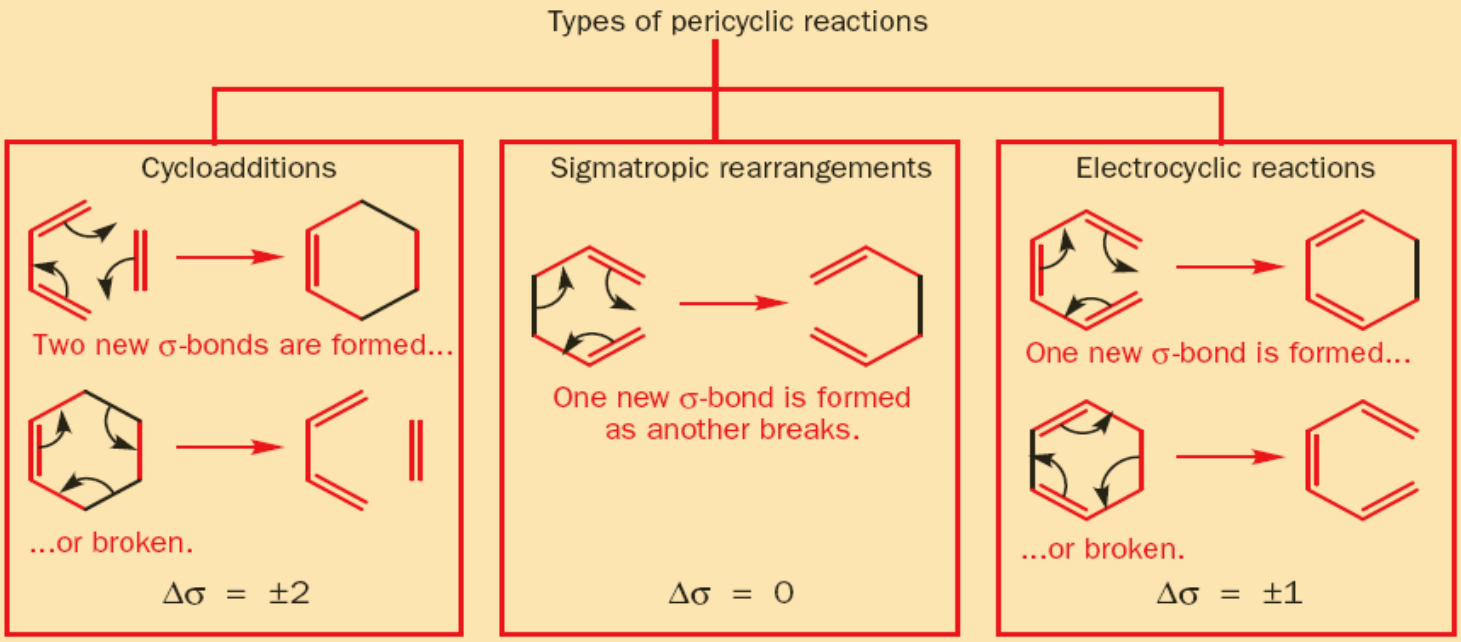
TÁMOP-4.1.1.F-14/1/KONV-2015-0006
SZTE TTIK, KTCS, 1a) Duális és moduláris képzésfejlesztés a mesterképzéshez

Periciklusos reakciók 2: elektrociklusos reakciók

Pálinkó István, egyetemi tanár

SZÉCHENYI 2020
MAGYARORSZÁG KORMÁNYA
Európai Unió
Európai Szociális Alap
BEFEKTETÉS A JÖVŐBE

The types of pericyclic reactions are distinguished by the number of σ bonds made or broken



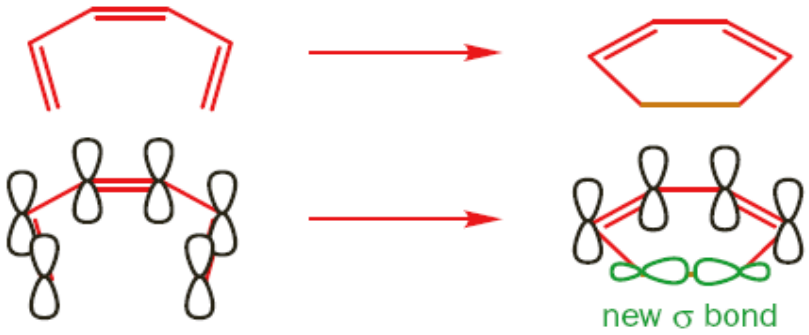
Electrocyclic reactions

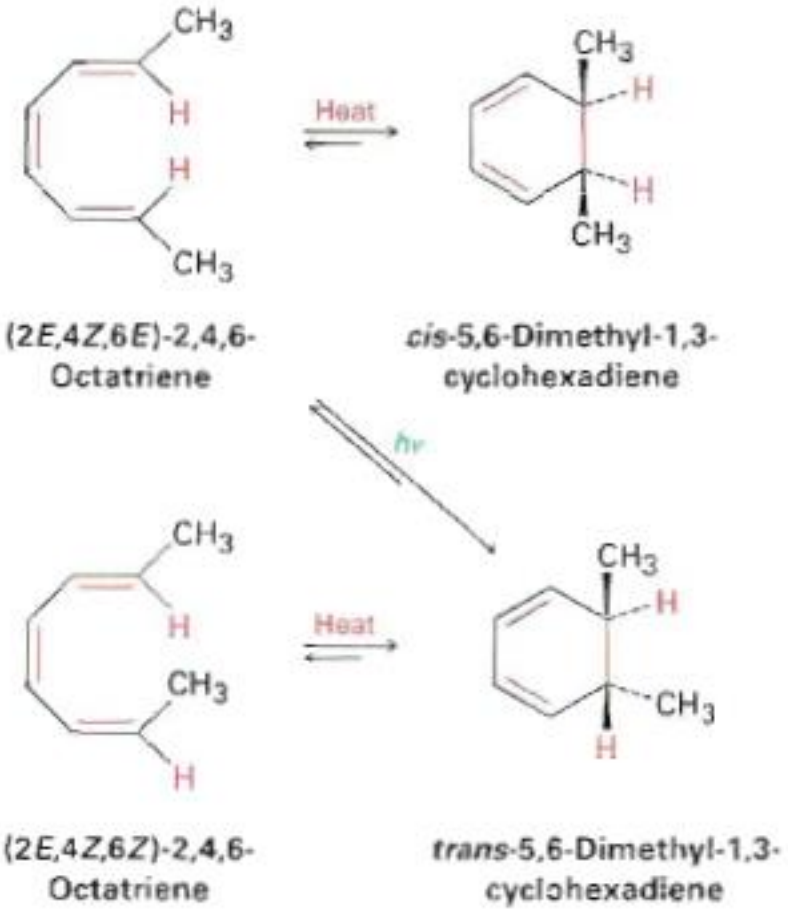
- An **electrocyclic reaction** is the formation of a new σ bond across the ends of a conjugated polyene or the reverse

It is important that you do not confuse electrocyclic reactions with pericyclic reactions. Pericyclic is the name for the family of reactions involving no charged intermediates in which the electrons go round the outside of the ring. *Electrocyclic* reactions, *cycloadditions*, and *sigmatropic* rearrangements are the three main classes of *pericyclic* reactions.

(4n+2) π elektronos rendszerek

nemcsak hő, hanem fénybesugárzás hatására is végbemegy


new σ bond


CH3
H
H
CH3
Heat
CH3
H
H
CH3
(2E,4Z,6E)-2,4,6-
Octatriene
cis-5,6-Dimethyl-1,3-
cyclohexadiene
hν
CH3
H
CH3
H
Heat
CH3
H
CH3
H
(2E,4Z,6Z)-2,4,6-
Octatriene
trans-5,6-Dimethyl-1,3-
cyclohexadiene

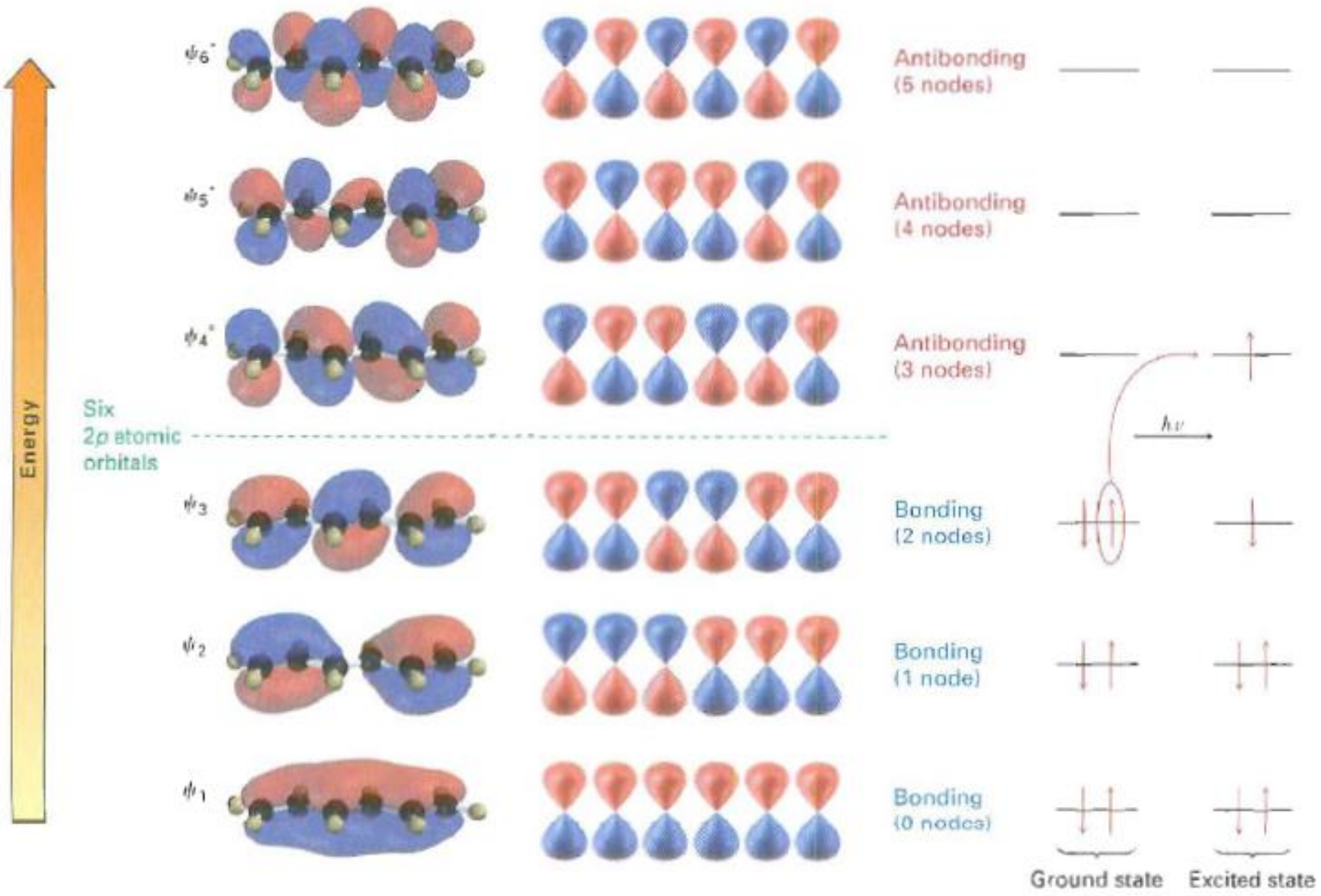
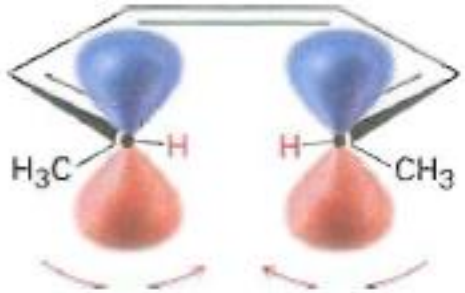


Figure 30.2 The six π molecular orbitals of 1,3,5-hexatriene. In the ground state, the three bonding MOs are filled. In the excited state, ψ_3 and ψ_4^* each have one electron.

A frontális molekulapálya modell a termikus ciklizációra [(4n+2) π elektron]

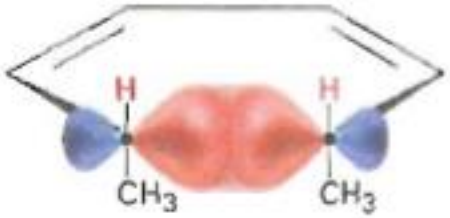
a HOMO



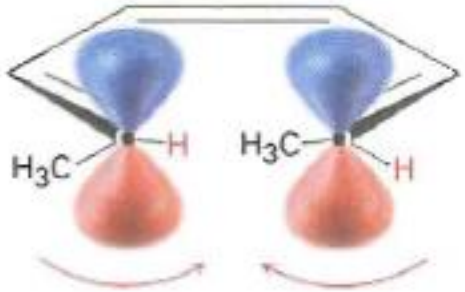
(2*E*,4*Z*,6*E*)-2,4,6-Octatriene

Heat

(Disrotatory)



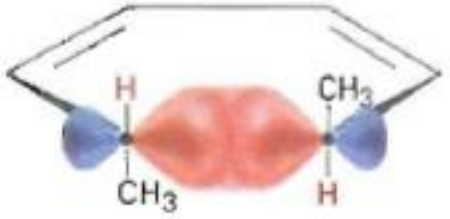
cis-5,6-Dimethyl-1,3-cyclohexadiene



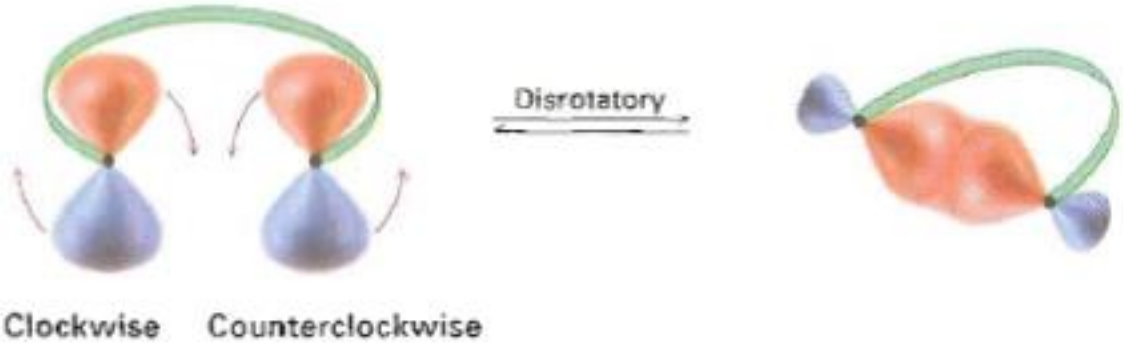
(2*E*,4*Z*,6*Z*)-2,4,6-Octatriene

Heat

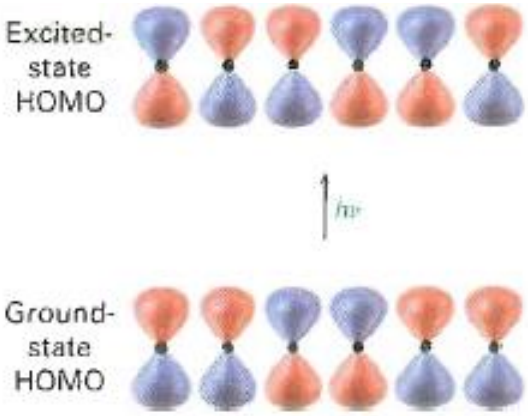
(Disrotatory)

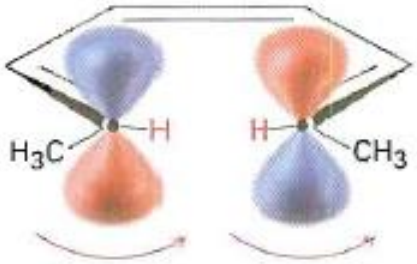


trans-5,6-Dimethyl-1,3-cyclohexadiene

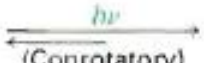

Disrotatory
Clockwise
Counterclockwise

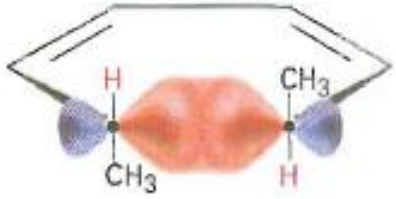
A frontális molekulapálya modell a fénybesugárzás hatására bekövetkező ciklizációra [(4n+2) π elektron]



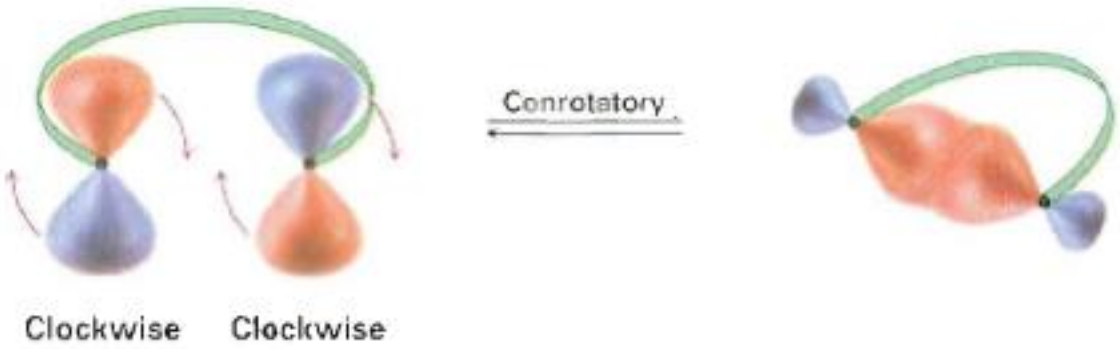


(2*E*,4*Z*,6*E*)-2,4,6-Octatriene

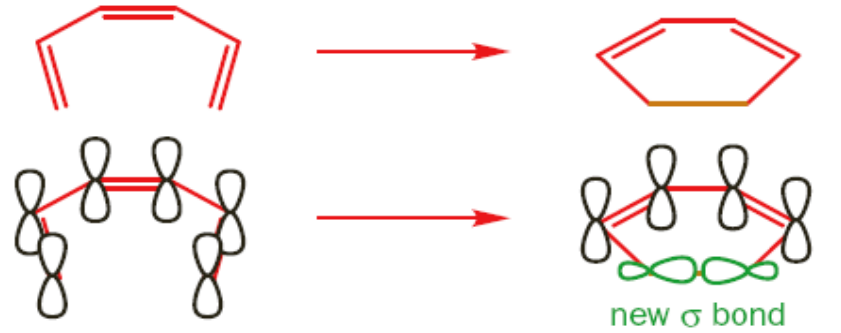




trans-5,6-Dimethyl-1,3-cyclohexadiene


Conrotatory
Clockwise
Clockwise

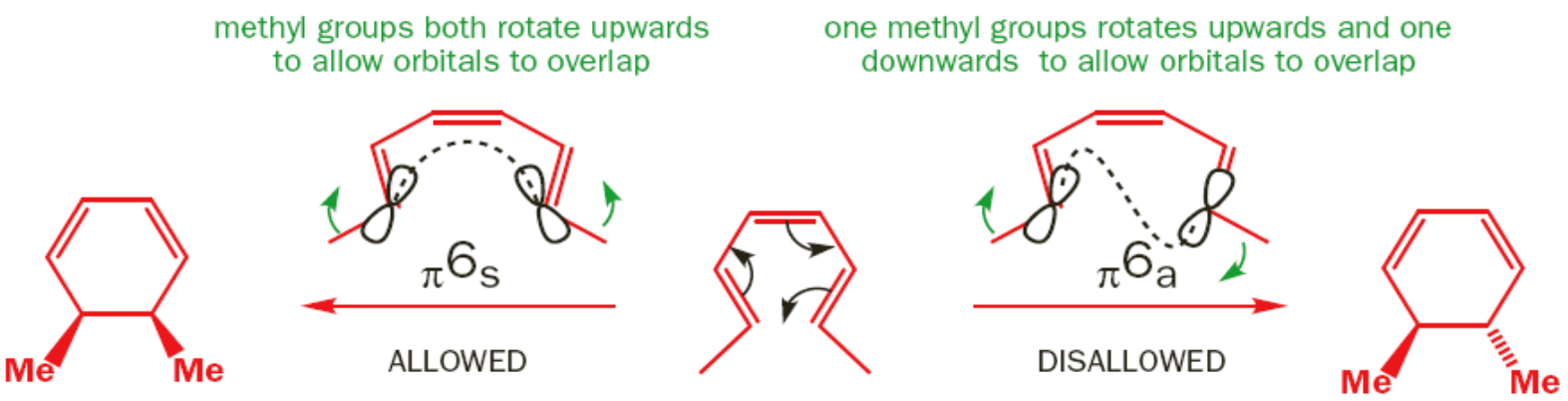
A Woodward-Hoffmann modell termikus elektrociklizációra (4n+2 π elektron)


new σ bond

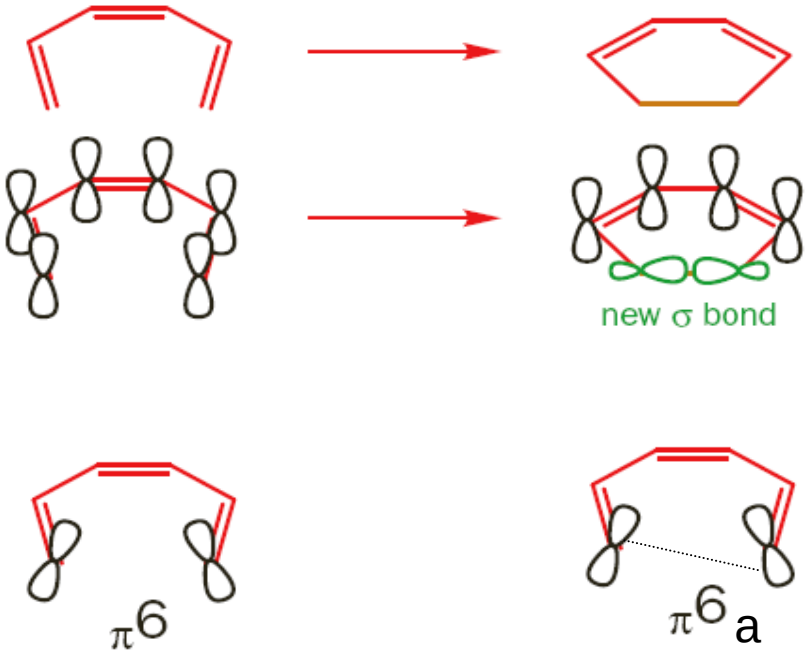

π6
π6s

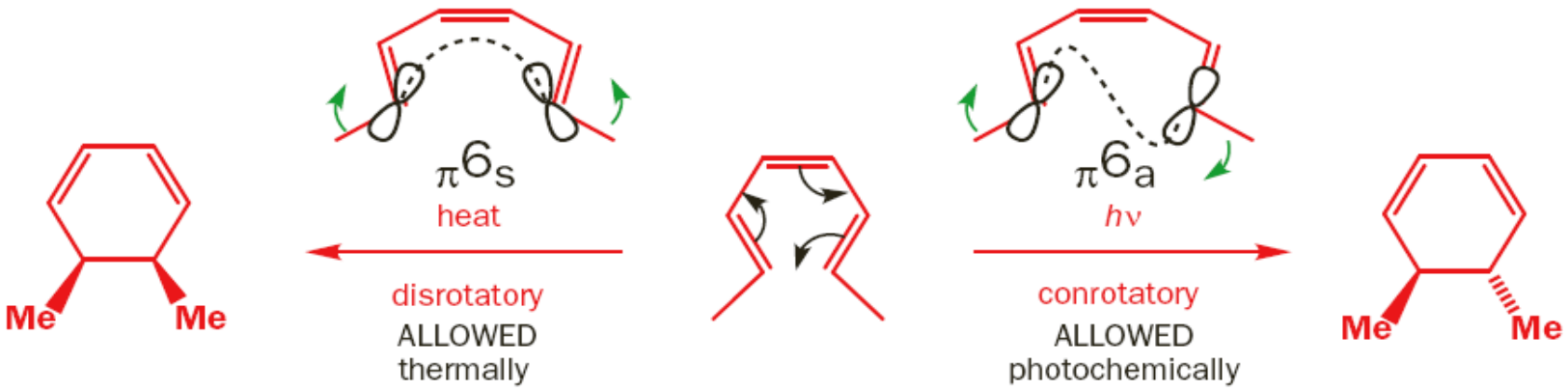
Woodward–Hoffmann rules

In a thermal pericyclic reaction the total number of $(4q + 2)_s$ and $(4r)_a$ components must be odd.


methyl groups both rotate upwards
to allow orbitals to overlap
one methyl groups rotates upwards and one
downwards to allow orbitals to overlap
Me
Me
π6s
ALLOWED
π6a
DISALLOWED
Me
Me

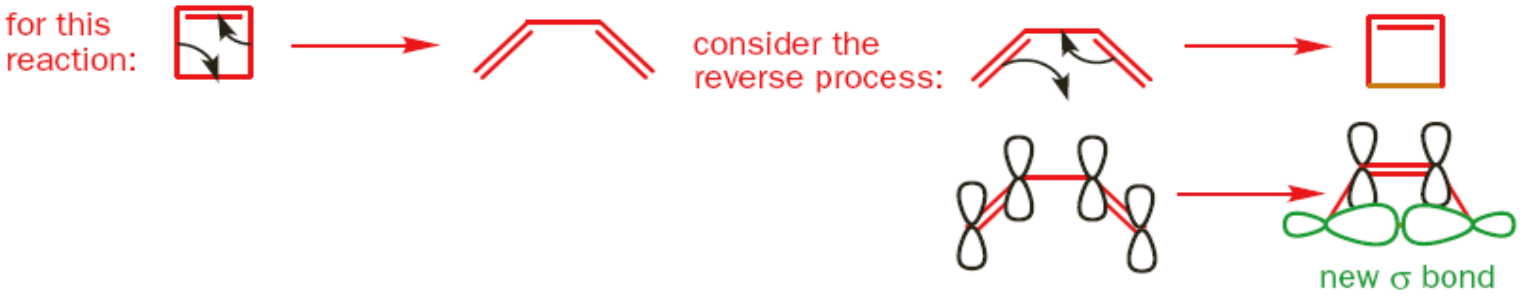
A Woodward-Hoffmann modell fény hatására végbemenő elektrociklizációra [(4n+2) π elektron]

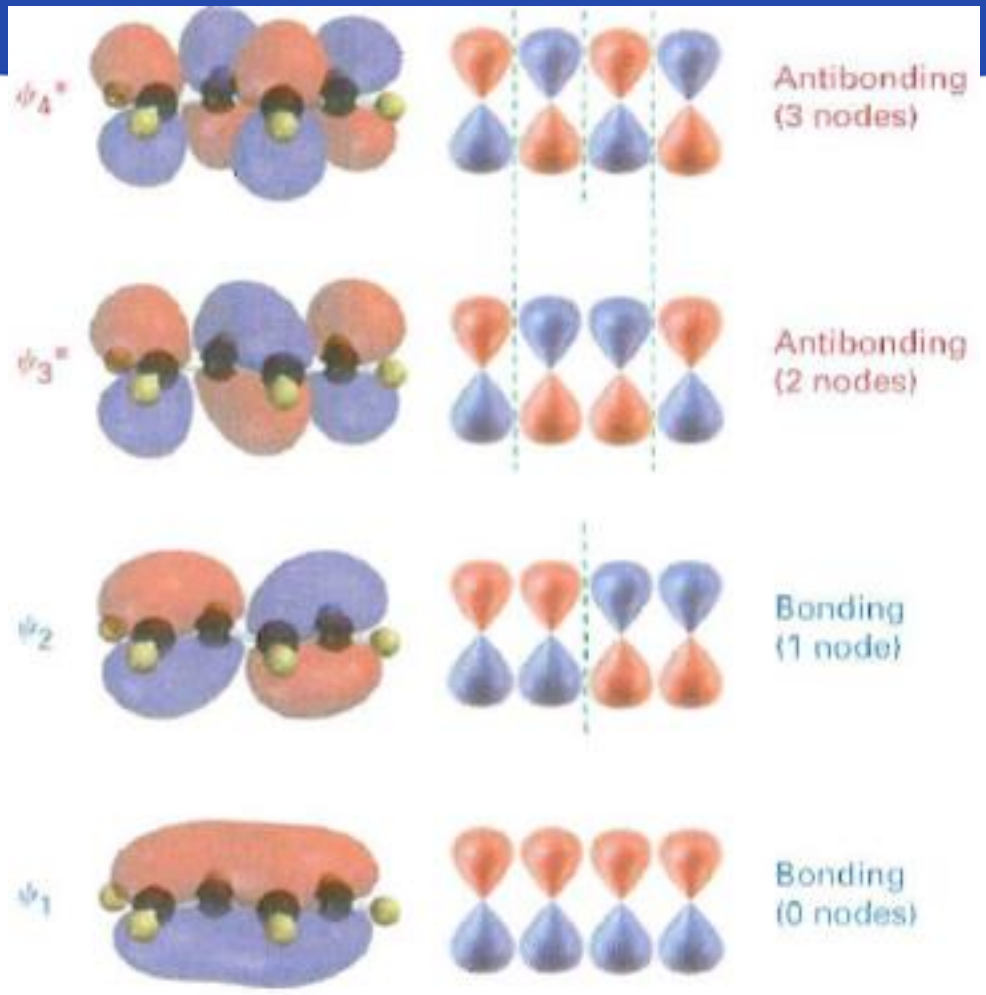

new σ bond
π6
π6a


Me
Me
π6s
heat
disrotatory
ALLOWED
thermally
π6a
hν
conrotatory
ALLOWED
photochemically
Me
Me

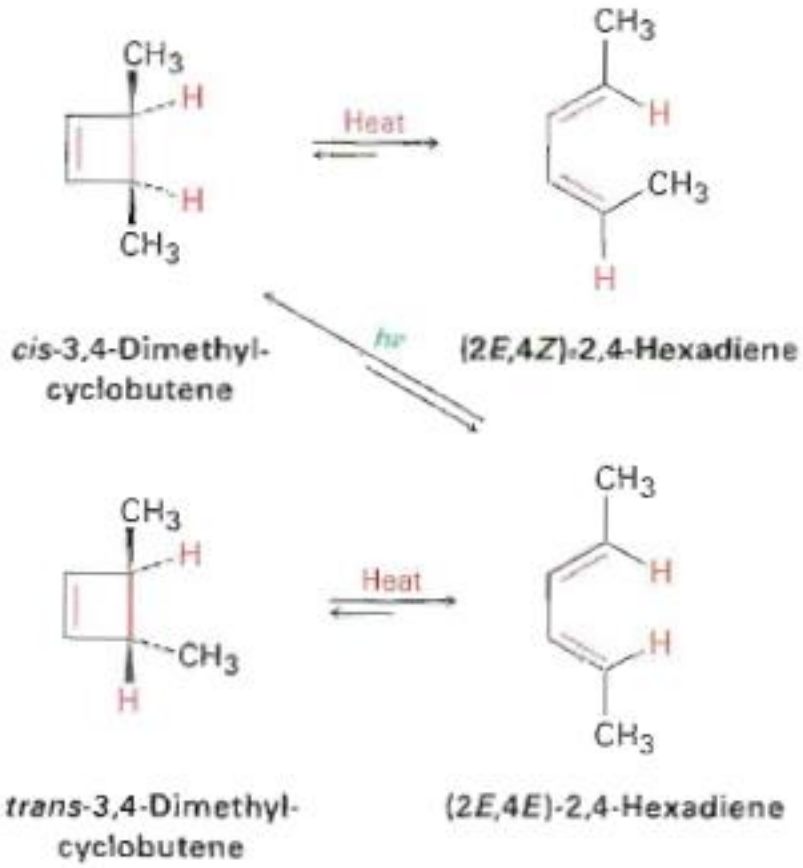
4n π elektronos rendszerek

nemcsak hő, hanem fénybesugárzás hatására is végbemegy

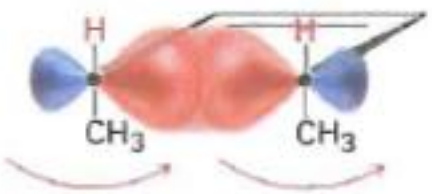

for this reaction:
consider the reverse process:
new σ bond



1,3-Butadiene

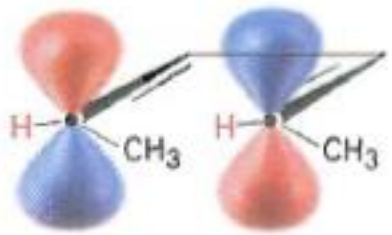

CH3
H
H
CH3
Heat
CH3
H
CH3
H
cis-3,4-Dimethyl-
cyclobutene
hν
(2E,4Z)-2,4-Hexadiene
CH3
H
CH3
H
Heat
CH3
H
H
CH3
trans-3,4-Dimethyl-
cyclobutene
(2E,4E)-2,4-Hexadiene

A frontális molekulapálya modell a termikus ciklizációra/ gyűrűfelnyílásra (4n π elektron)

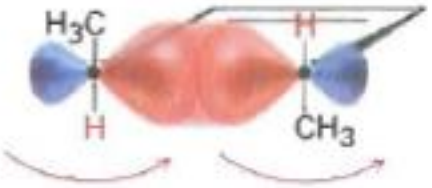


cis-3,4-Dimethylcyclobutene

Heat
(Conrotatory)

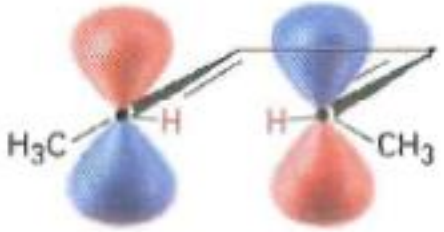


(2*E*,4*Z*)-2,4-Hexadiene

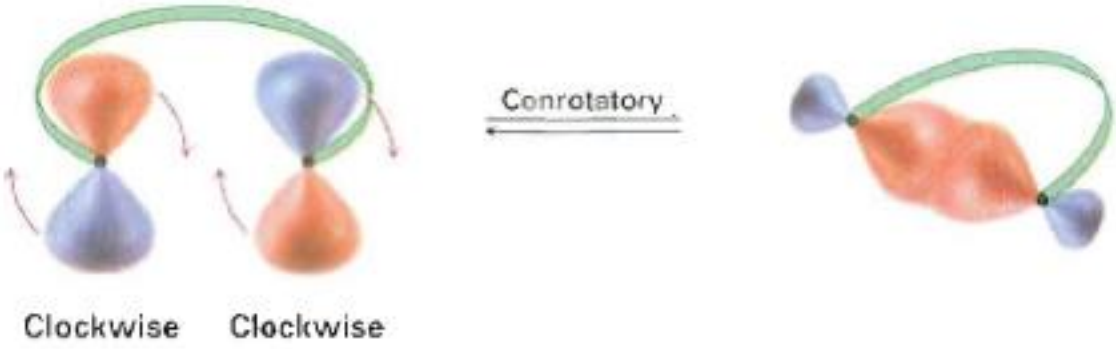


trans-3,4-Dimethylcyclobutene

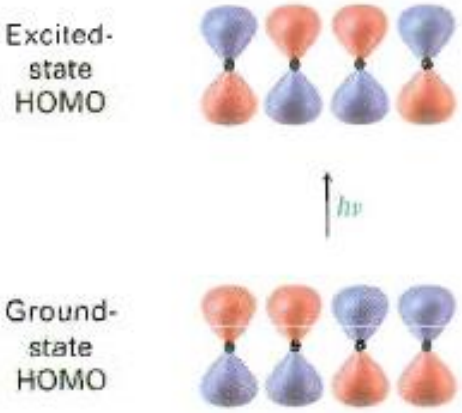
Heat
(Conrotatory)

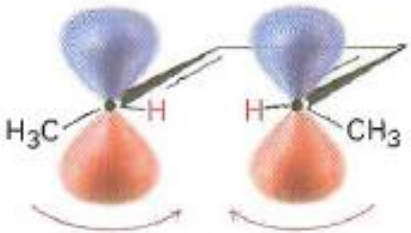


(2*E*,4*E*)-2,4-Hexadiene

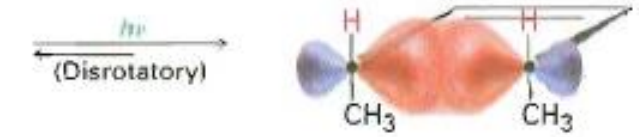

Conrotatory
Clockwise
Clockwise

A frontális molekulapálya modell a fénybesugárzás hatására bekövetkező ciklizációra/gyűrűfelnyílásra (4n π elektron)

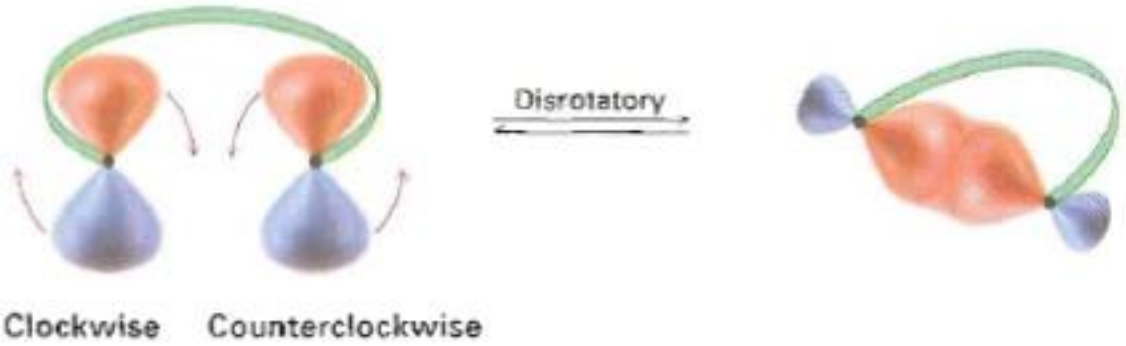




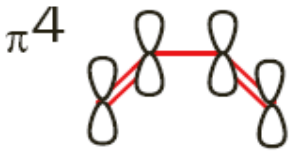
(2*E*,4*E*)-2,4-Hexadiene



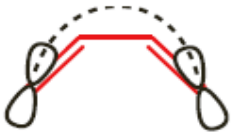
cis-3,4-Dimethylcyclobutene


Disrotatory
Clockwise
Counterclockwise

A Woodward-Hoffmann modell termikus elektrociklizációra/ gyűrűfelnyílásra (4n π elektron)


π4


π4


π4s

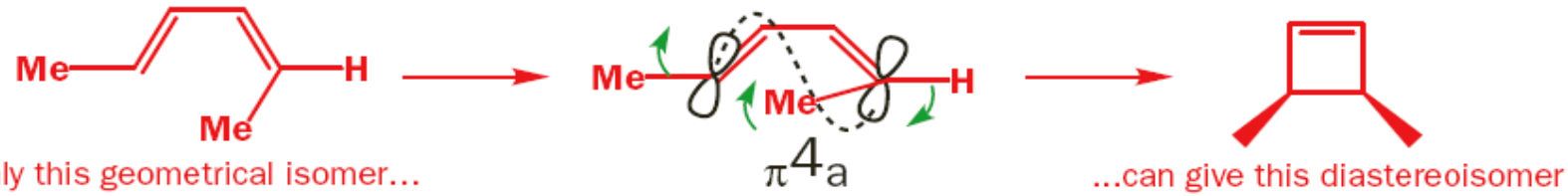

π4a

Woodward–Hoffmann rules

In a thermal pericyclic reaction the total number of $(4q + 2)_s$ and $(4r)_a$ components must be odd.

$\pi 4_a$

both methyl groups rotate upwards
to allow orbitals to overlap

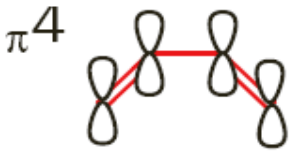


only this geometrical isomer...

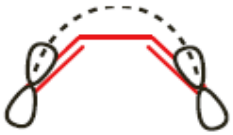
π^4_a

...can give this diastereoisomer

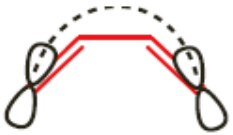
A Woodward-Hoffmann modell fény hatására végbemenő elektrociklizációra/gyűrűnyitásra (4n π elektron)


π4


π4


π4s

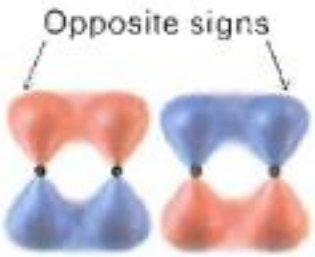

π4a



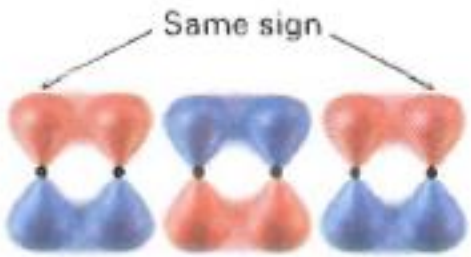
$\pi 4_S$

Rules for electrocyclic reactions

- All electrocyclic reactions are allowed
- Thermal electrocyclic reactions involving $(4n + 2)$ π electrons are *disrotatory*
- Thermal electrocyclic reactions involving $(4n)$ π electrons are *conrotatory*
- In *conrotatory* reactions the two groups rotate in the *same* way: *both* clockwise or *both* anticlockwise
- In *disrotatory* reactions, *one* group rotates *clockwise* and *one anticlockwise*

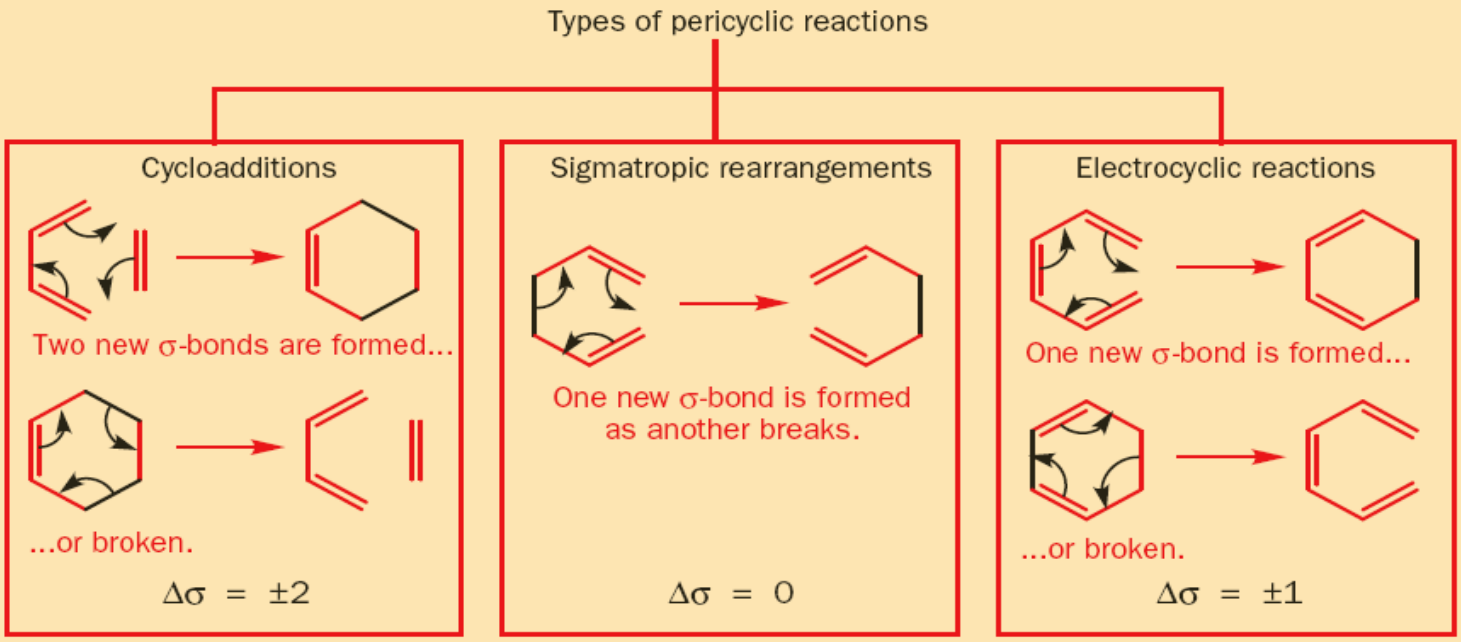


Diene HOMO



Triene HOMO

The types of pericyclic reactions are distinguished by the number of σ bonds made or broken



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SZÉCHENYI 2020

MAGYARORSZÁG KORMÁNYA

Európai Unió
Európai Szociális Alap

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