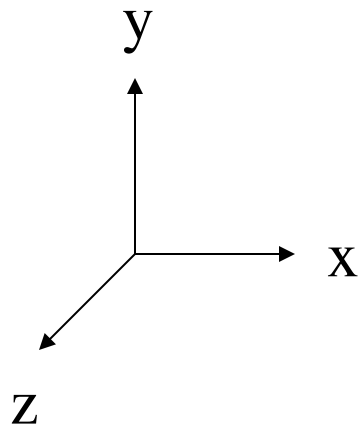


*More on:*

*Molecular Orbitals*

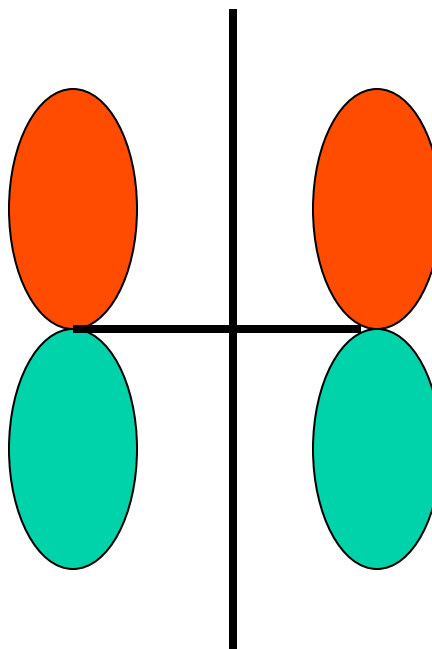
*Pericyclic Reactions*

*Electrocyclic Reactions*

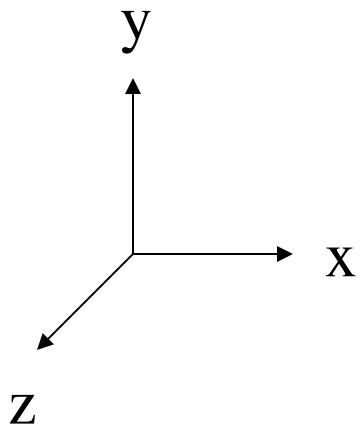


Pi Bonding MO  
(bond along x-axis;  
orbitals in xy plane)

mirror in yz plane

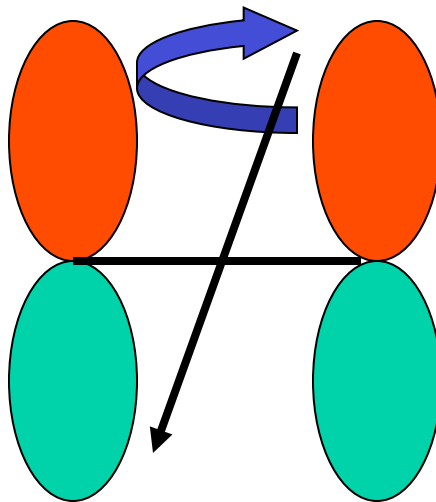


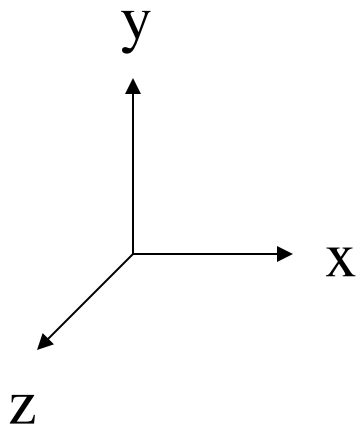
Symmetrical mirror plane (yz)



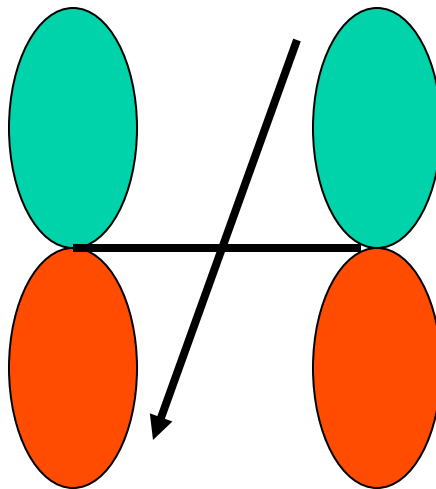
Pi Bonding MO  
(bond along x-axis;  
orbitals in xy plane)

rotate  $180^\circ$   
about z-axis  
in xy-plane

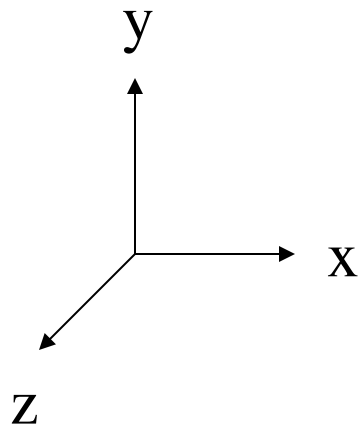




Pi Bonding MO  
(bond along x-axis;  
orbitals in xy plane)

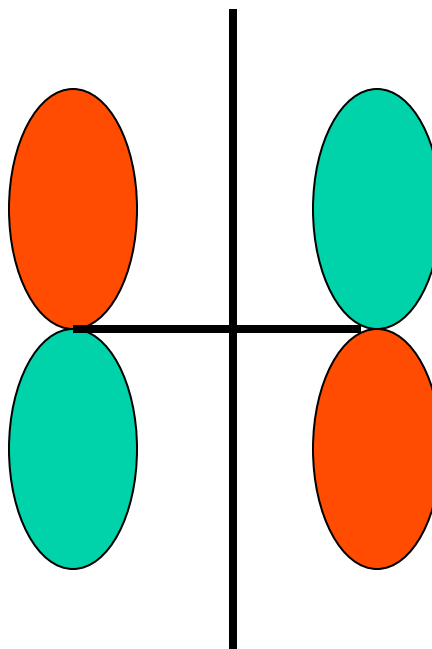


Antisymmetric about the  $C_2$  axis

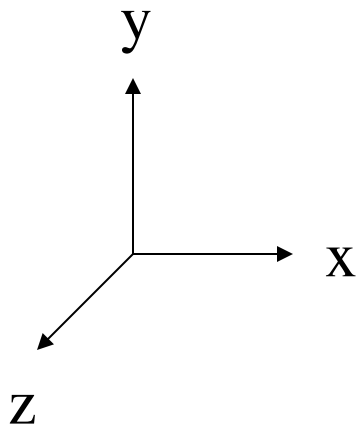


Pi Antibonding MO  
(bond along x-axis;  
orbitals in xy plane)

mirror in yz plane

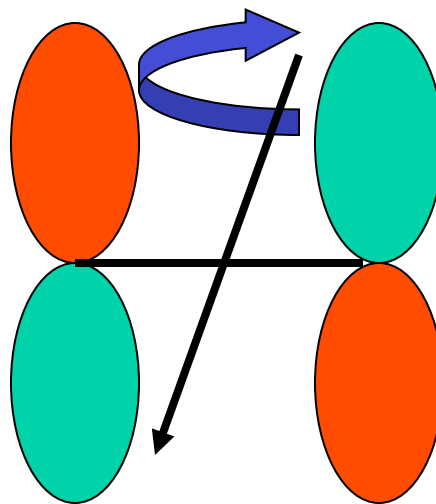


Antisymmetric mirror plane (yz)



Pi Bonding MO  
(bond along x-axis;  
orbitals in xy plane)

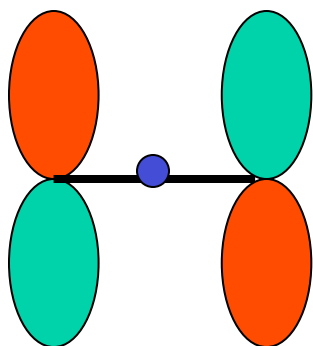
rotate  $180^\circ$   
about z-axis  
in xy-plane



Symmetric about  $C_2$  axis

# Pi Bond MO

Antibonding



node

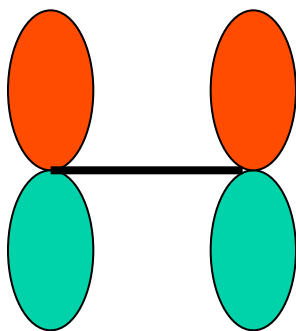
Mirror

A

$C_2$  - axis

S

Bonding

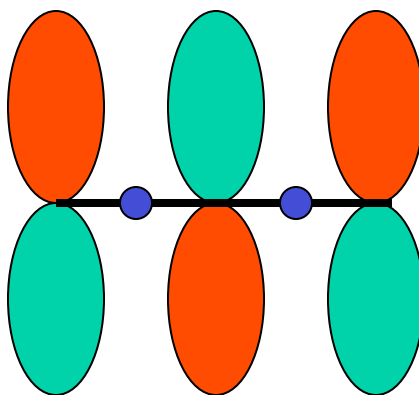


S

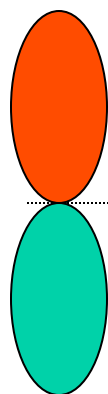
A

# Allylic Resonance

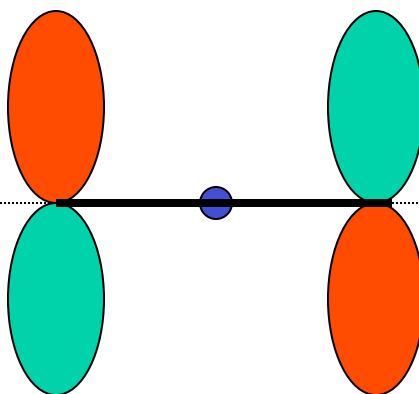
anti-bonding -  $\pi_3^*$   
 Energy of an  
 isolated p-orbital  
 2 nodes

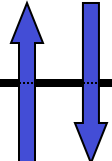


SA —

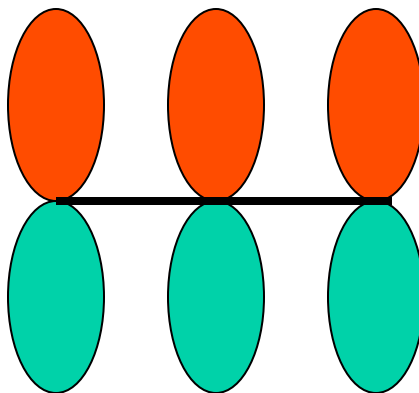


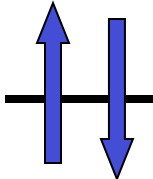
non-bonding -  $\pi_2$   
 1 node



AS 

bonding -  $\pi_1$   
 0 nodes

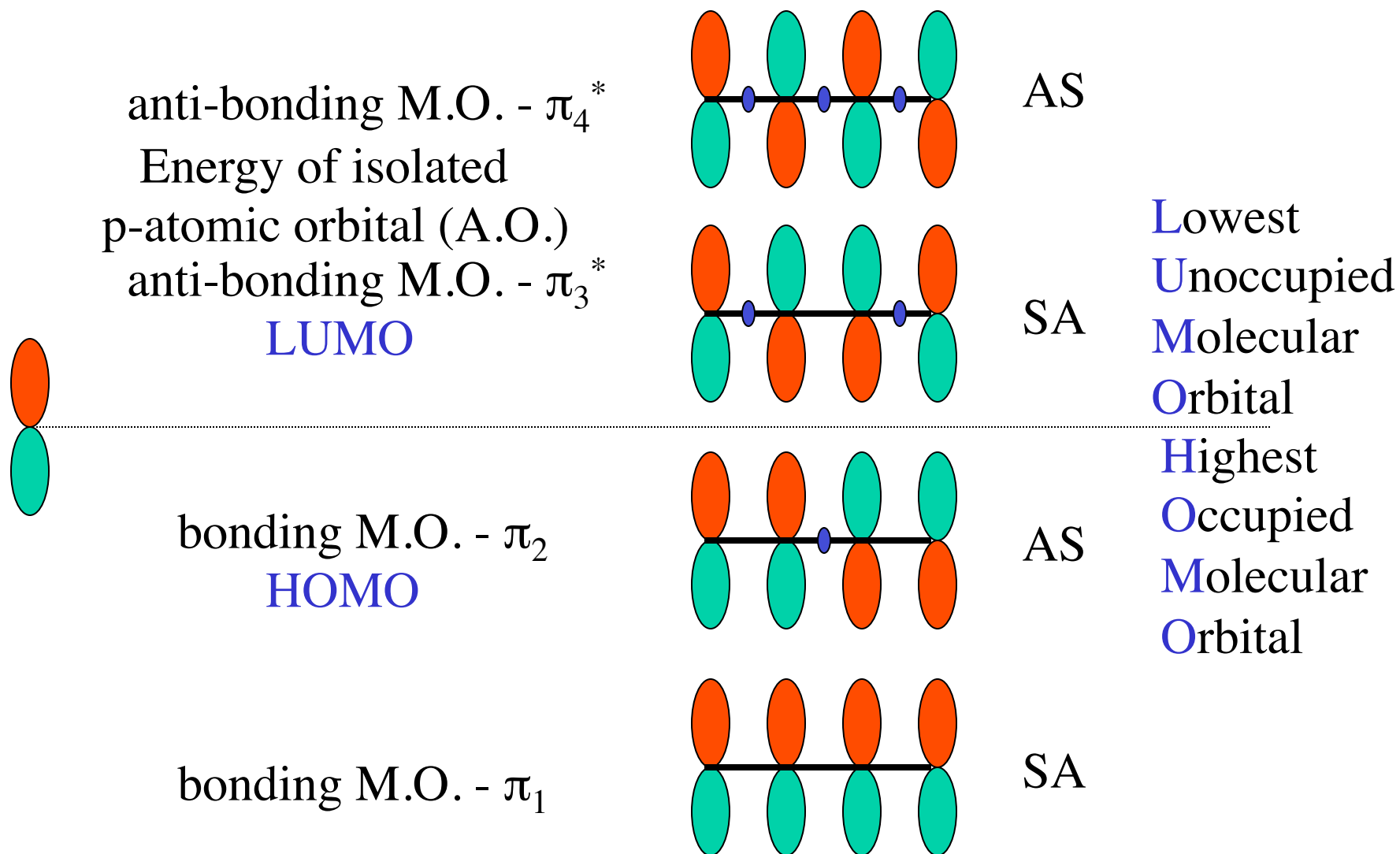


SA 

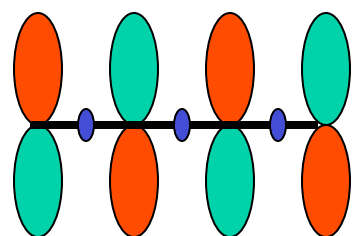
allylic radical



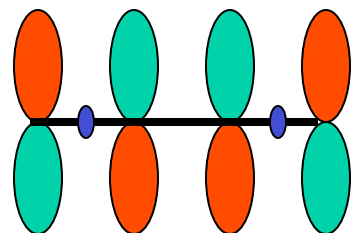
# M.O.s of 1,3-Butadiene



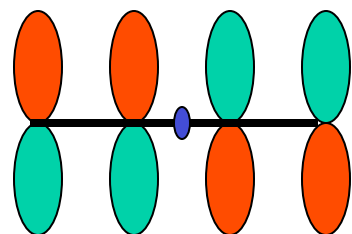
# Orbital Symmetry in the Diels-Alder Reaction



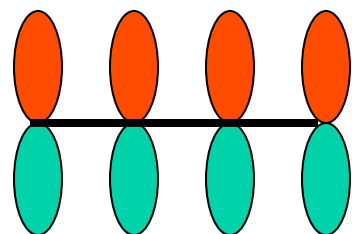
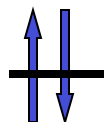
AS



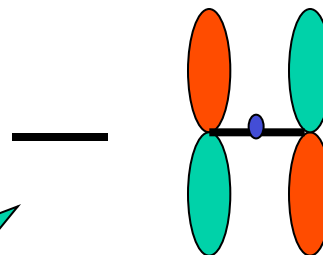
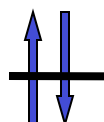
SA



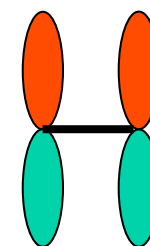
AS



SA



AS



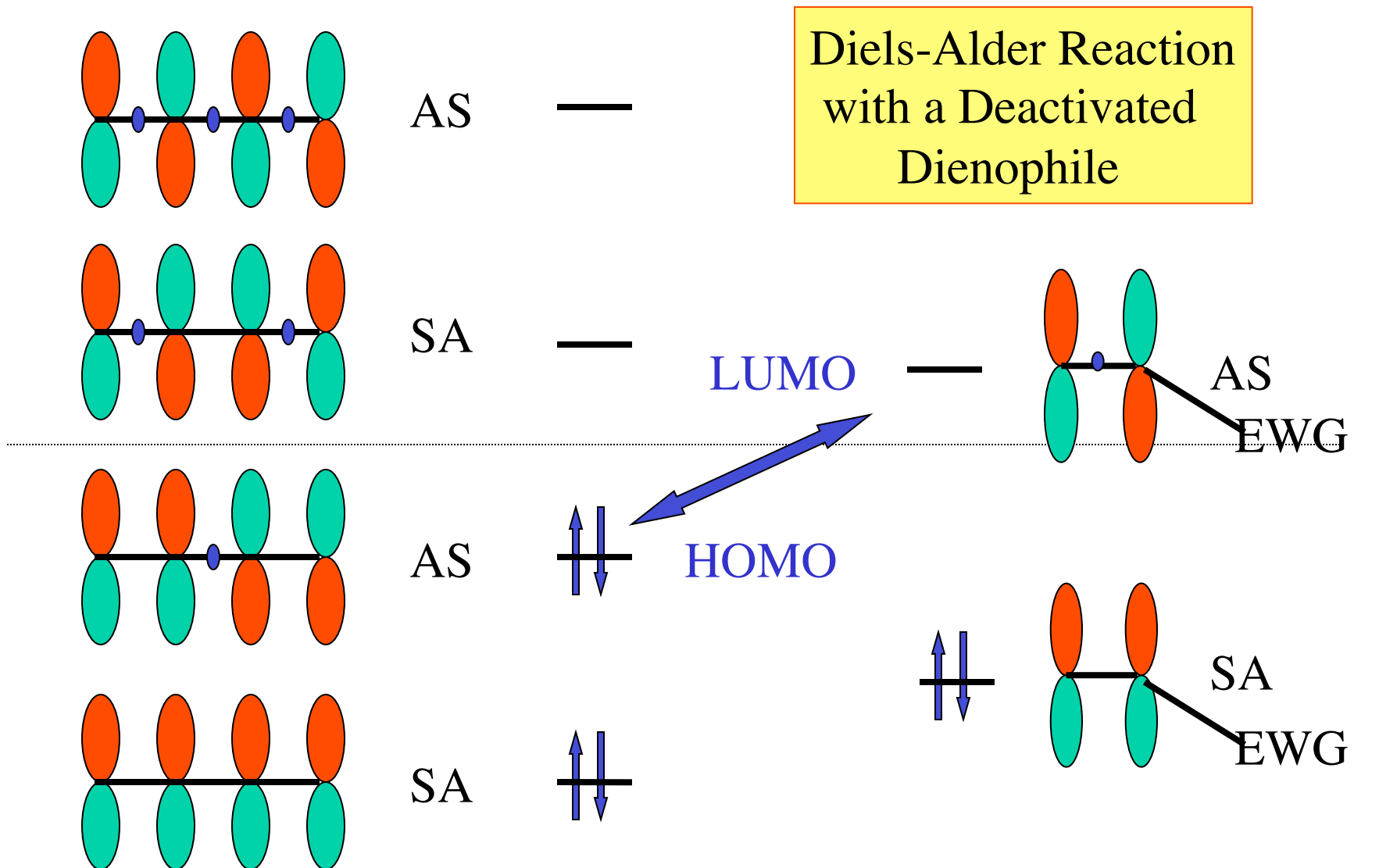
SA

LUMO

HOMO

Equal HOMO-LUMO  
Energy Difference

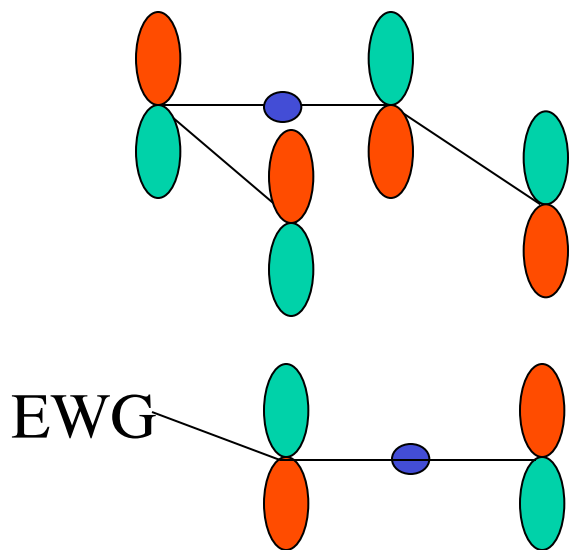
Diels-Alder Reaction  
with a Deactivated  
Dienophile



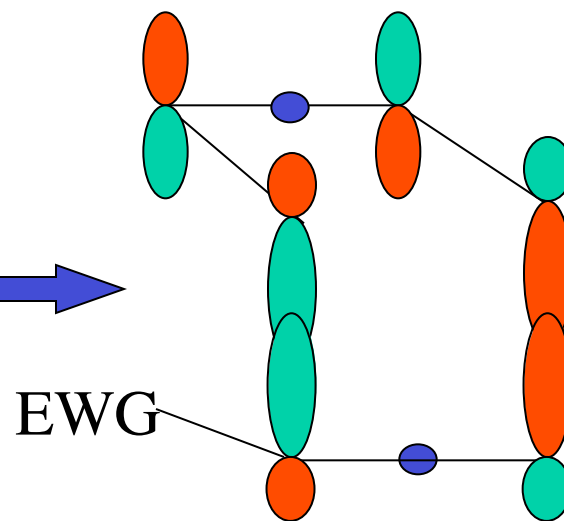
EWG Lowers LUMO Energy

## The Diels-Alder Reaction Transition State

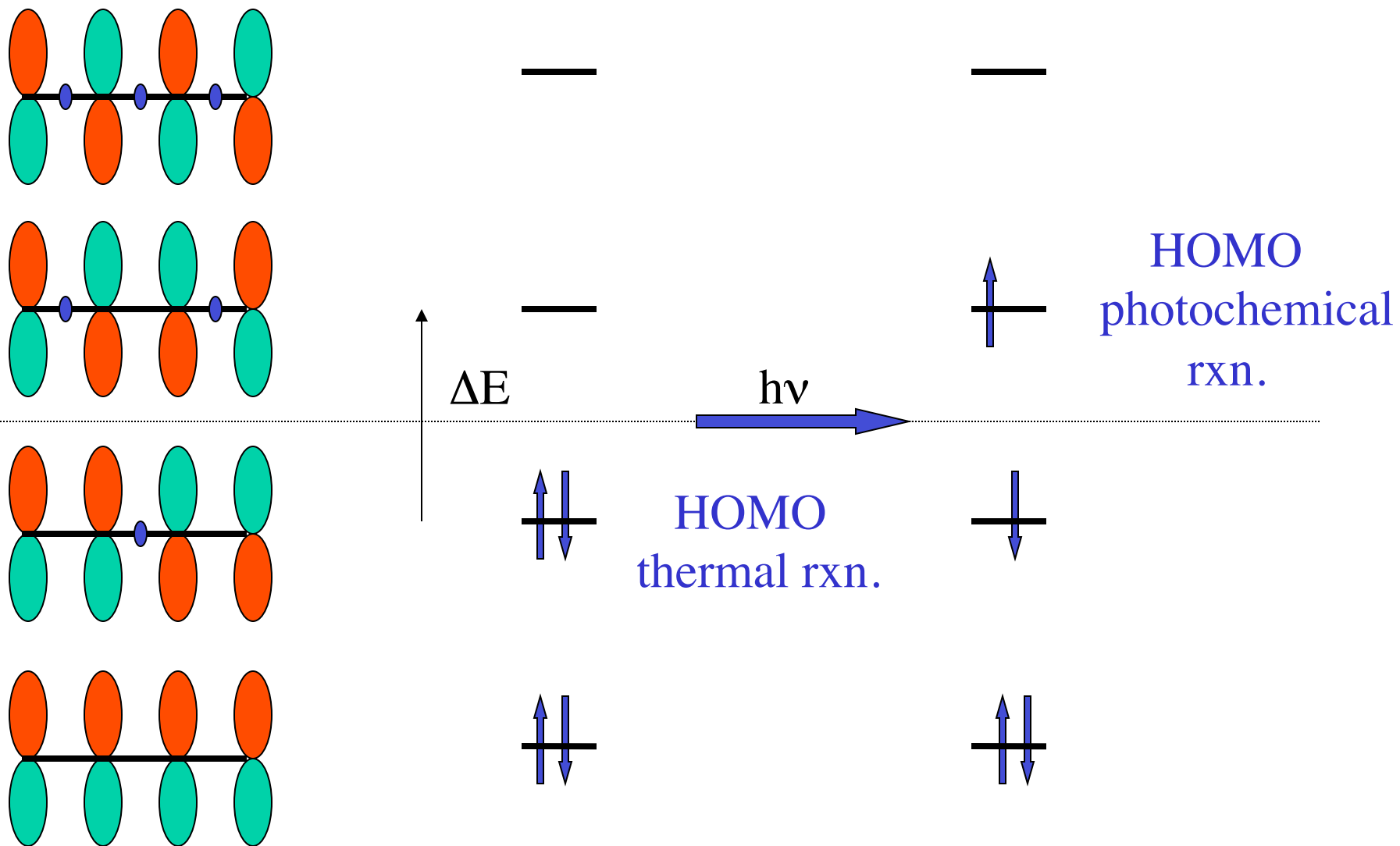
Diene  
HOMO ( $\pi_2$ )



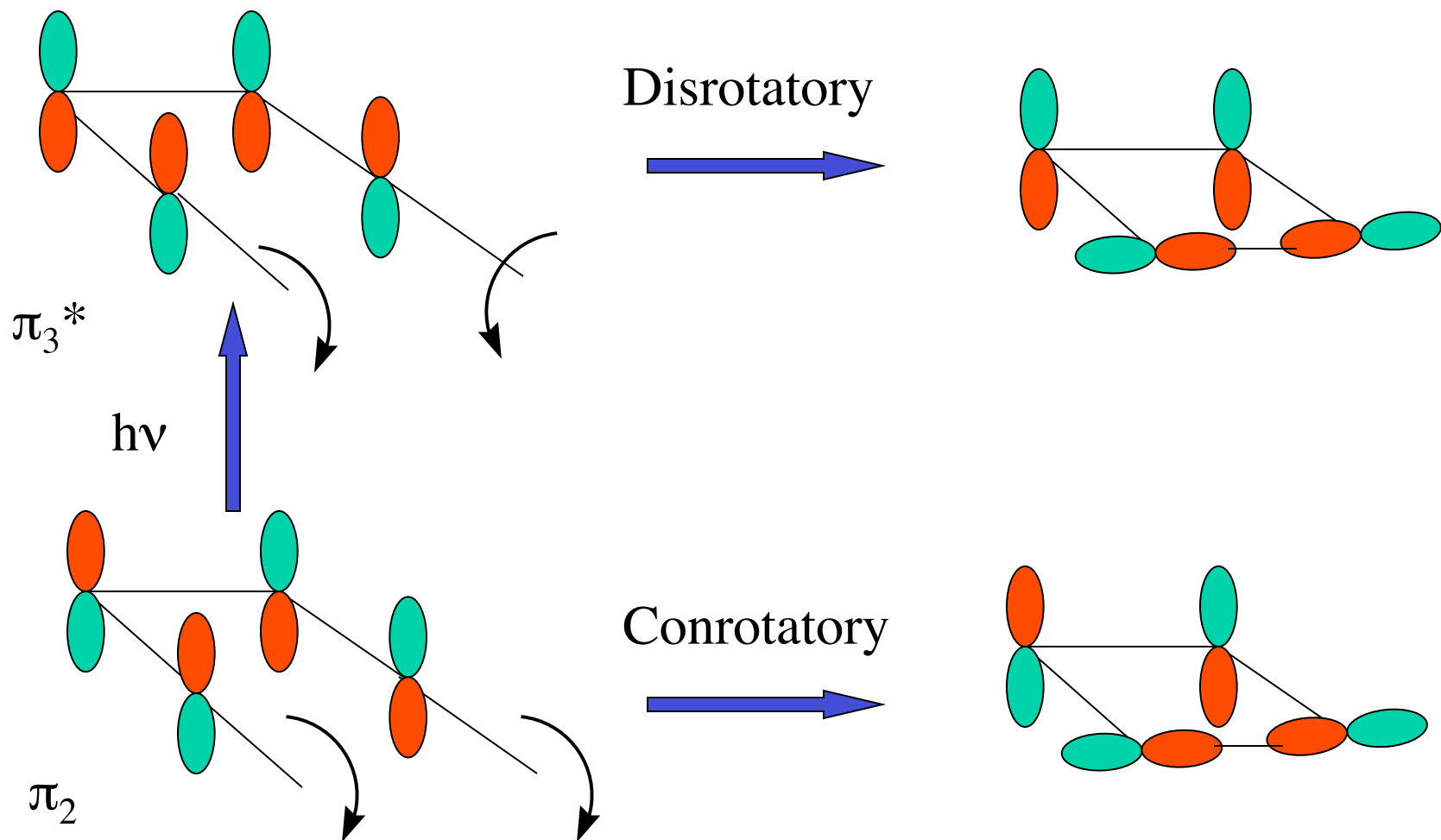
Dienophile  
LUMO ( $\pi_3^*$ )



# Photochemical Excitation in 1,3-Butadiene



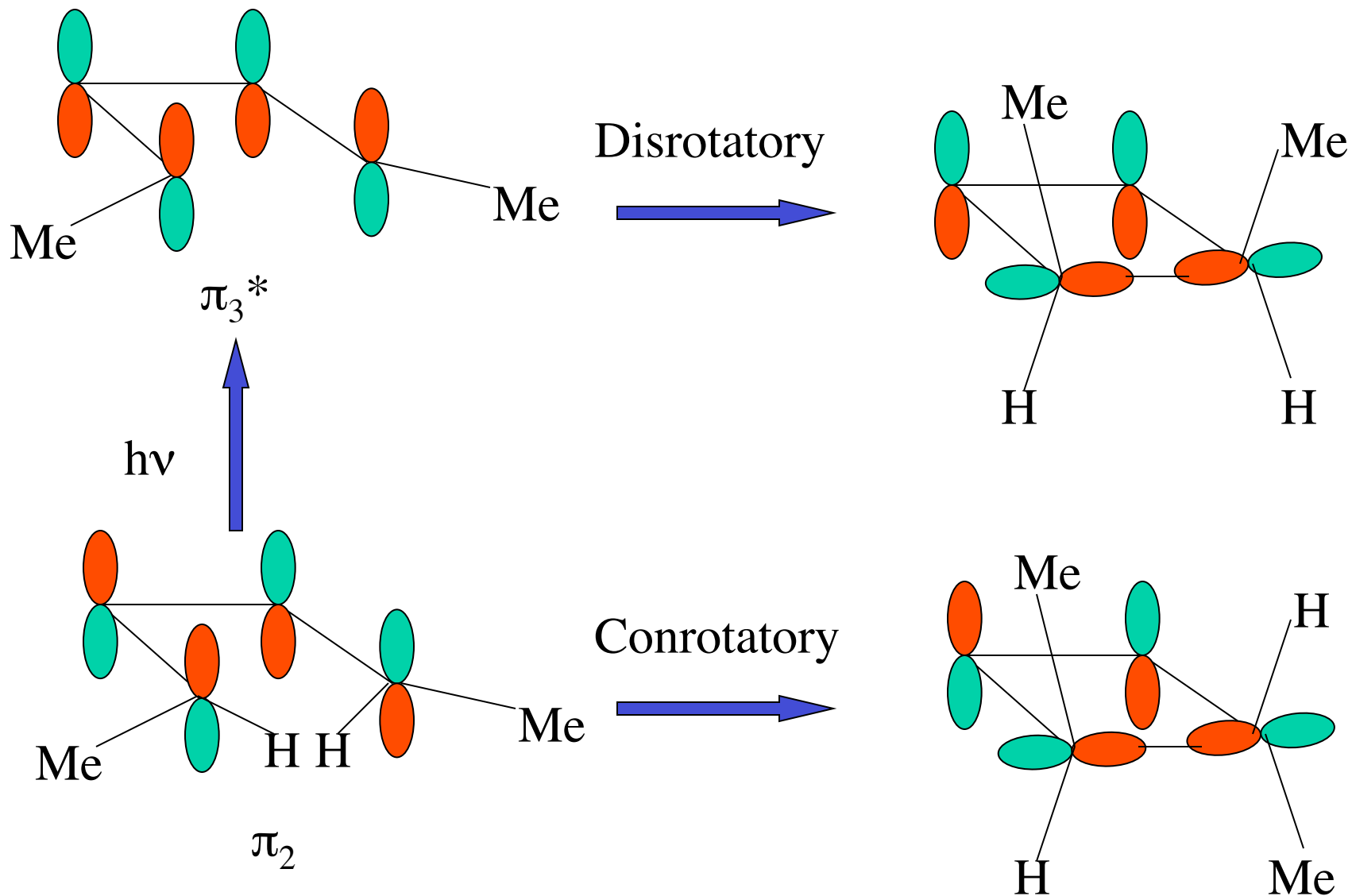
1,3-Butadiene  $\longrightarrow$  Cyclobutene



but one cyclobutene is just like another cyclobutene

enter stereochemistry

1,3-Butadiene  $\longrightarrow$  Cyclobutene





# Stereocontrol in the 1,3-Diene Cyclization

