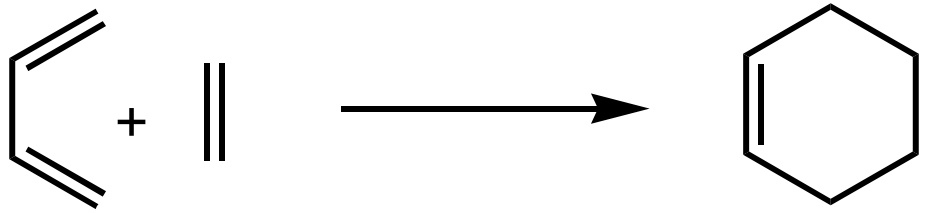
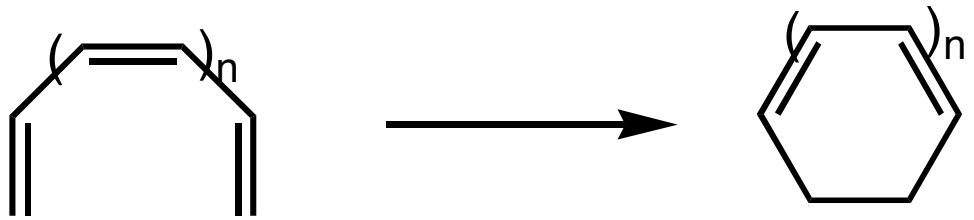
Pericyclic Reactions

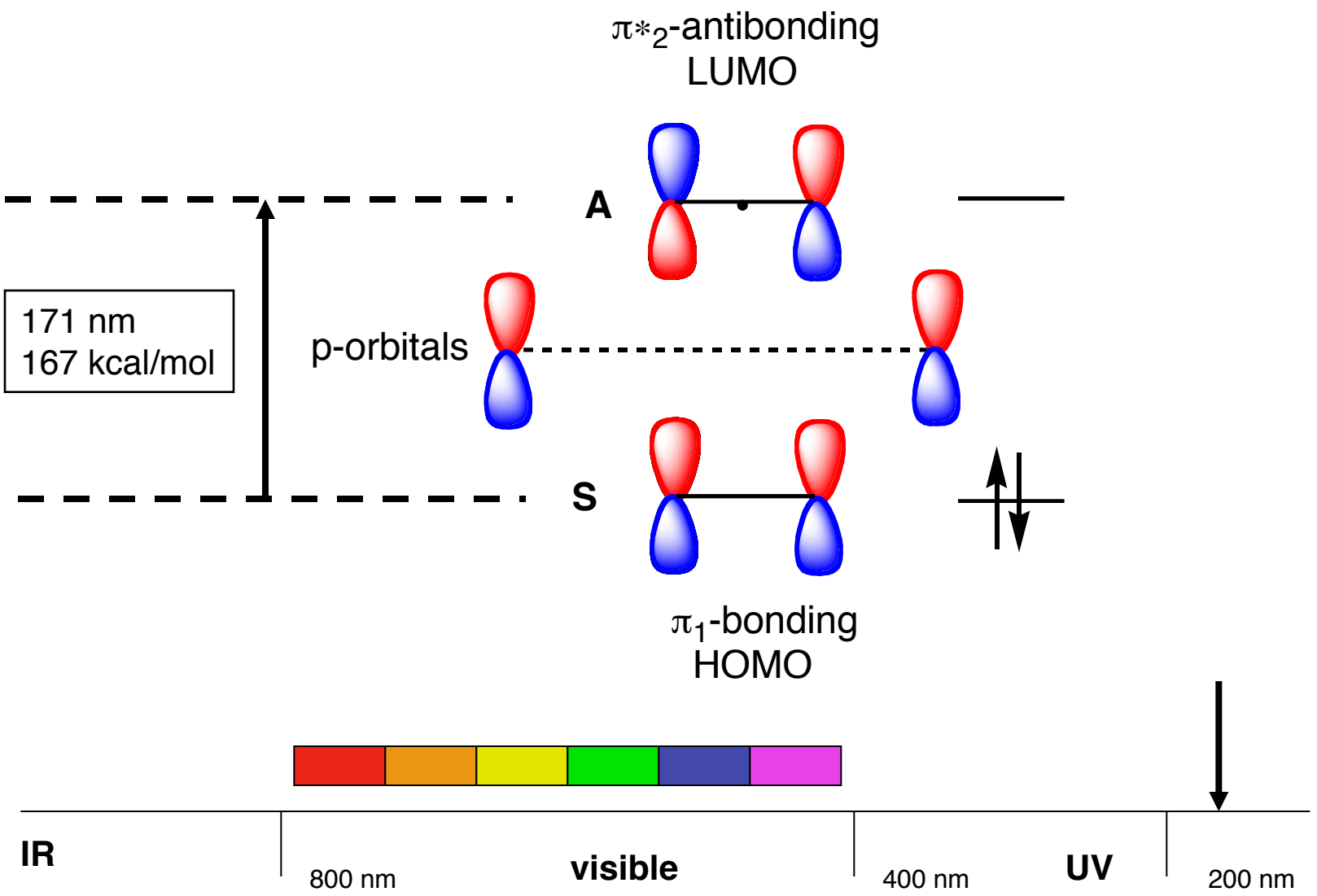
Cycloaddition



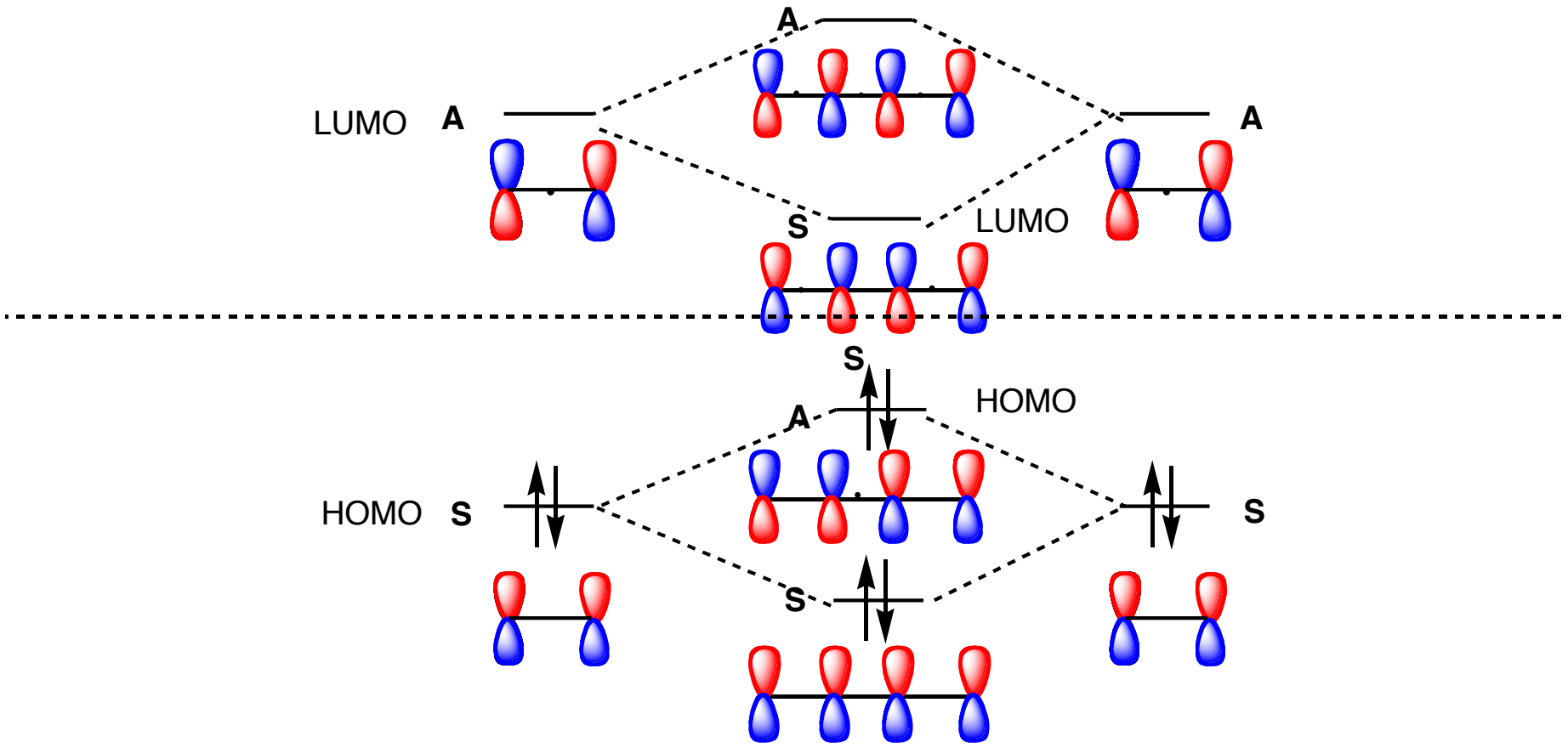
Electrocyclization



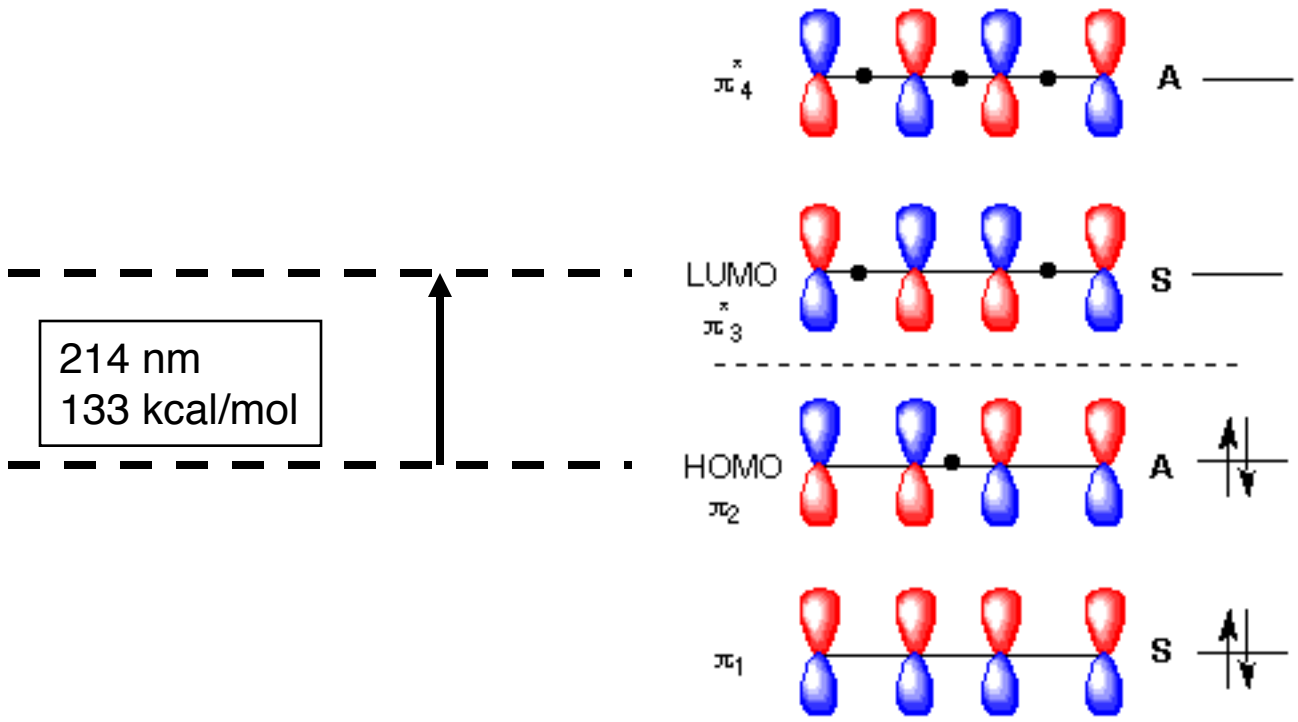
Ethylene π-Molecular Orbitals

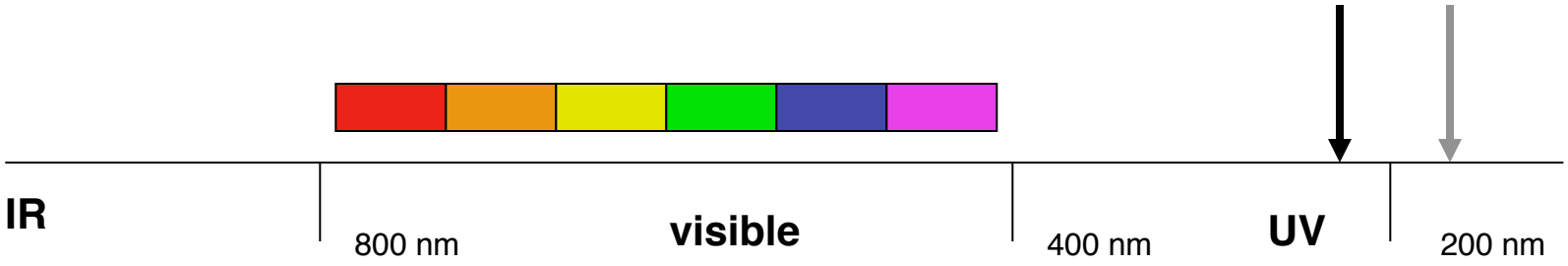


1,3-Butadiene from Ethylene

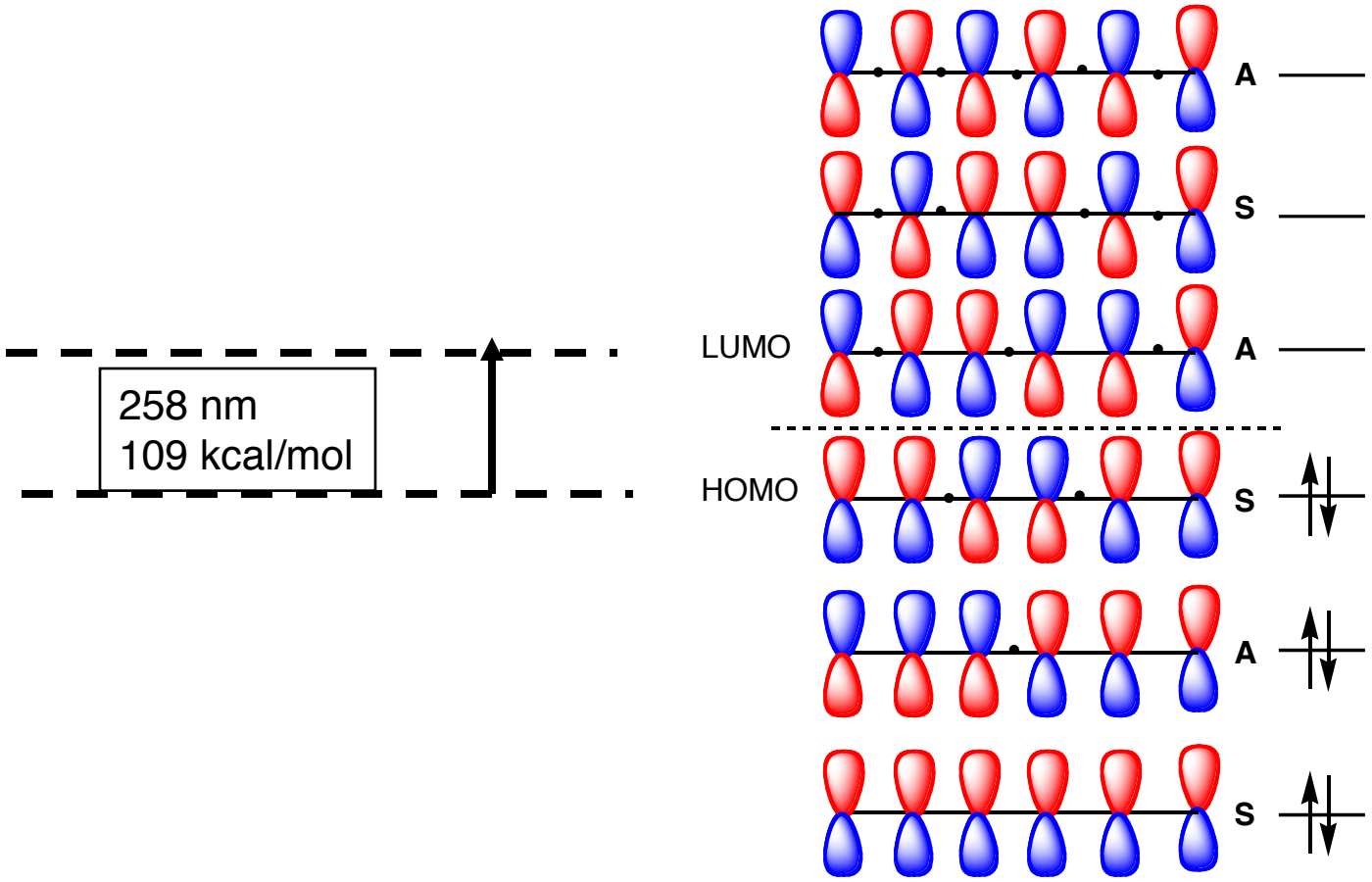


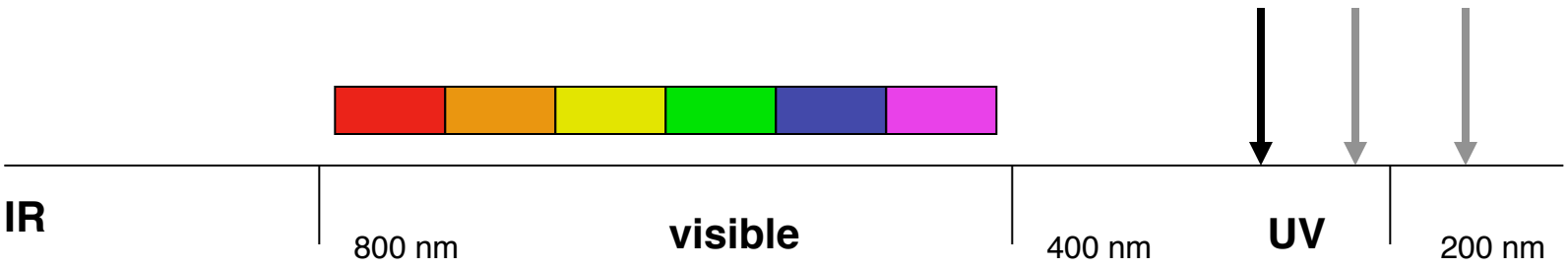
1,3-Butadiene π-Molecular Orbitals



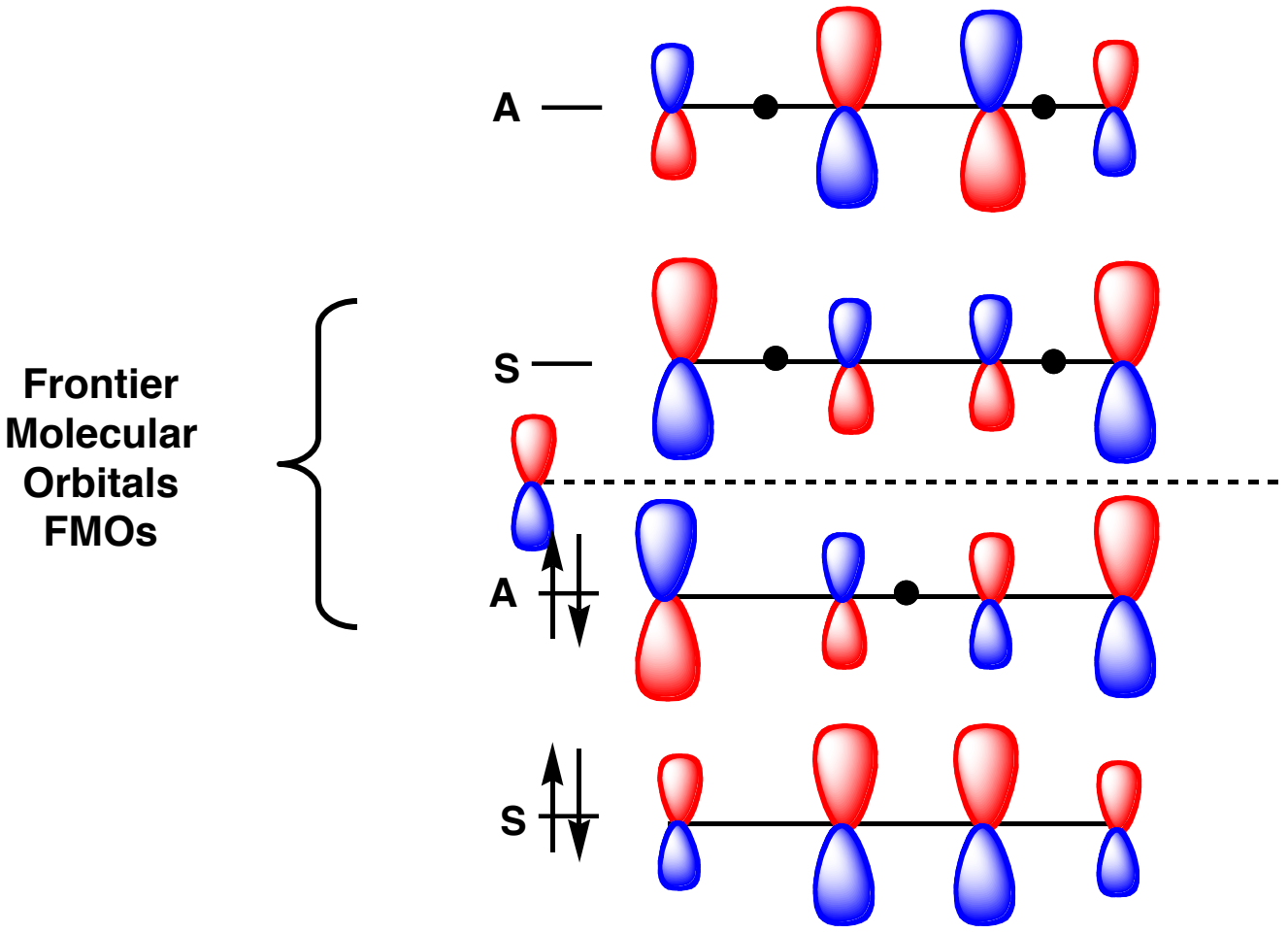


1,3,5-Hexatriene π-Molecular Orbitals

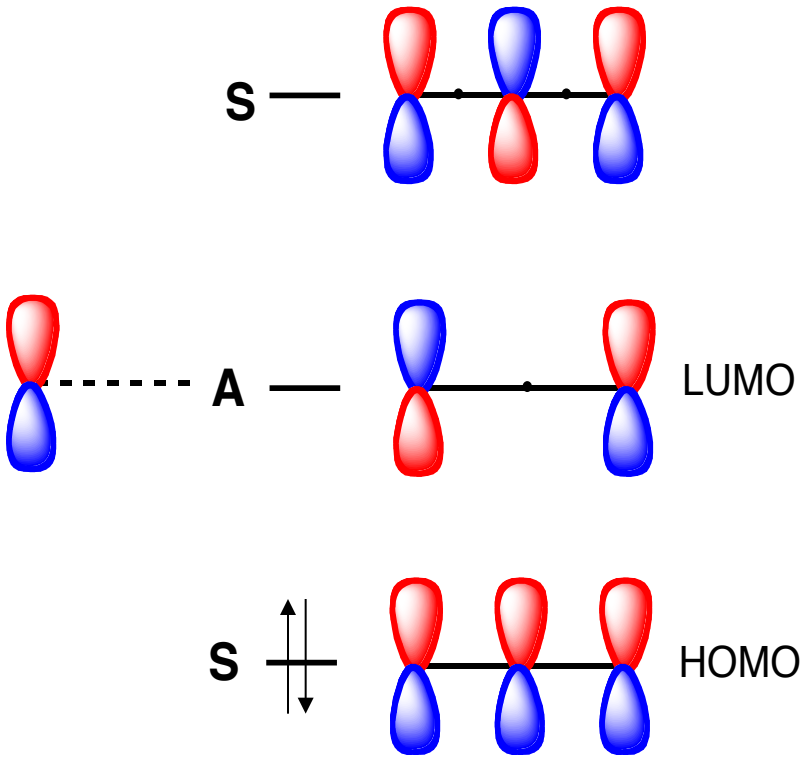


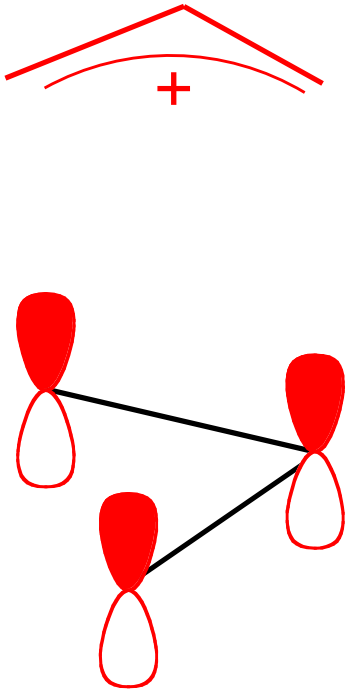


Butadiene: Orbital Coefficients

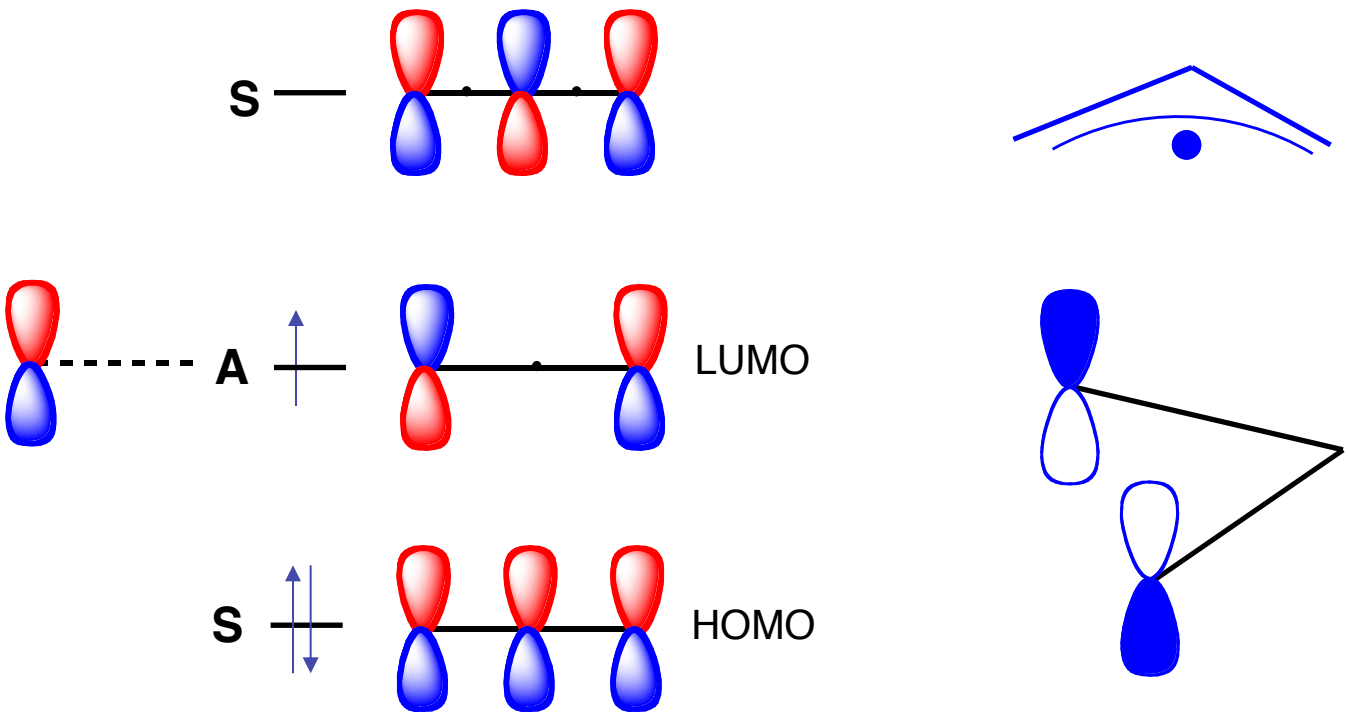


The Allylic System: Allyl Cation

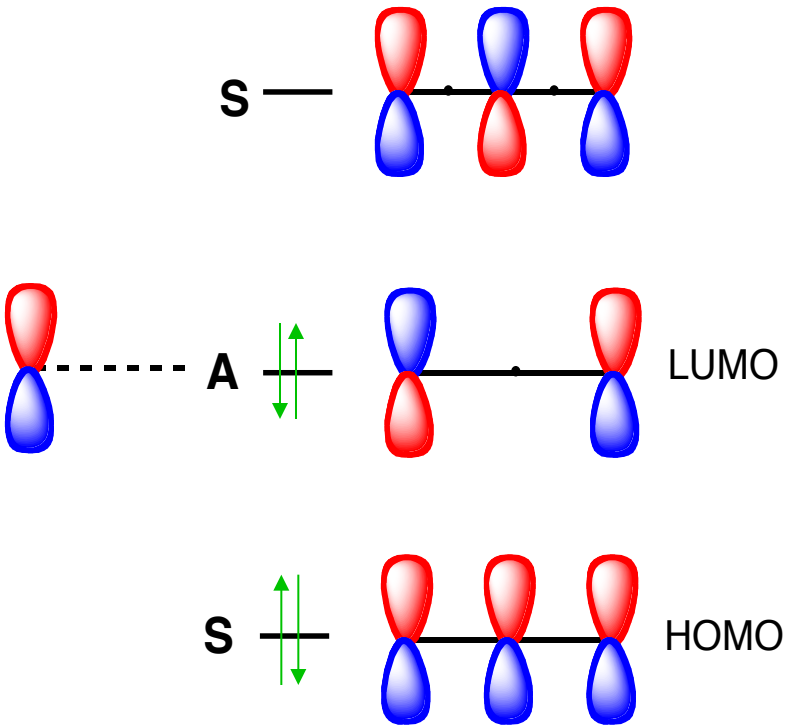


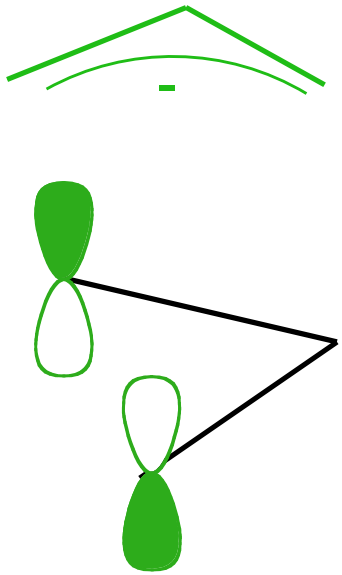


The Allylic System: Allyl Radical

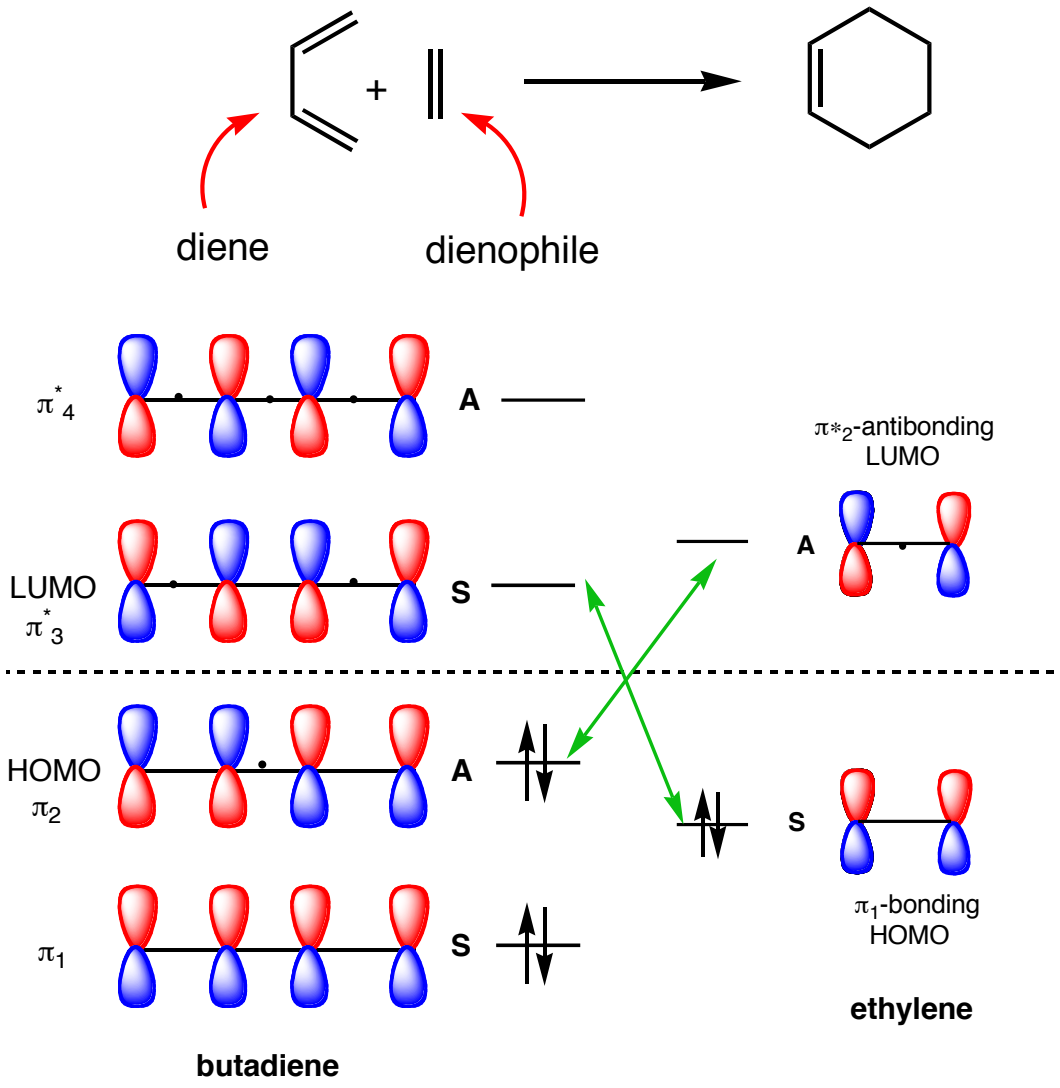


The Allylic System: Allyl Anion

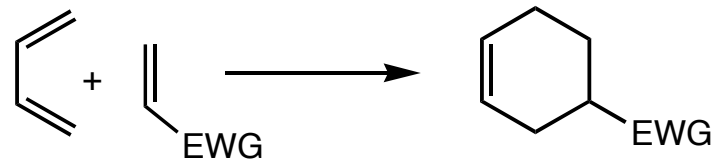




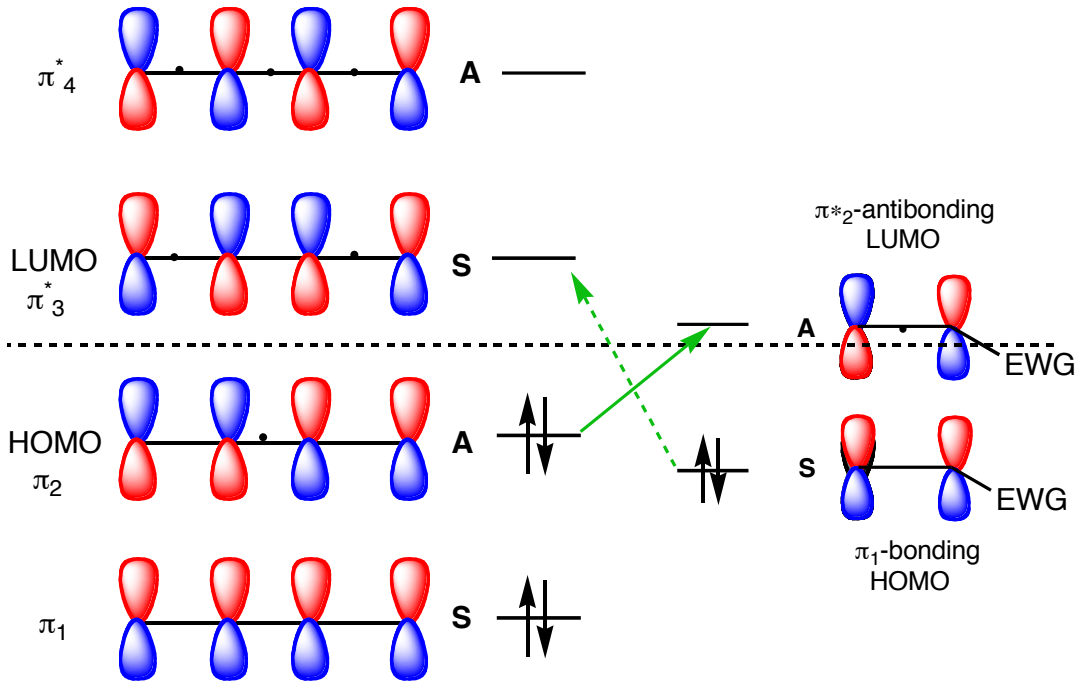
Cycloaddition: Diels-Alder Reaction
An Allowed [4+2] Cycloaddition



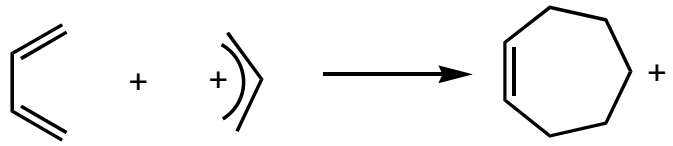
Diels-Alder Reaction:
The Effect of Electron Withdrawing Groups

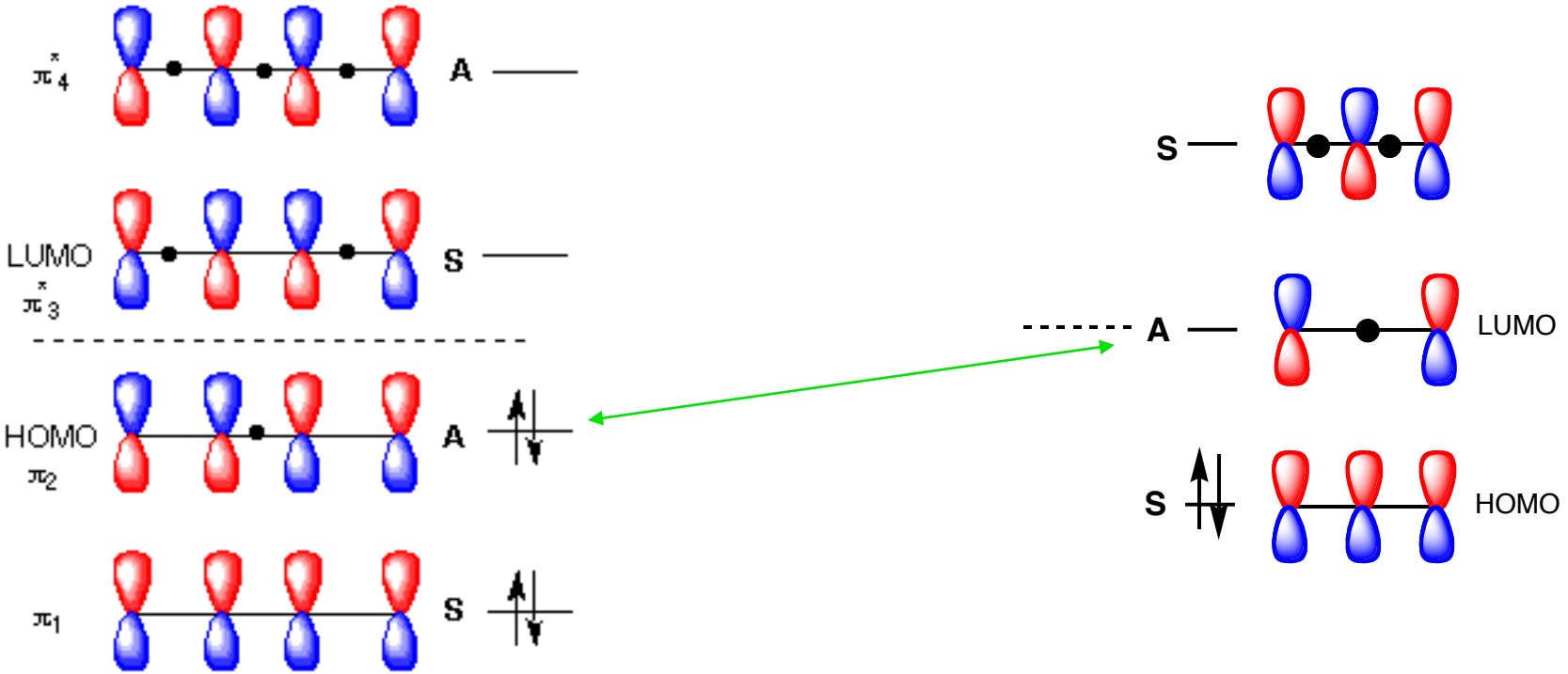


diene dienophile

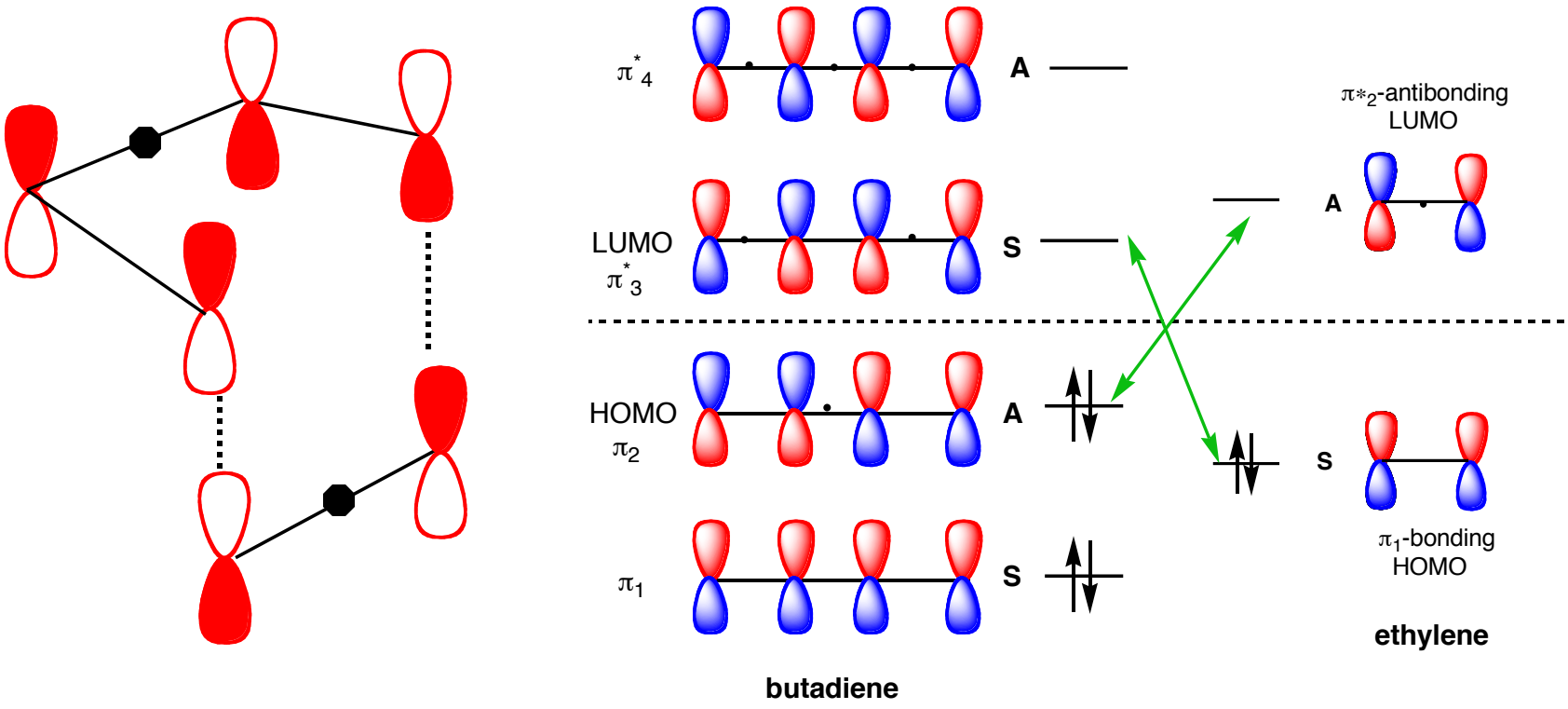


[4+2]-Cycloadditions

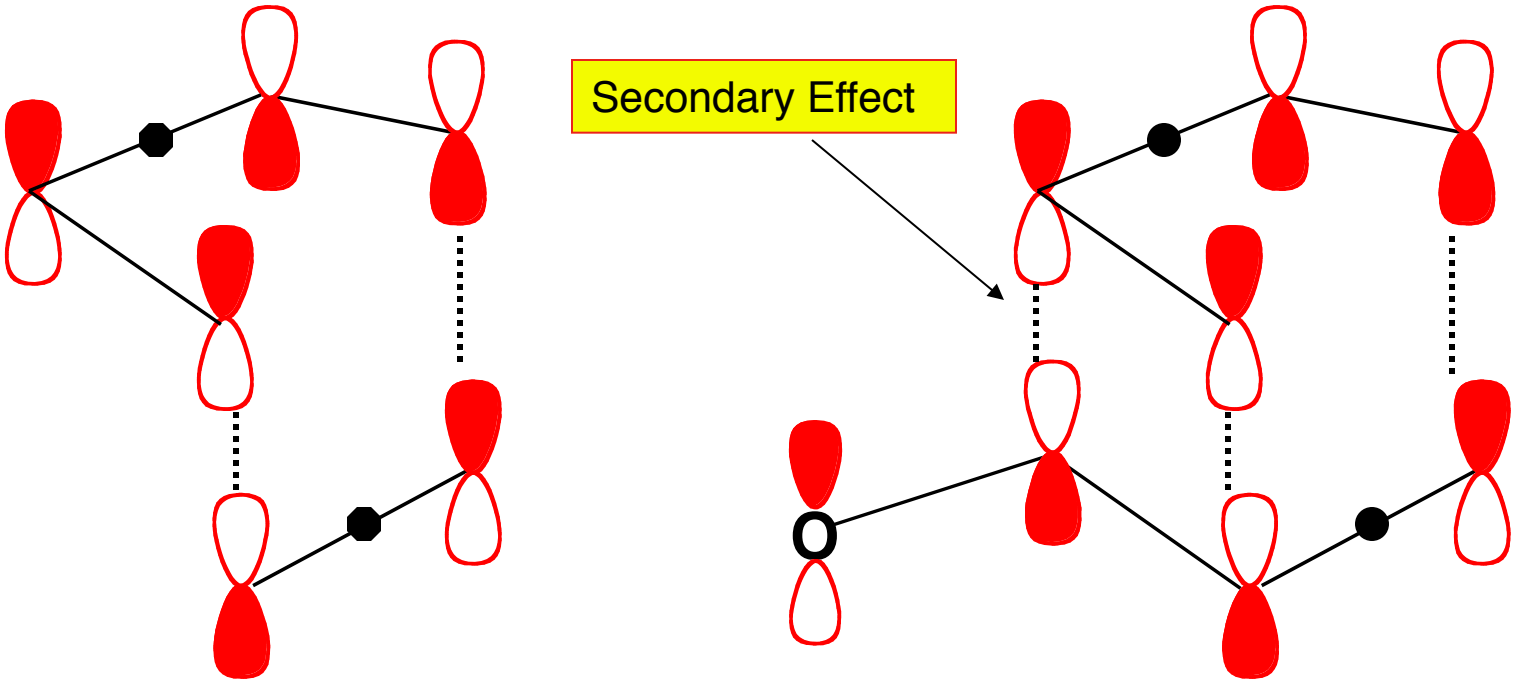




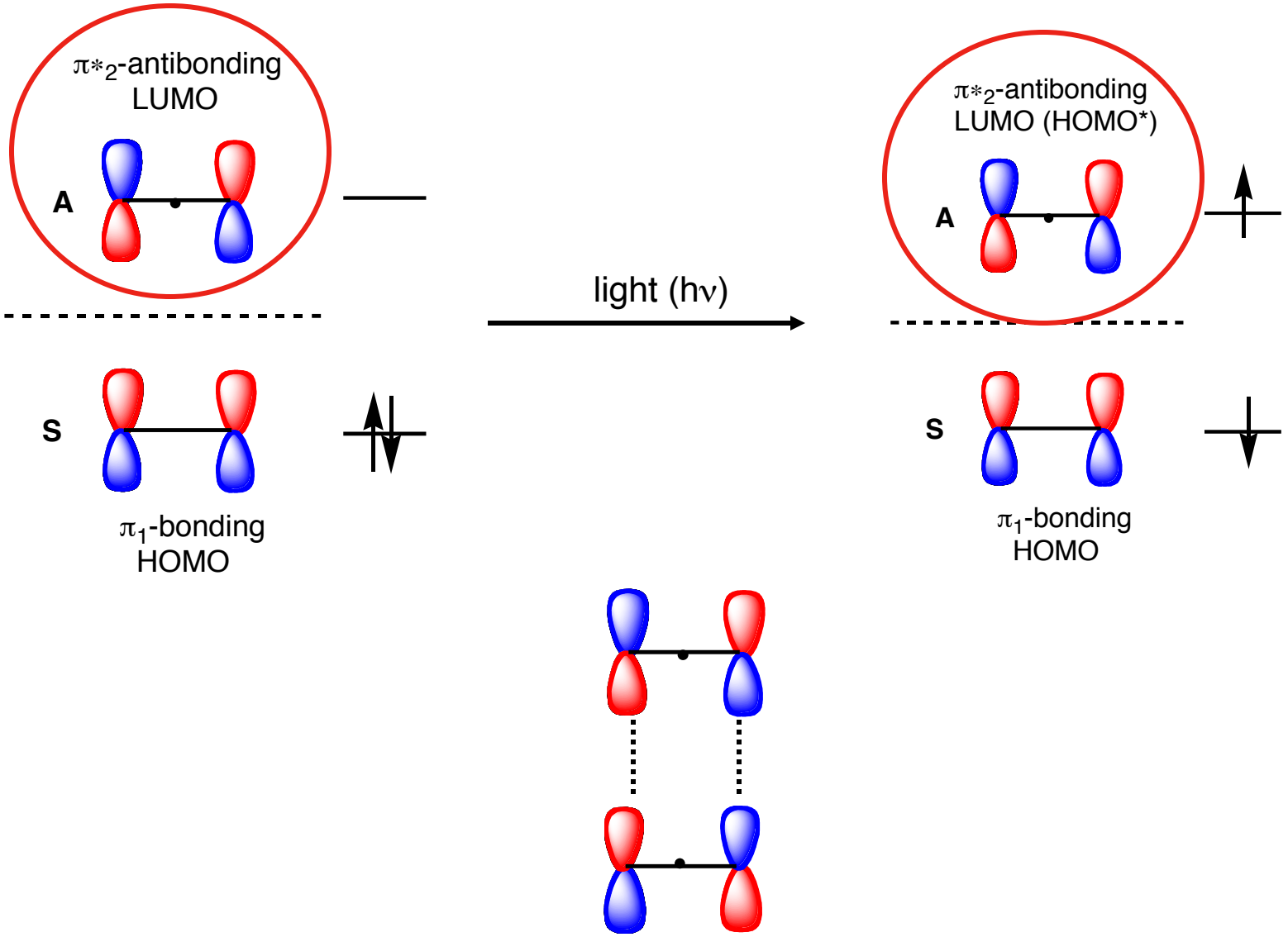
Diels-Alder Reaction: Mechanism



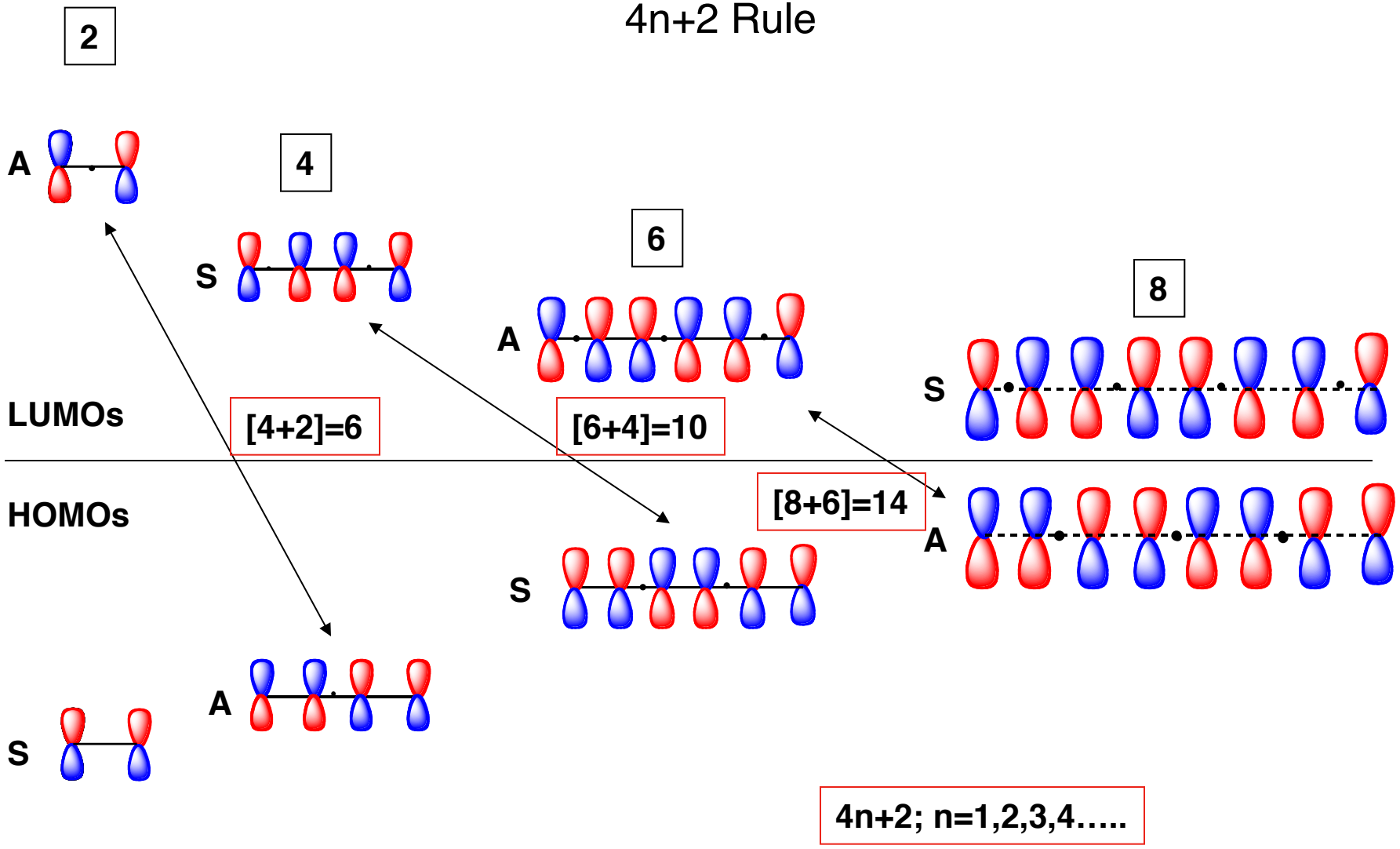
Diels-Alder Reaction: The Endo Effect



What About a [2+2] Cycloaddition?

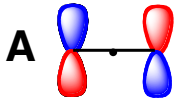


Thermally Allowed Cycloadditions
4n+2 Rule

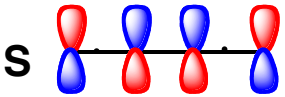


Photochemically Allowed Cycloadditions
4n Rule

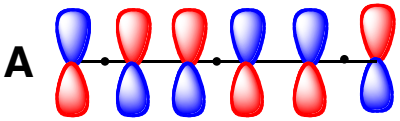
2 [2+2]=4



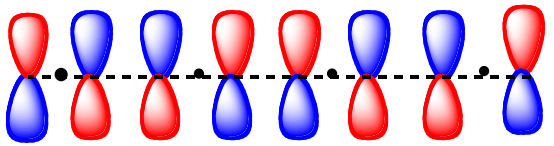
4 [4+4]=8



6 [6+6]=12

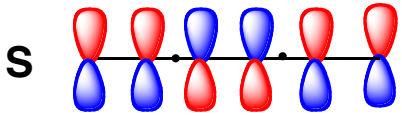


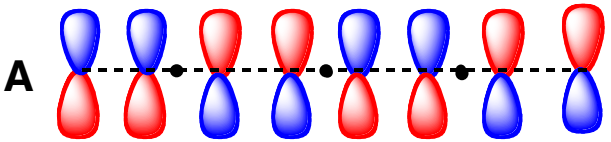
8 [8+8]=16

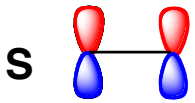


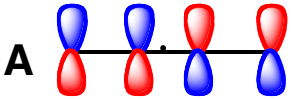
LUMOs

HOMOs









4n; n=1,2,3,4…..

and [2+6]=8; [8+4]=12

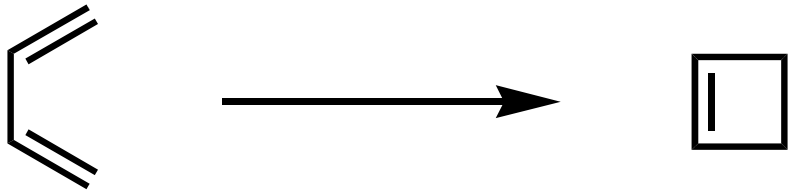
Summary of Cycloadditions

Thermal 4n+2

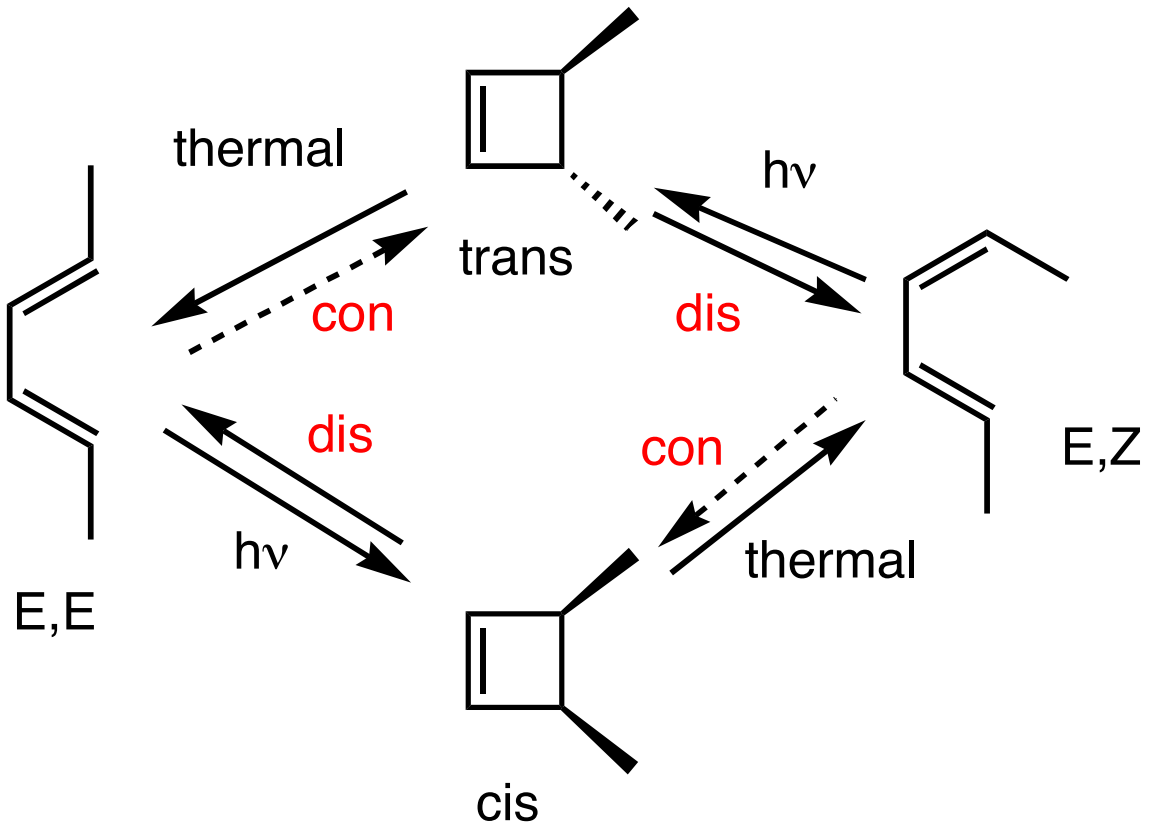
Photochemical 4n

	2	4	6	8	10
2	P	T	P	T	P
4	T	P	T	P	T
6	P	T	P	T	P
8	T	P	T	P	T
10	P	T	P	T	P

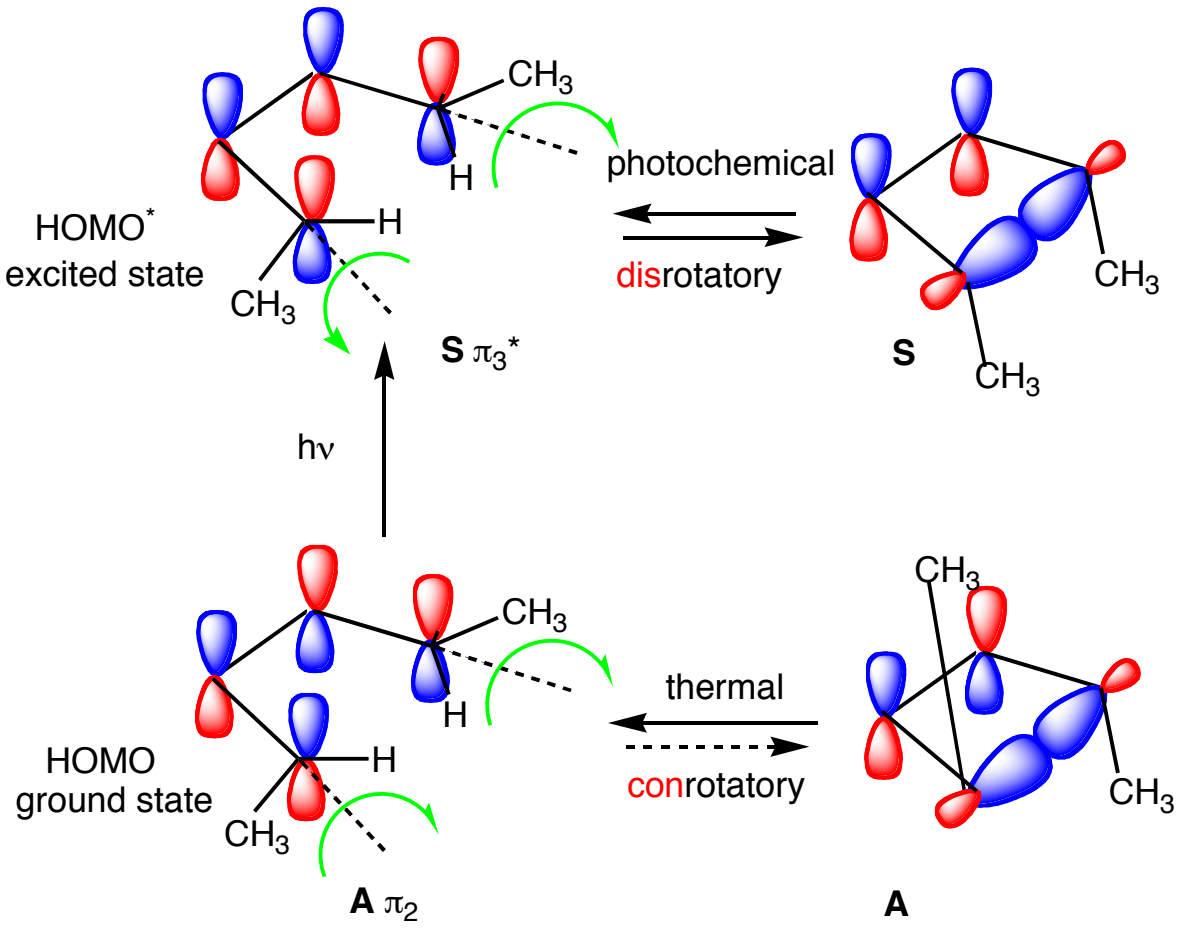
Electrocyclizations



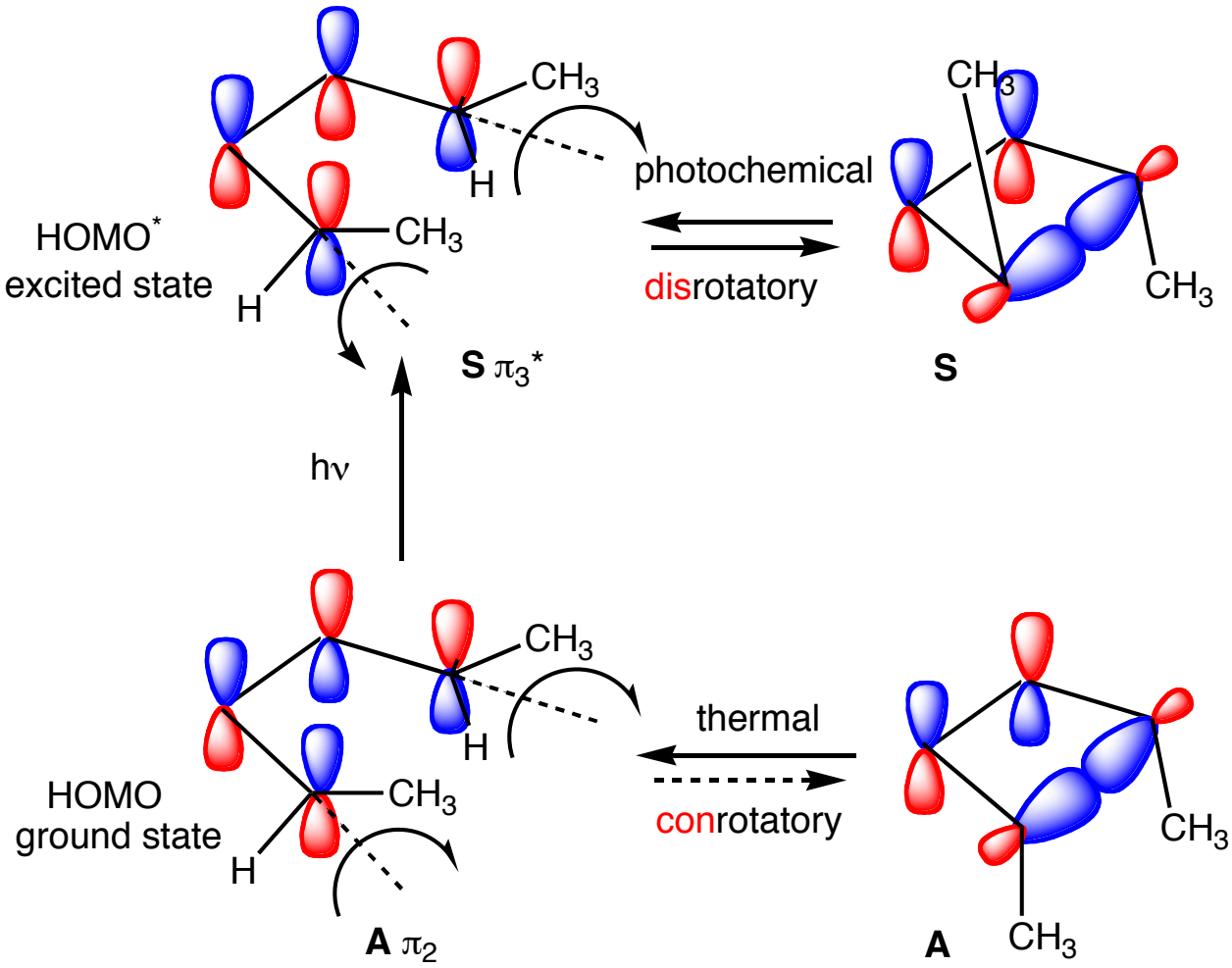
1,3-Butadiene-Cyclobutene



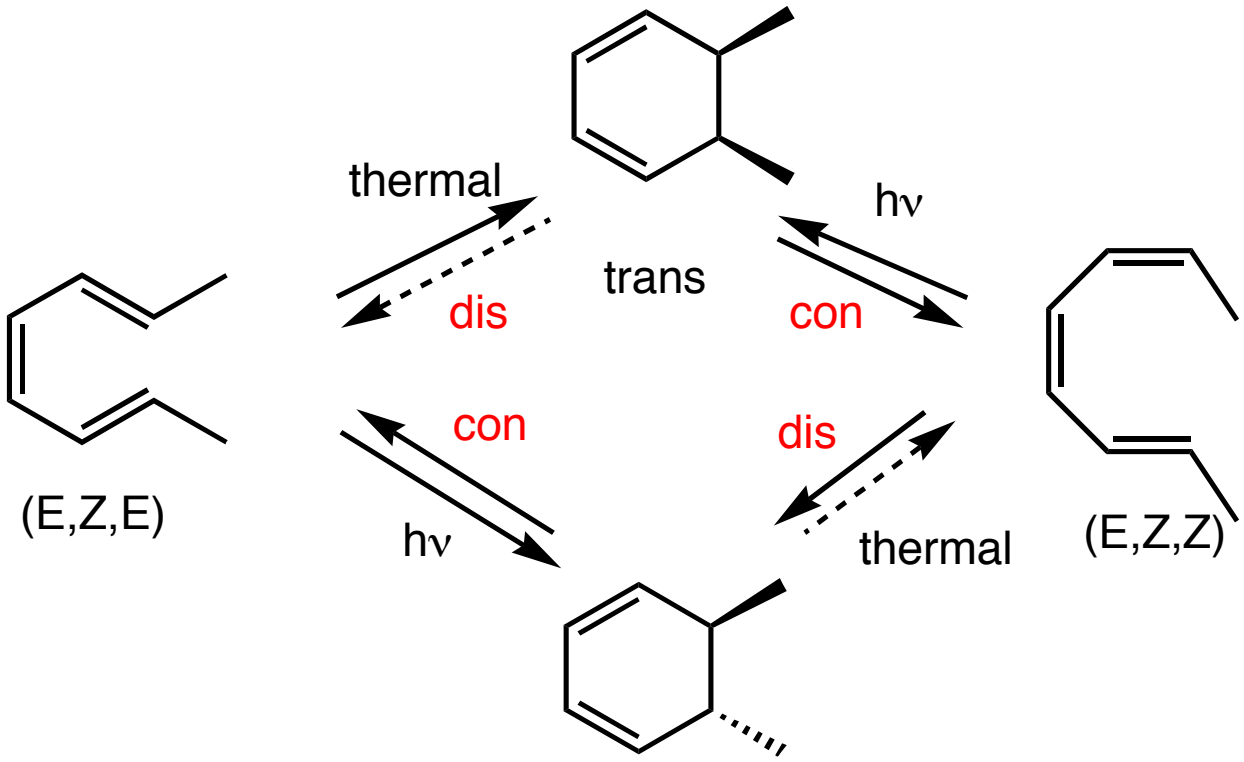
(*E,E*)-1,3-Butadiene-Cyclobutene



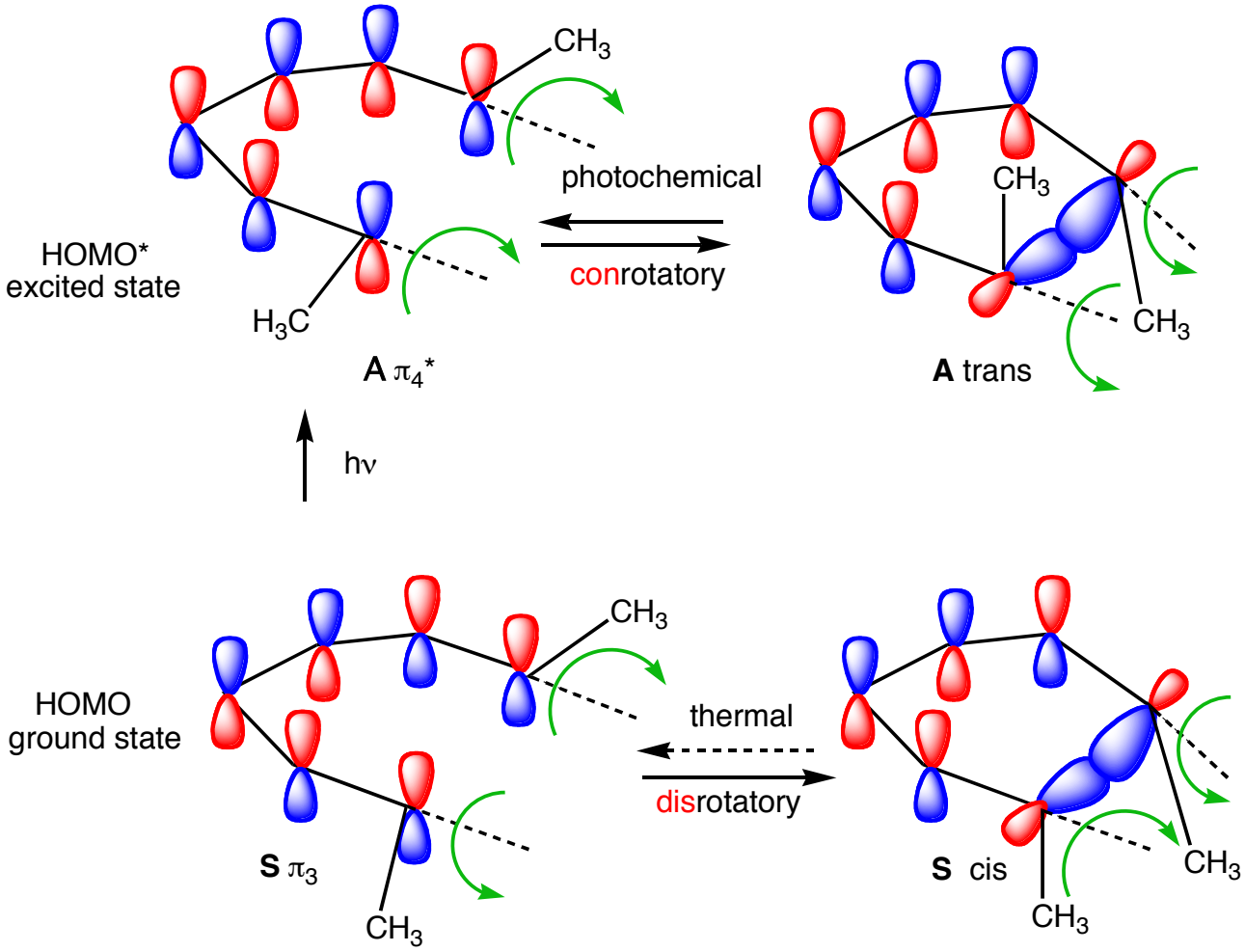
(*E,Z*)-1,3-Butadiene-Cyclobutene



(*E,Z,E*)-1,3,5-Hexatriene-Cyclohexadiene



(*E,Z,E*)-1,3,5-Hexatriene-Cyclohexadiene Orbitals



Electrocyclizations

n=1,2,3,4…	thermal	photochemical
4n	con	dis
4n+2	dis	con

Violations

“There are none!”

Woodward and Hoffmann, *The Conservation of Orbital Symmetry*