CHEM 342 – Lecture 5 *20/01/15*

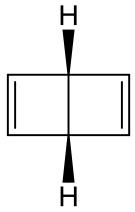
Overheads: - Today's Outline

Quiz #1

Recap Thursday: Woodward-Hoffman Rule for Electrocyclic Reactions

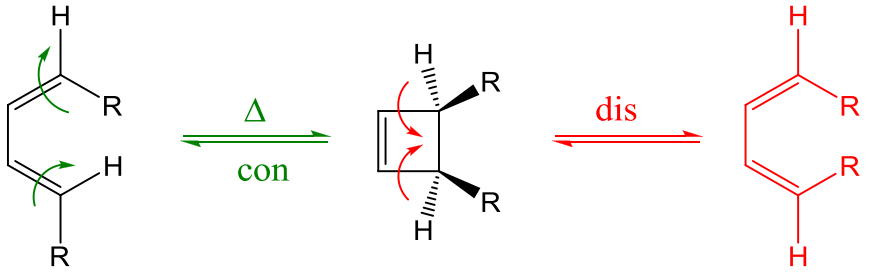
4n / even	Δ	con
	hν	dis
4n+2 / odd	Δ	dis
	hν	con

Cool example: "Dewar Benzene"



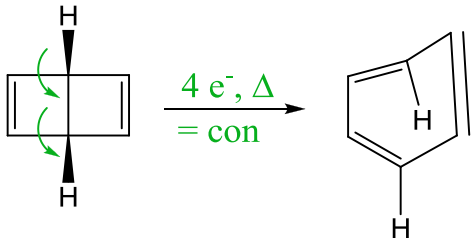
looks very unstable (very strained)
but stable at room temperature!

Compare to:



- imagine the R groups are the rest of the benzene ring
- in order to get "normal" benzene, need to do a disrotary ring opening (reverse of electrocyclic reaction), which is symmetry forbidden!

**Note that WH rule is same for reverse reaction (*ie* electrocyclic ring opening)

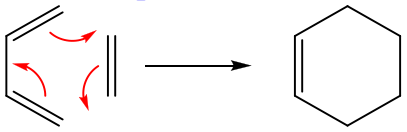


con ring opening would give "trans benzene"

→ electrocyclic ring opening of dewar benzene to give benzene is symmetry-forbidden, so dewar benzene is unexpectedly stable
→ however, heating above RT gives benzene (by another mechanism)

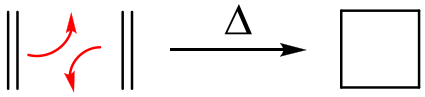
2) Cycloaddition Reactions

- two components add to make ring

e.g. 

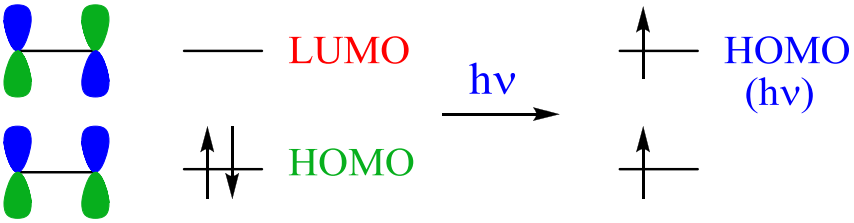
- to determine if "allowed" need to look at MO's of both
*HOMO of one reacts with LUMO of the other

e.g. [2+2] cycloaddition (each component has two π e⁻):



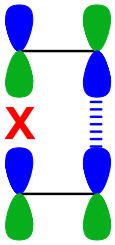
is it allowed?

MO's:



To react: LUMO of molecule B:

HOMO of molecule A:



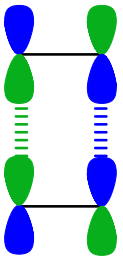
Can't overlap :-(

What about photochemical reaction?

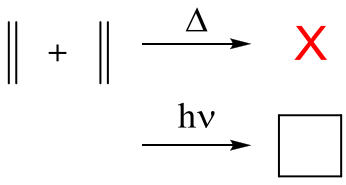
→ HOMO of excited state reacts with LUMO of ground state molecule.

LUMO of molecule B:

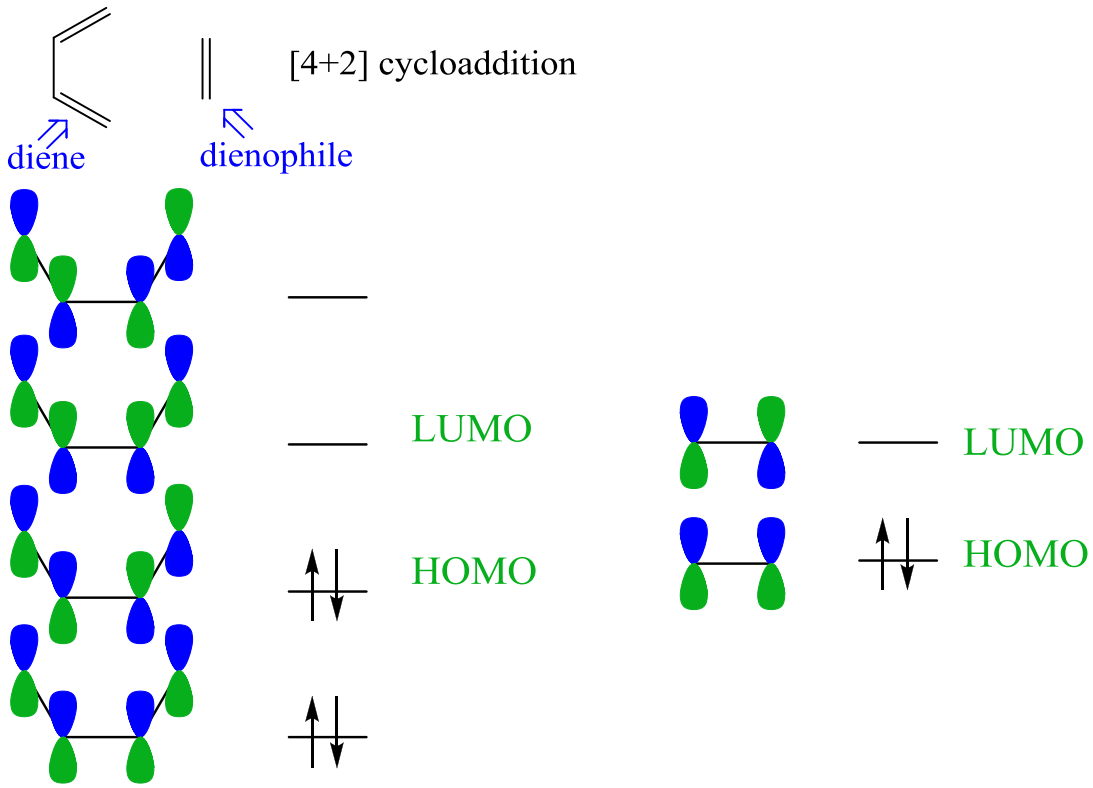
HOMO* of molecule A (excited state):



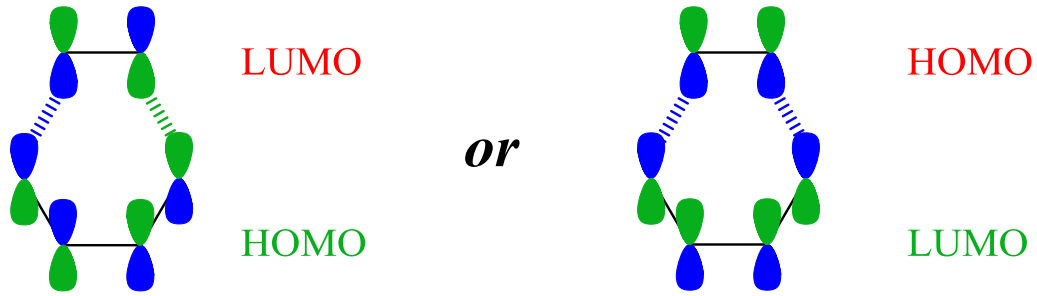
:-)

∴ 

Diels-Alder Reaction

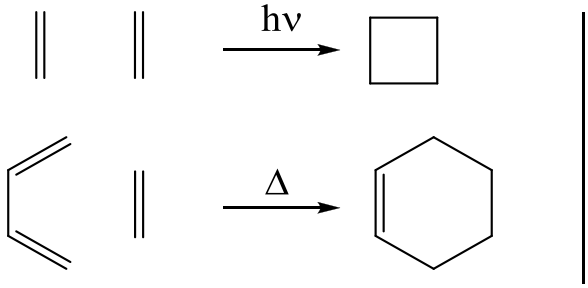


Combine HOMO of one with LUMO of the other:



- Works either way!

Summary:

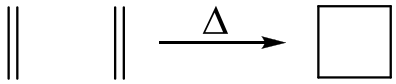


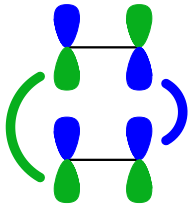
In general

even π bonds (4n) = hν

odd π bonds (4n+2) = Δ

Are the other reactions really "forbidden"?





In order to react, one must twist around
to form bond from other side

Suprafacial: → both new bonds form from same side of π system
→ "straight-on" overlap

Antarafacial: → two new bonds are formed on opposite sides
(uses top of one end of orbital and bottom of other end)
→ "twisted" overlap
→ much more difficult (only works for big rings; > 6 C's)

Woodward-Hoffman Rule for cycloadditions

4n π e (even pairs)	Δ	= antarafacial
	hν	= suprafacial
4n+2 π e (odd pairs)	Δ	= suprafacial
	hν	= antarafacial

= Diels-Alder!

→ remember any one, change one part get opposite