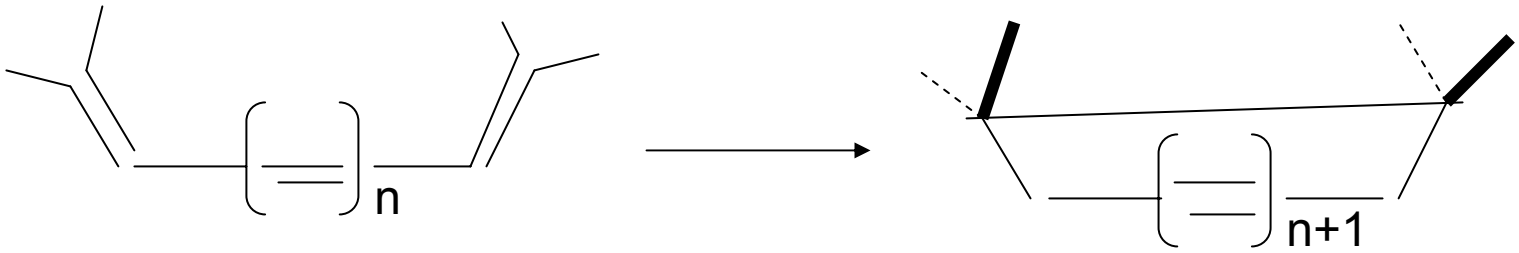
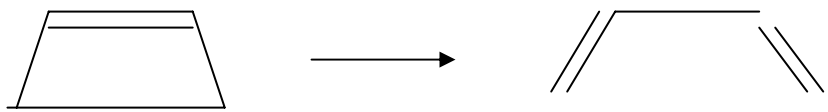
Cyclization of polyenes

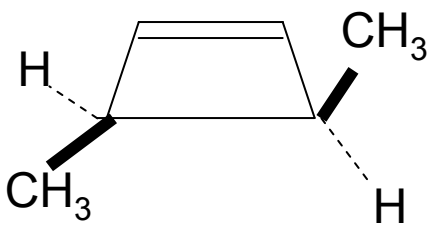


n=0- cyclization of cis-butadiene

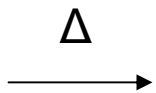
Reaction is endothermic- difficult to run in the gas phase

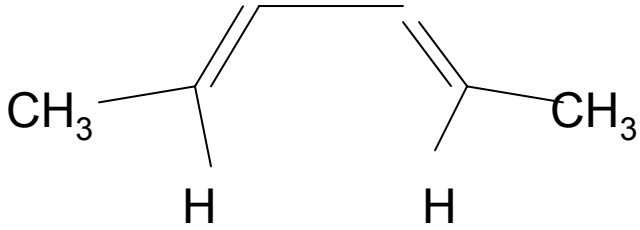
Let us consider reverse reaction- ring opening, which is exothermic and easier for experiment





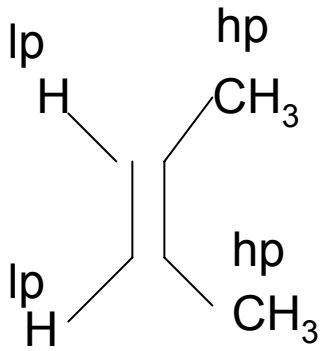
“trans”



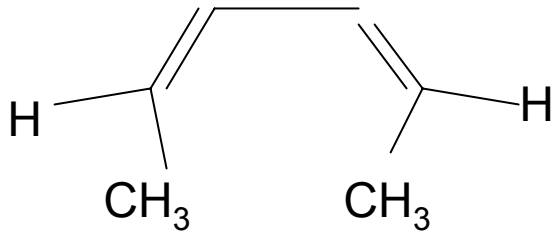


E,E-diene only the product

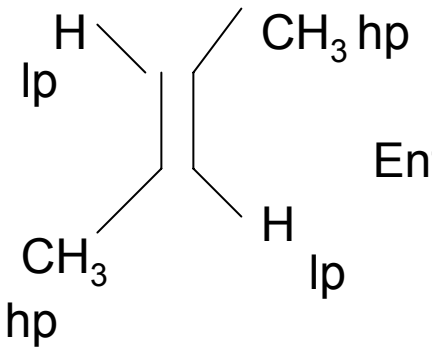
No Z,Z or E,Z



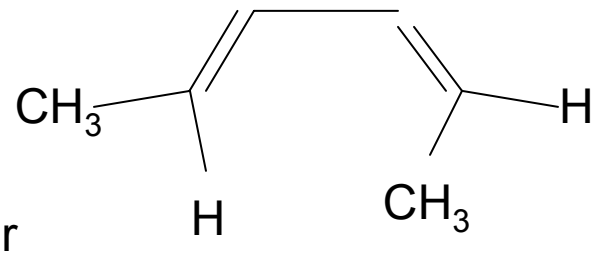
Zusammen (same side) Z-isomer



Z,Z-diene

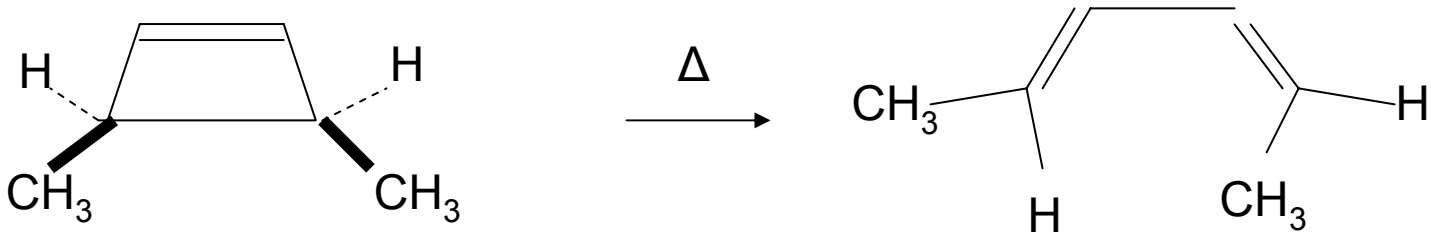


Entgegen (opposite side) E-isomer



E,Z-diene

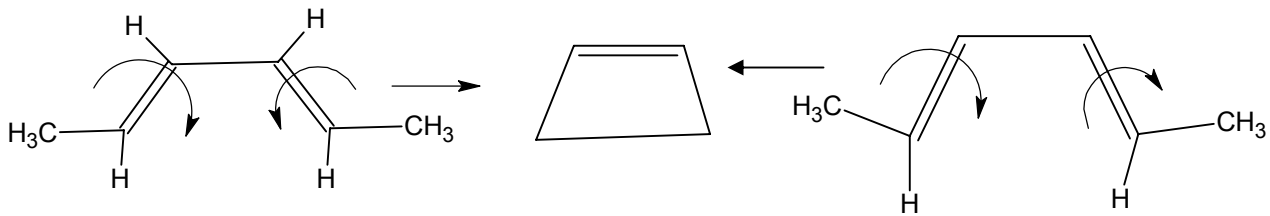
lp-low priority (H), hp- high priority (CH_3)



"cis"

E,Z-diene only the product

There are two different pathways for ring opening: disrotatory and conrotatory

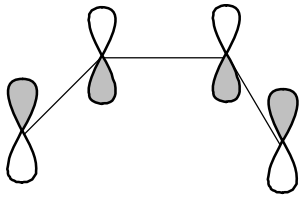


disrotatory

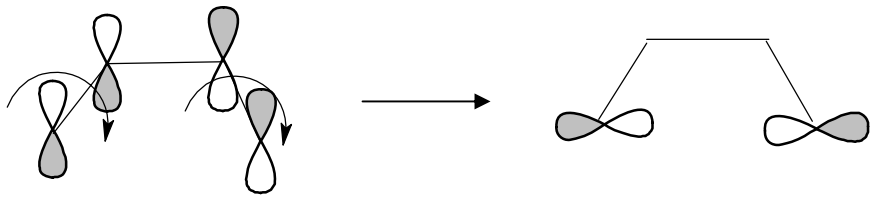
conrotatory

Thermal reaction (ground state)

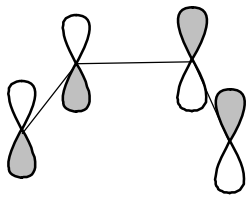
LUMO



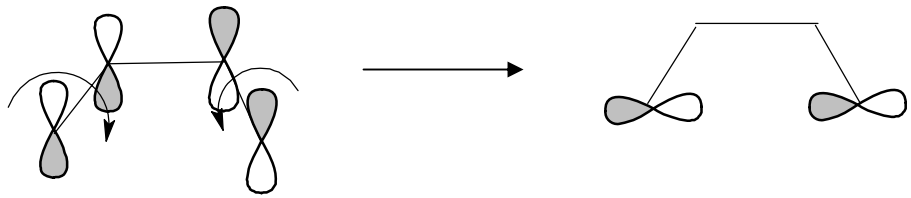
Conrotatory-allowed

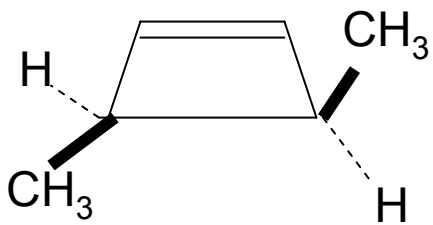


HOMO



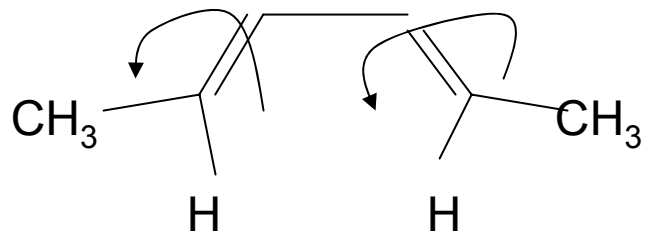
Disrotatory-forbidden





"trans"

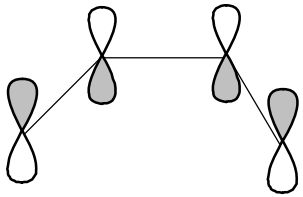
Δ



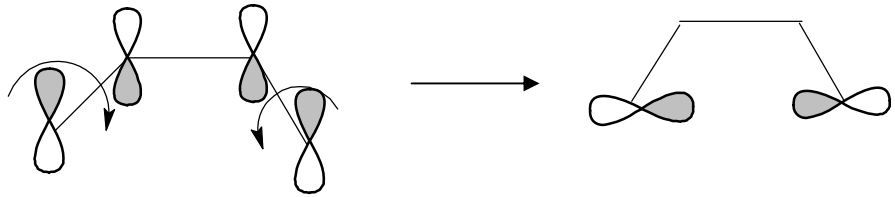
E,E-diene only the product

hv -reaction

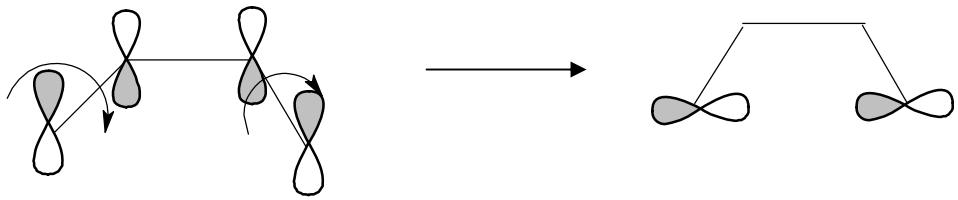
LUMO



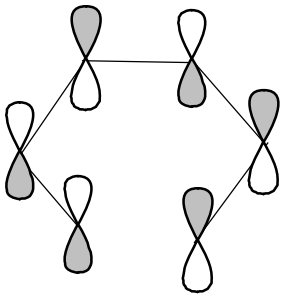
Disrotatory- allowed



Conrotatory-forbidden

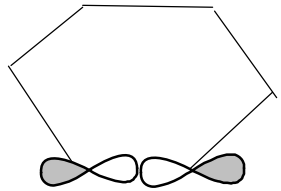


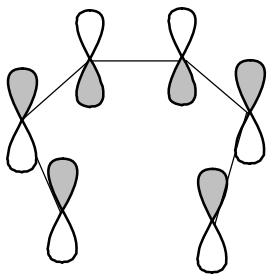
n=1, hexatriene cyclization



LUMO

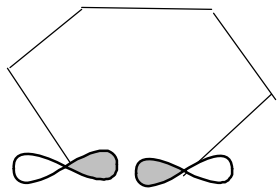
hv, conrotatory
allowed



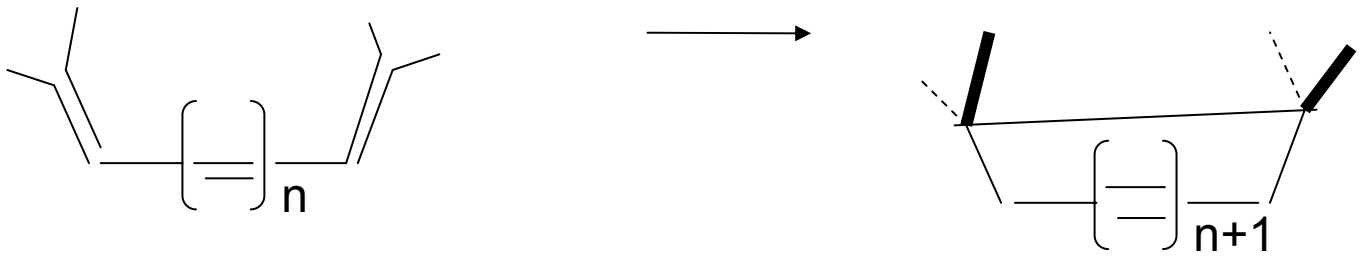


HOMO

Δ, disrotatory
allowed



Selection rules for electrocyclic reactions



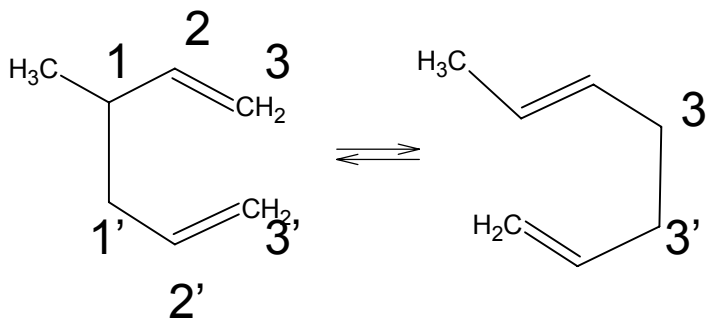
n	Number of π-electrons	Δ	hv
0,2,4	4q	con	dis
1,3,5	4q+2	dis	con

Sigmatropic reactions. Selection rules

Sigmatropic reactions ([i,j]-shift): migration of a σ-bond flanked by one or more π-systems to location i over j positions.

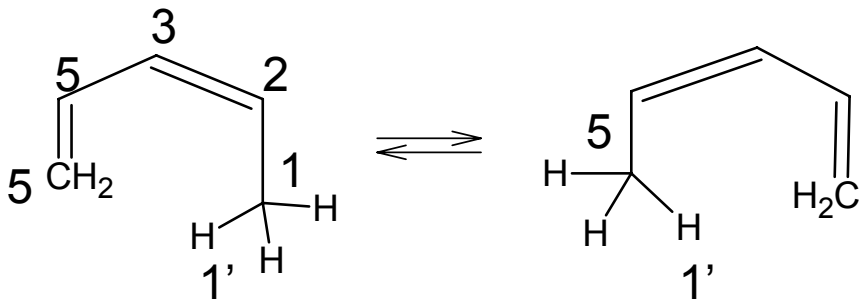
H- and alkyl-group migrations, Cope rearrangement, etc.

Cope rearrangement

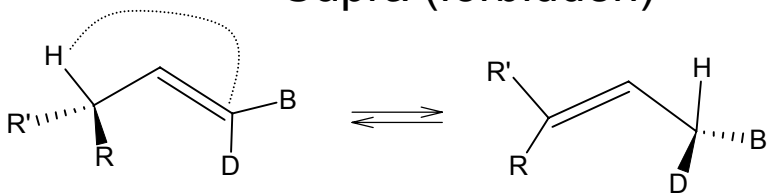


3,3-sigmatropic shift

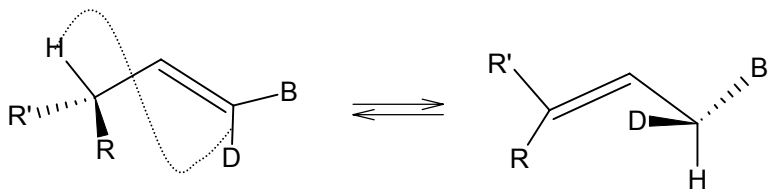
[1,5]-H-shift



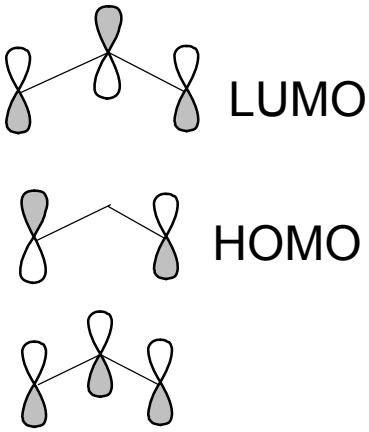
Supra (forbidden)



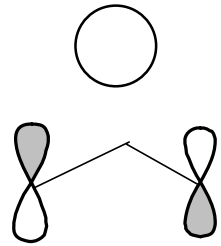
Antara (fallowed)



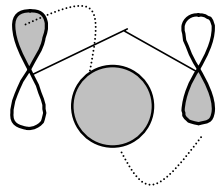
[1,3] H• shift in allyl radical



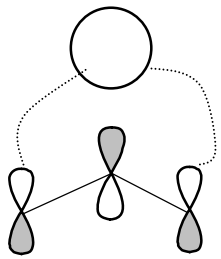
Δ, supra- forbidden



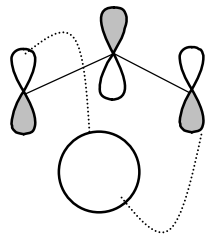
Δ, antara- allowed



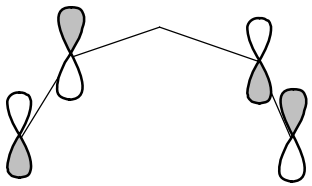
hv, supra- allowed



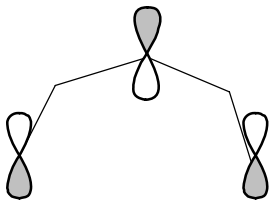
hv, antara- forbidden



[1,5] H-shift

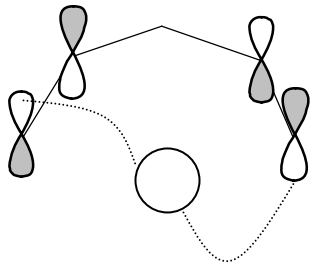


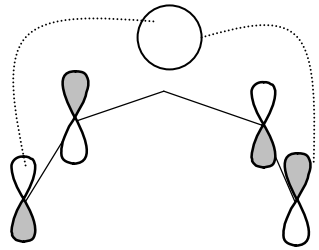
LUMO



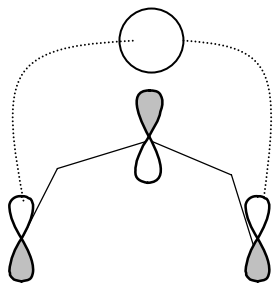
HOMO

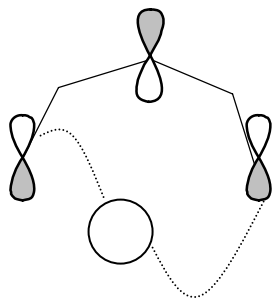
hv (excited state)- supra forbidden, antara- allowed





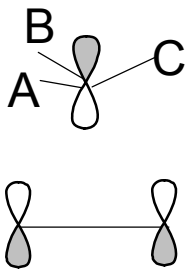
Δ (ground state)- supra allowed, antara-forbidden





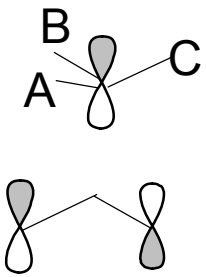
Flip the selection rule when : change in number of pi-electrons (4n, 4n+2); change in sterochemistry (supra, antara), change in electronic state (ground or excited)

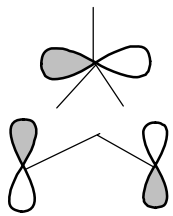
Migration of CH_3- inversion or retaining of configuration



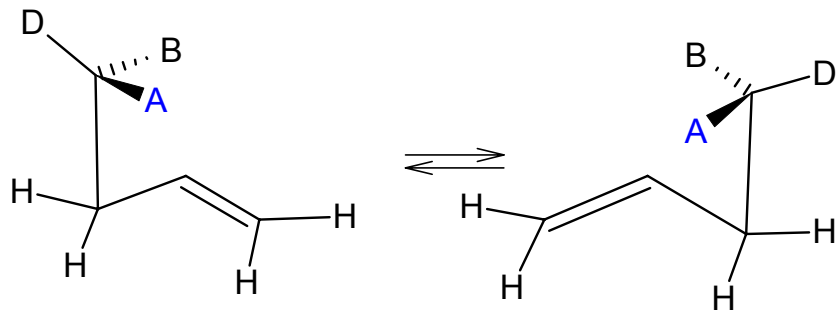
1,2-shift, supra- allowed, retaining of configuration

1,3-shift, supra, with retaining of configuration- forbidden

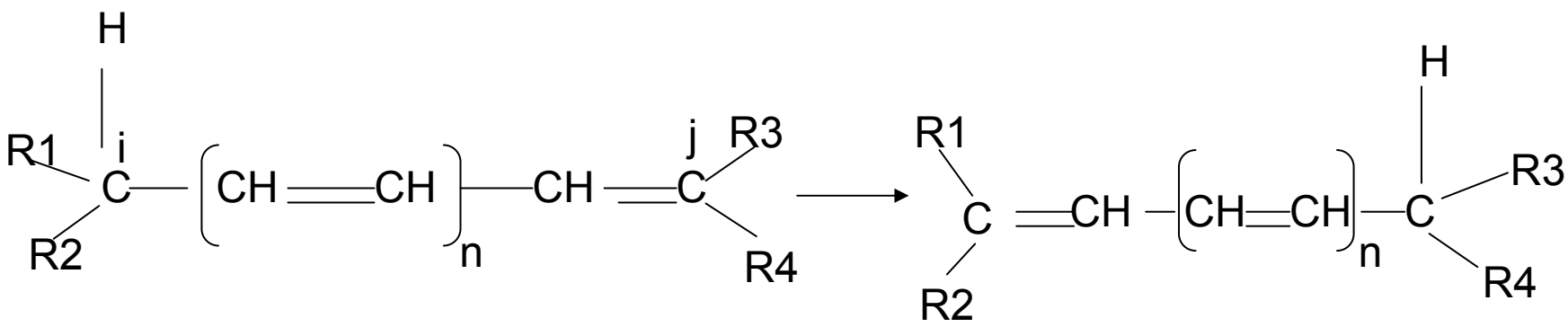




1,3 shift with inversion of configuration is allowed



[1,J]-H SHIFT SELECTION RULES



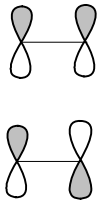
Allowed H-shifts

Number of e	neutral	polyene cation	anion-	Δ	hv
2	-	[1,2]	-	s	a
4	[1,3]	[1,4]	[1,2]	a	s
6	[1,5]	[1,6]	[1,4]	s	a
4q	[1, 4q-1]	[1,4q]	[1,4q-2]	a	s
4q+2	[1,4q+1]	[1,4q+2]	[1,4q]	s	a

Another useful approach: aromaticity of transition states (Evans, Zimmerman)

For allowed rxn, TS is aromatic, for forbidden rxn, TS is antiaromatic

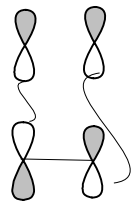
cyclic dimerization of ethylene:



π^2 (s) + π^2 (s)

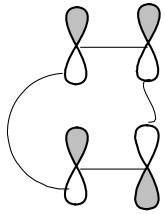
Antibonding
forbidden

4π-antiaromatic



π^2 (s) + π^2 (a)

bonding
allowed

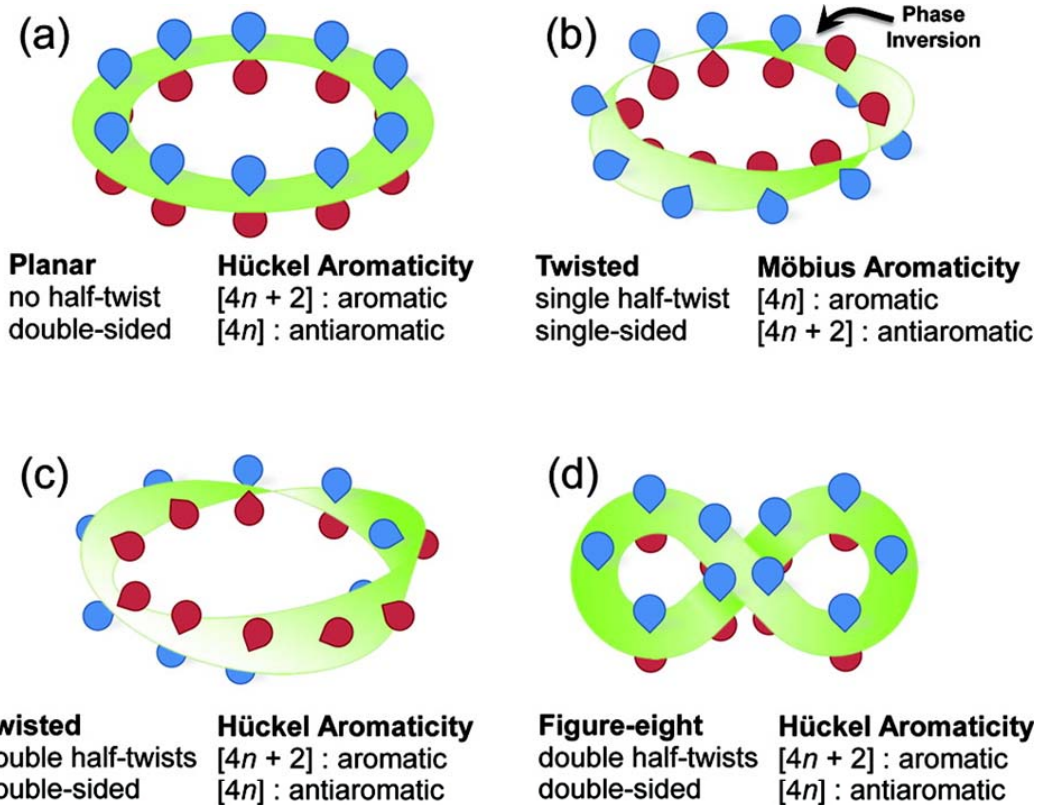


π^2 (a) + π^2 (s)

bonding
allowed

Aromaticity for antara?

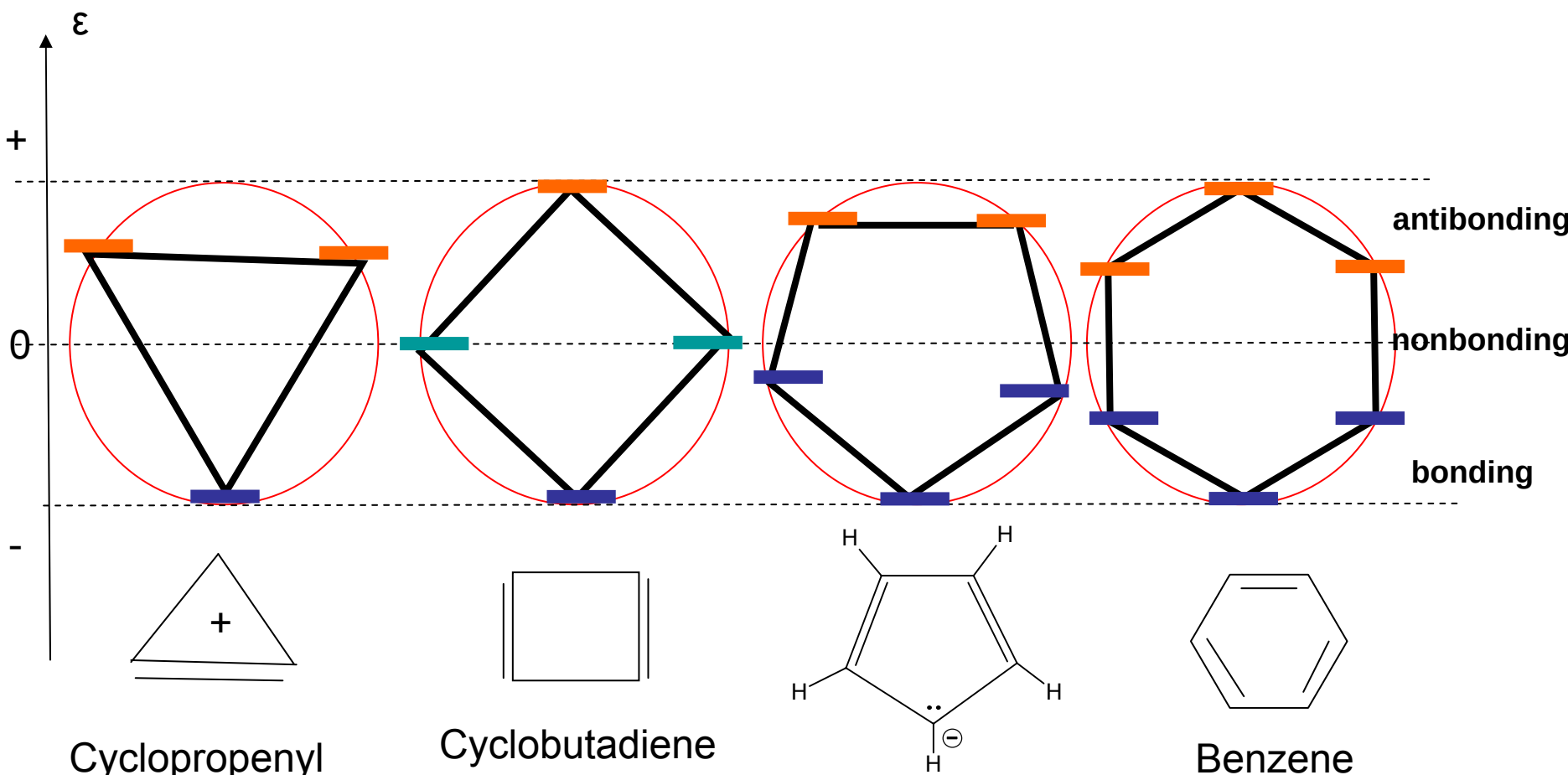
Hückel and Möbius aromaticity (topology)



Under Hückel topology, there are even number of nodes (0, 2,4)
Under Möbius topology- odd number of nodes (1,3,5…)

Published in: Min-Chul Yoon; Pyosang Kim; Hyejin Yoo; Soji Shimizu; Taro Koide; Sumito Tokuji; Shohei Saito; Atsuhiro Osuka; Dongho Kim; *J. Phys. Chem. B* Article ASAP
DOI: 10.1021/jp207731k

The circle method – Huckel topology



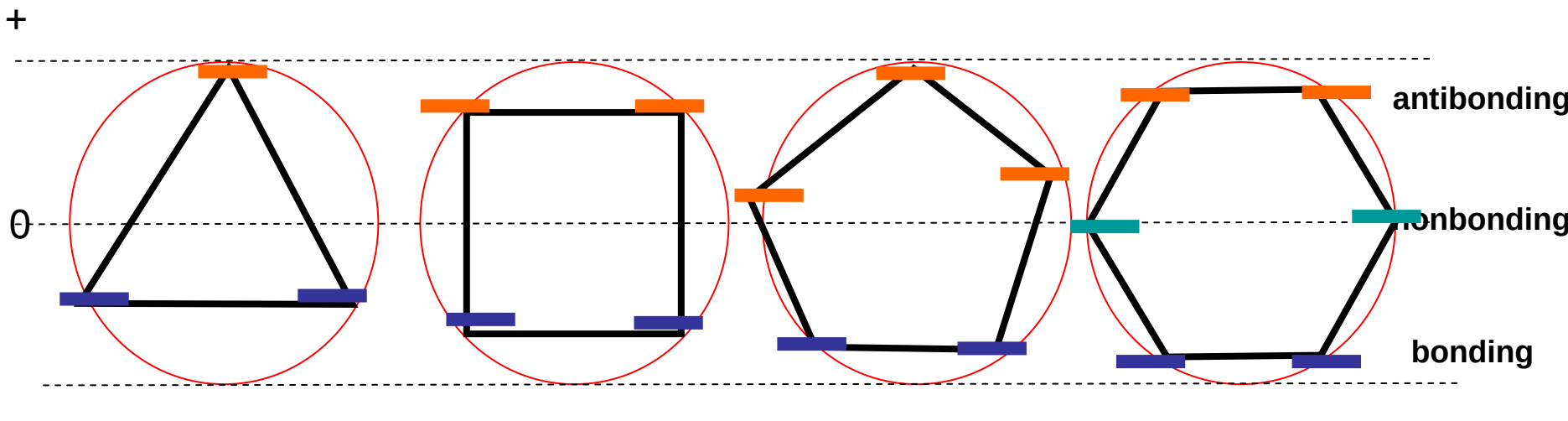
Cyclopropenyl cabocation
2π electrons
(4n+2), n=0
aromatic

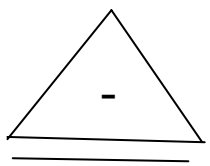
Cyclobutadiene
4π electrons –
antiaromatic (not stable). Dication and dianion-aromatic

Cyclopentadienyl anion
6π electrons –
aromatic

Benzene
6π electrons –
aromatic

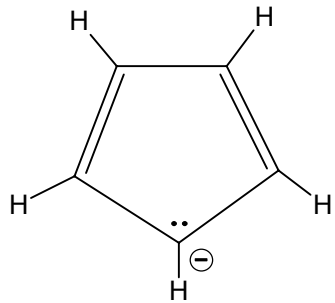
For Mobius topology, the rules are reversed and so are orientation of rings in the circles



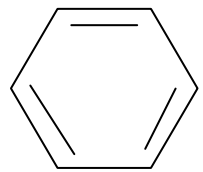


Twisted cyclopropenyl anion
4π electrons
aromatic

Twisted cyclobutadiene
4π electrons
aromatic

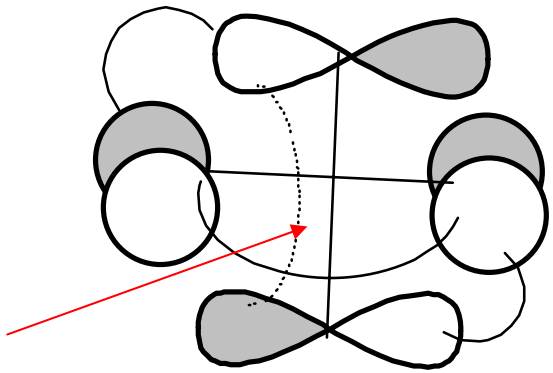


Twisted cyclopentadienyl cation
4π electrons –
aromatic



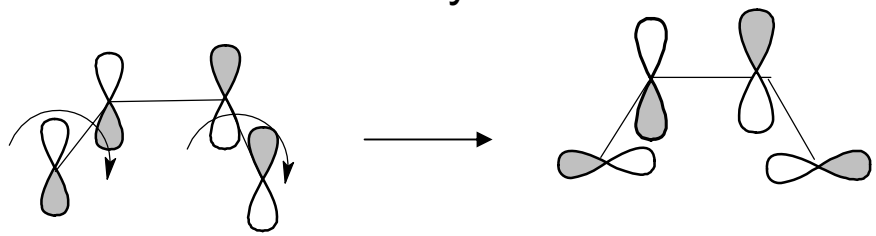
Twisted benzene
6π electrons –
antiaromatic

Allowed $\pi^2_s + \pi^2_a$ addition (Möbius 4 π aromatic)



One node (Möbius)

Conrotatory-allowed



Möbius 4π-aromatic TS!

Absolutely generalized Woodward-Hoffman rule (you do not have to know anything but a script of rxn)

A pericyclic rxn is allowed if the number of 4n+2 suprafacial plus 4m antarafacial component is odd

For example:

π^2 (s) + π^2 (s)

First term: supra, n=0, second term: supra, n=0
Zero + zero= 2 components (even)- forbidden

π^2 (s) + π^2 (a)

First term: supra, n=0,
second term: antara, does not fit the 4m formula, discard
Result: one zero = 1 component, odd, allowed

π^4 (s) + π^2 (s)

First term: supra, n=4, does not fit 4n+2, discard
second term: supra, n=0
One zero= 1 component (odd)- allowed