

Qualitative approach to prediction of reaction barriers.

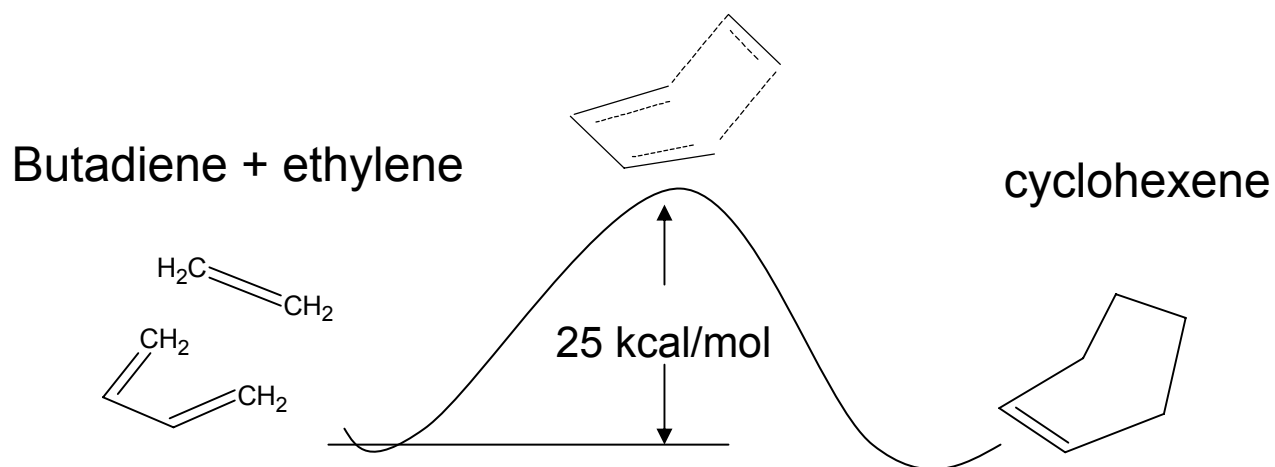
For stepwise reactions, which proceed via reaction intermediates, the reaction barriers could be estimated using relative stabilities of the RIs.

For concerted reaction (no RIs) ??? “No-mechanism” reactions (early 60th)

Many concerted reactions proceed via a cyclic transition state- pericyclic reactions

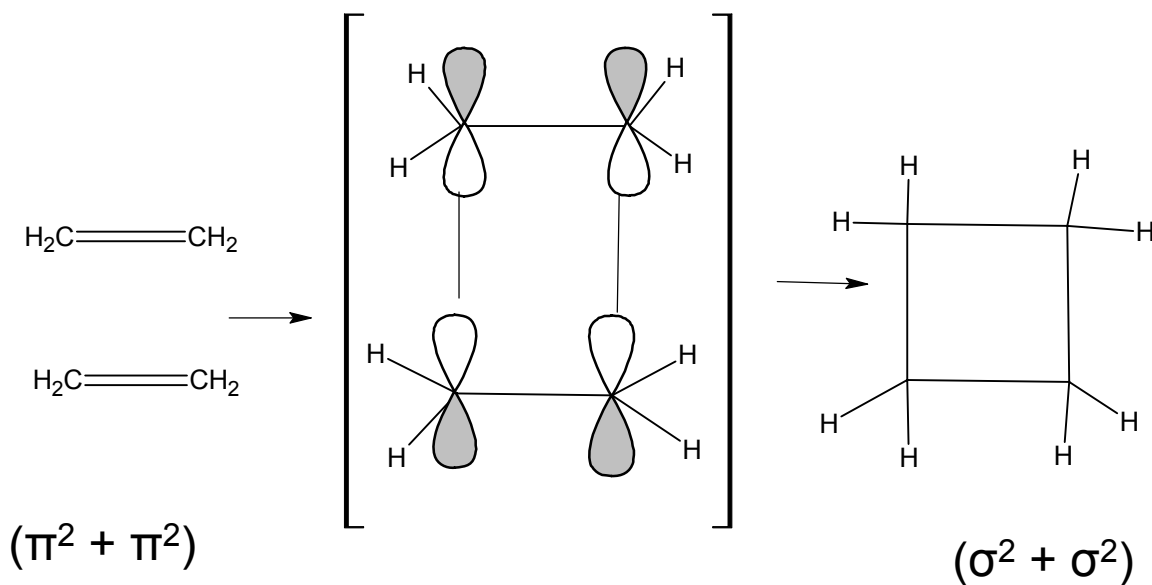
S_{N2} rxn is concerted but not pericyclic

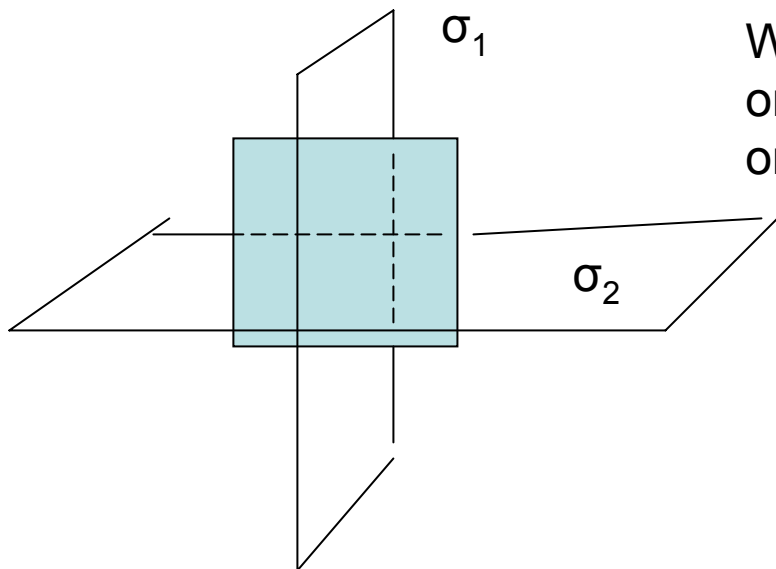
Diels-Alder rxn: concerted and pericyclic



Woodward and Hoffmann idea: pericyclic concerted reactions proceed readily if the symmetry of the occupied MO of reactants corresponds to the symmetry of the occupied MOs of products.

Simply: conservation of orbital symmetry in pericyclic concerted reactions.



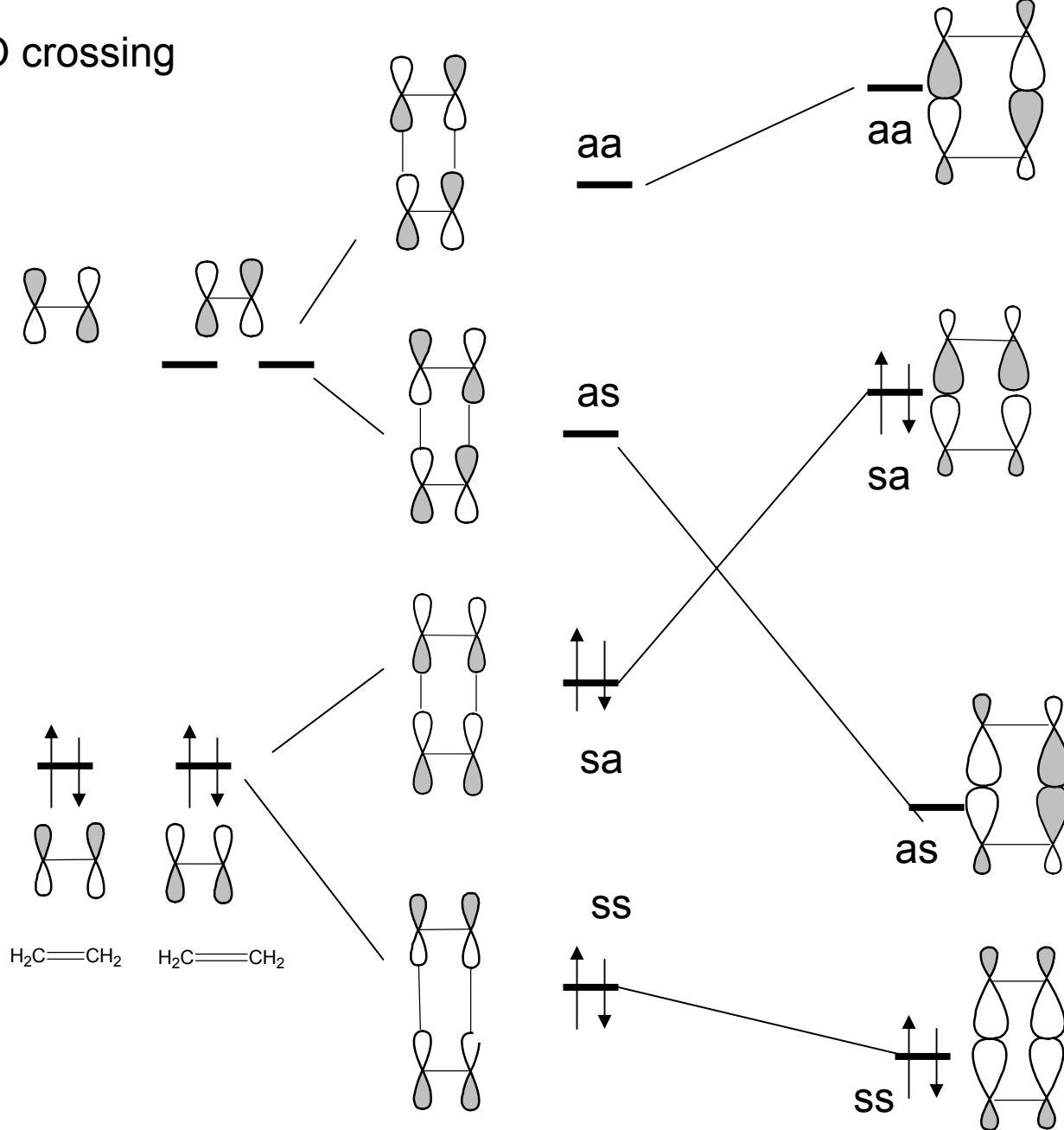


We do not need ALL symmetry elements but only planes which contain bonds being broken or formed

We do not need ALL molecular orbitals but only HOMO and LUMO of reactants!

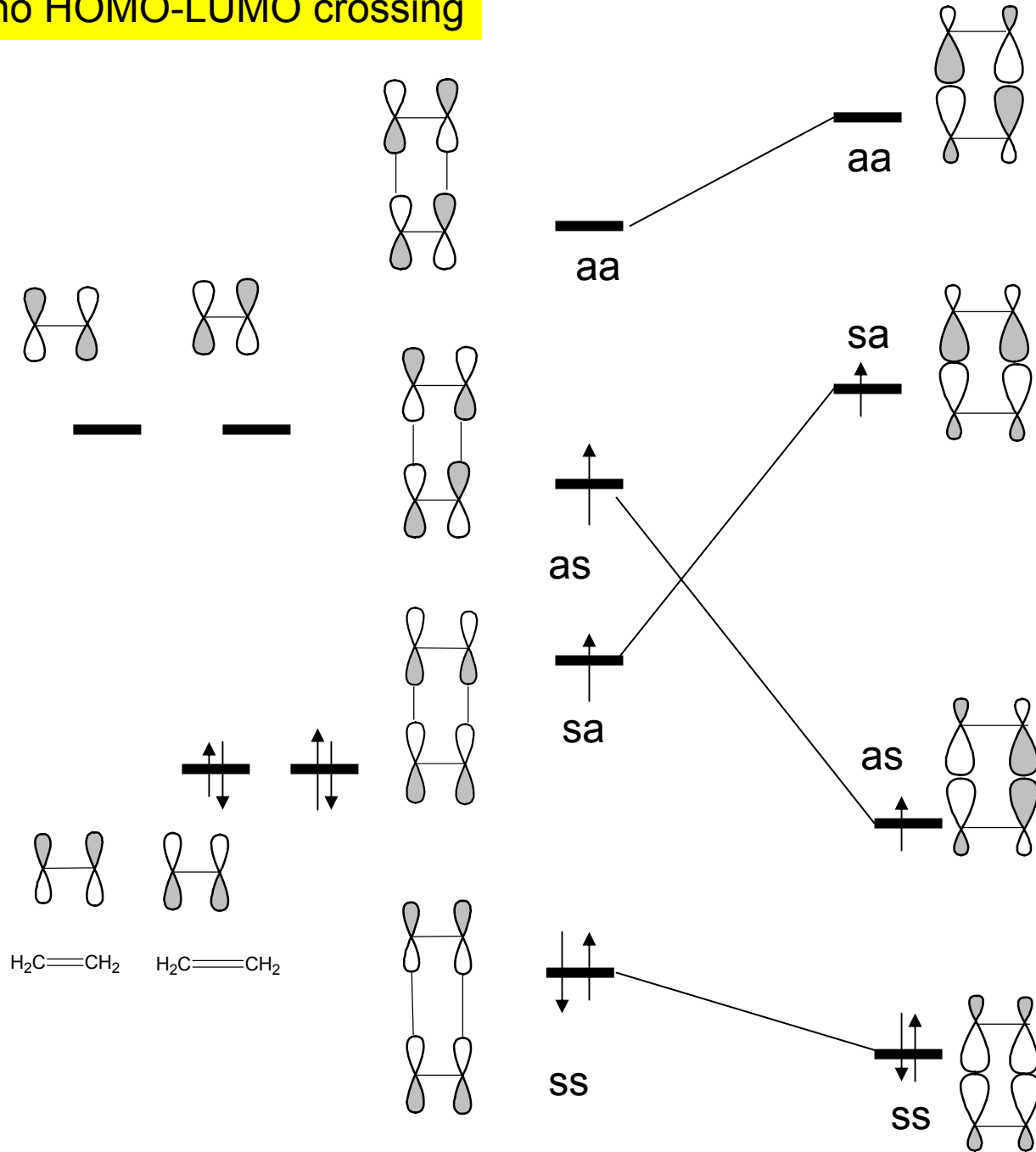
Let us work with the ground electronic states (no excited states). So, we run reaction thermally (Δ), not photochemically ($h\nu$).

HOMO-LUMO crossing



Ground state of the reactants correlates with the doubly-excited state of the product

There is no HOMO-LUMO crossing



Ground state (thermal) ($\pi^2 + \pi^2$) – addition is symmetry forbidden (proceeds with a high barrier)

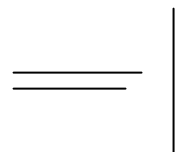
Excited state (photochemical) ($\pi^2 + \pi^2$) – addition is symmetry allowed (proceeds with a lower barrier)

Stereochemistry of pericyclic reactions

Face-to-face approach, as in above example: **suprafacial**. All bonds being broken or formed are on the same side of the molecular surface

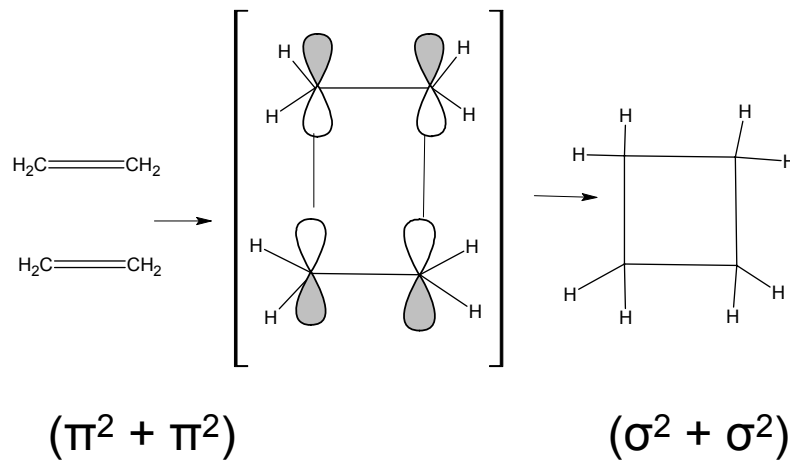


alternative approach (**antarafacial**). Bonds to be formed are on the opposite side of the molecular surface

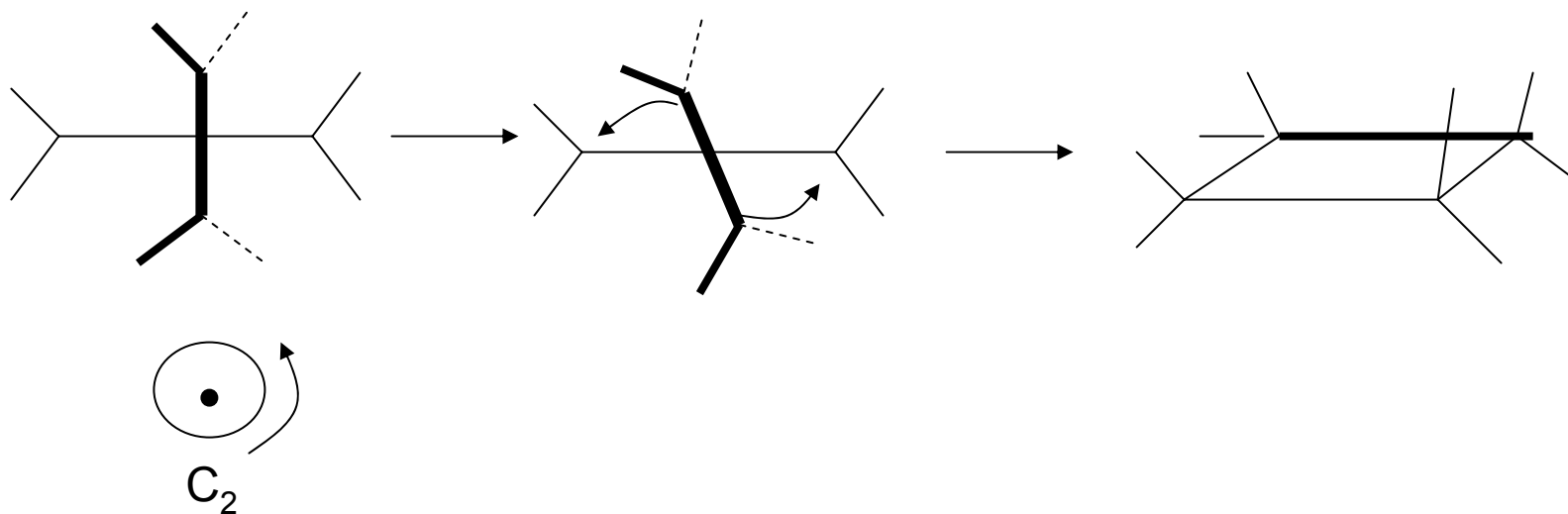


Stereochemistry of cycloaddition

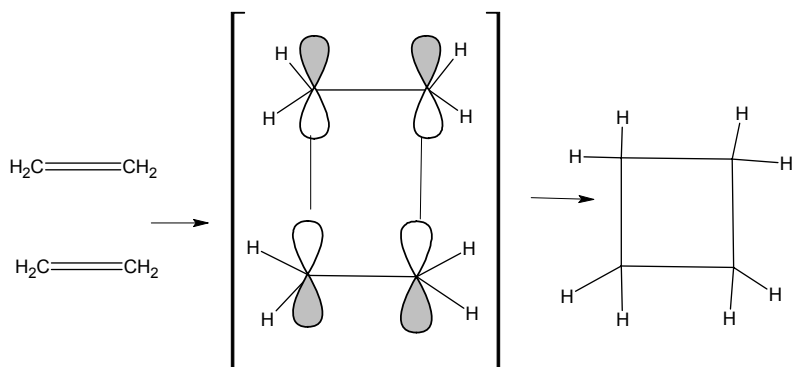
Supra faced



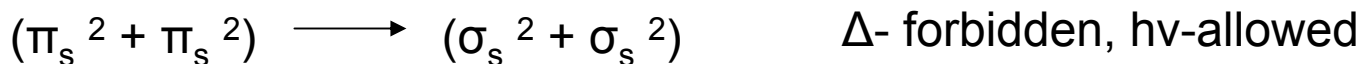
Antara faced



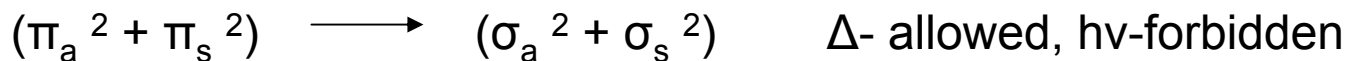
Supra faced



More detailed stereochemistry:



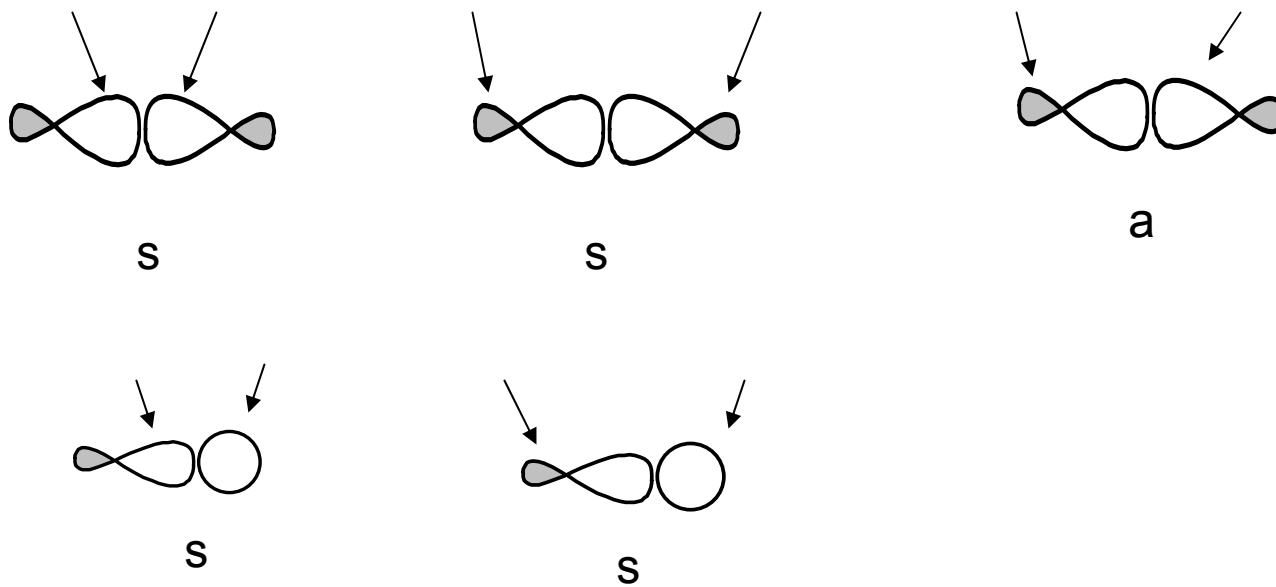
Change in stereochemistry for the reaction (from a to s) flips the selection rule:



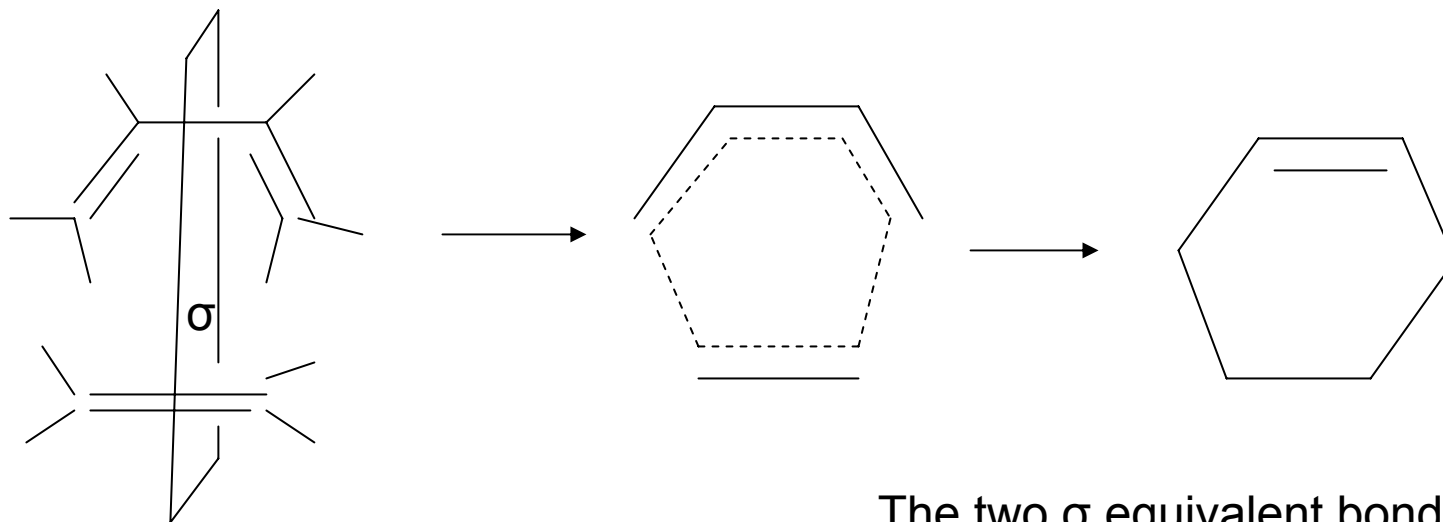
Antara- supra-facial stereochemistry is difficult to achieve due to steric effects- rare case in reality



For σ -orbitals: out-out and in-in lobes are supra, in-out lobes-antara



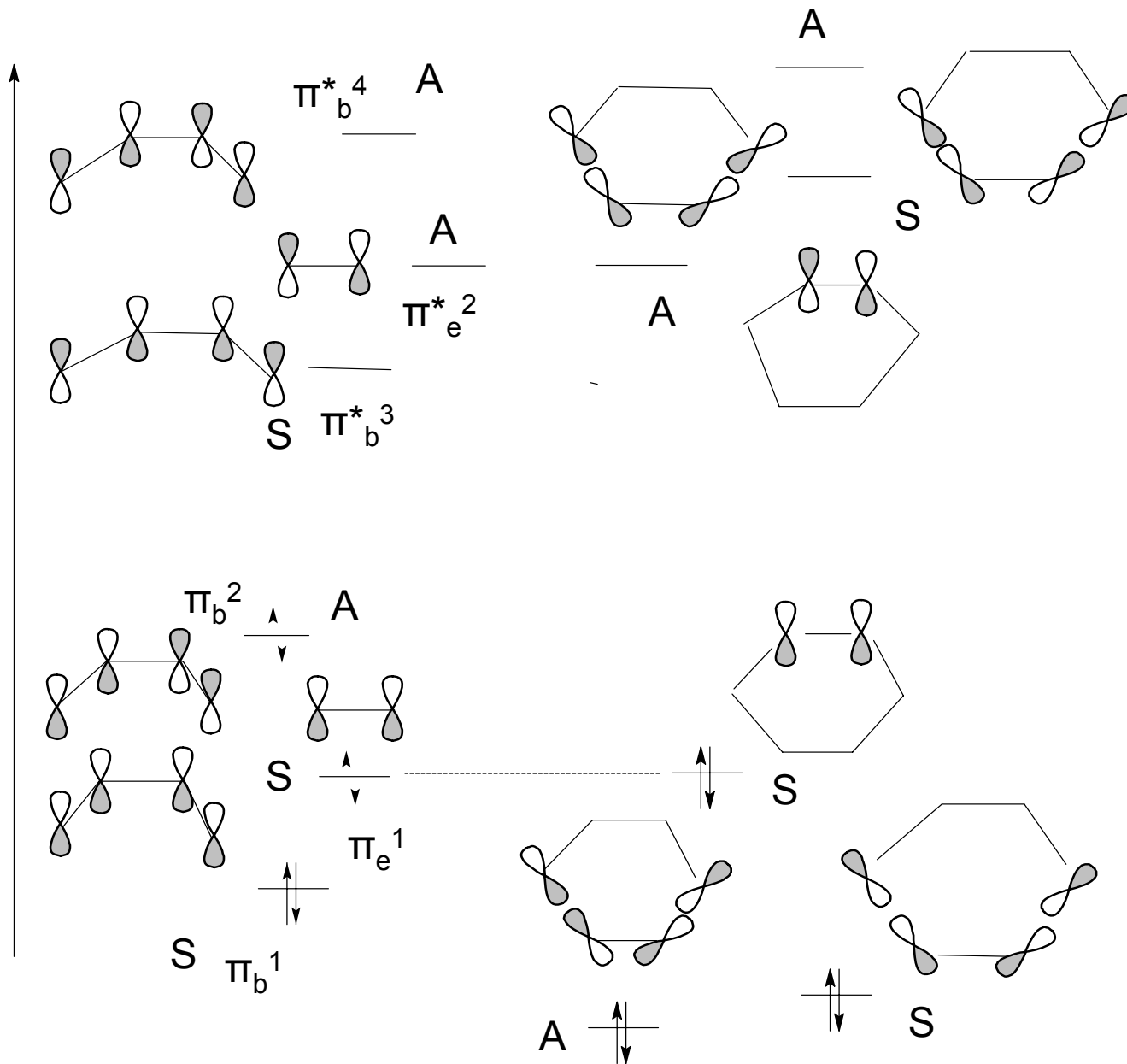
MO correlation diagram for $4n+2$ cycloaddition (n-number of π electrons)



$$\pi_s^2 + \pi_s^2 + \pi_s^2 \rightarrow \pi_s^2 + \sigma_s^2 + \sigma_s^2$$

The two σ equivalent bonds are not proper symmetry combination with respect to the σ -plane

Still we can apply symmetry rules for this rxn. MOs better be calculated



MOs of reactants correlate with MOs of product- Δ -allowed, hv- forbidden

Selection rules for cycloaddition reactions

$$p_{\pi e} + q_{\pi e}$$

Δ -allowed

h ν -allowed

$$4n$$

$$p_{\pi e} (a) + q_{\pi e} (s)$$

$$p_{\pi e} (s) + q_{\pi e} (s)$$

$$p_{\pi e} (s) + q_{\pi e} (a)$$

$$p_{\pi e} (a) + q_{\pi e} (a)$$

$$4n+2$$

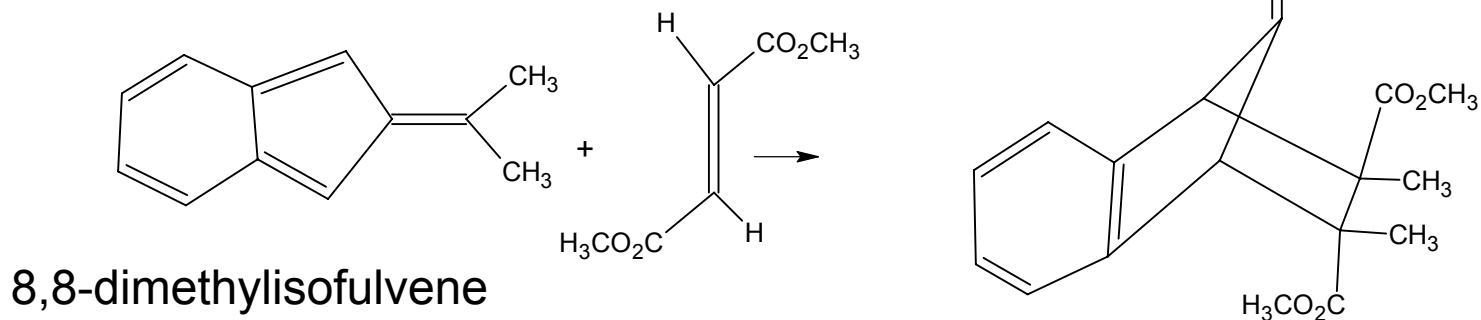
$$p_{\pi e} (s) + q_{\pi e} (s)$$

$$p_{\pi e} (a) + q_{\pi e} (s)$$

$$p_{\pi e} (a) + q_{\pi e} (a)$$

$$p_{\pi e} (s) + q_{\pi e} (a)$$

$\pi^8 (s) + \pi^2 (s)$ cycloaddition- s,s thermally allowed

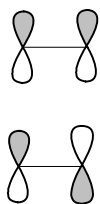


Fukui (shared Noble prize with Hoffmann in 1981) – **FMO** theory (frontier MO)

FMO for pericyclic reactions: HOMO and LUMO symmetries should be only considered

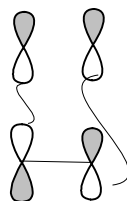
If HOMO-LUMO interaction leads to bonding interaction then reaction is allowed, antibonding interaction- forbidden

For example, for dimerization of ethylene:



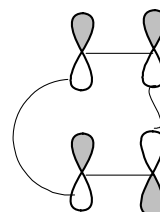
π^2 (s) + π^2 (s)

Antibonding
forbidden



π^2 (s) + π^2 (a)

bonding
allowed



π^2 (a) + π^2 (s)

bonding
allowed