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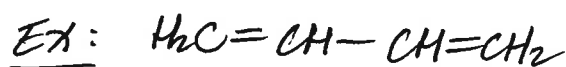
Ch 15 Dienes Resonance & Aromaticity.

"Diene" = hydrocarbon containing 2. C=C double bonds.

- 1) Cumulenes & Allenes: one carbon is involved in both double bonds.

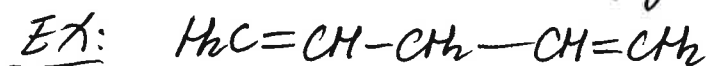


- 2) Conjugated Dienes: double bond immediately adjacent to one another

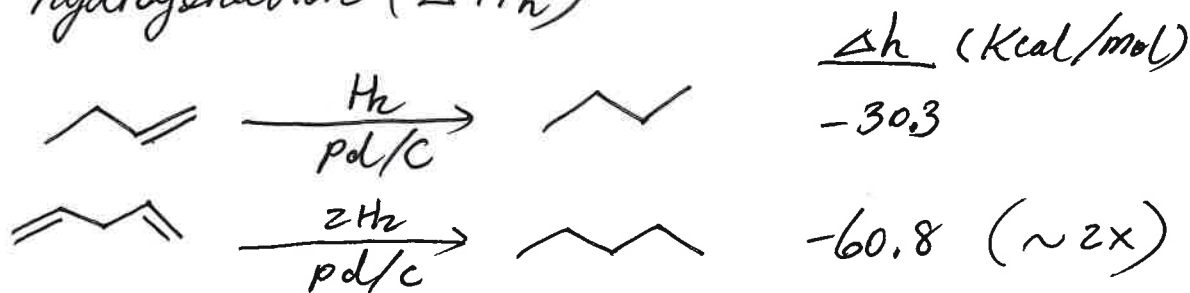


* special bonding & reactivity properties

- 3) ordinary Dienes: > 1 sat. C between double bonds.
(non-conjugated)



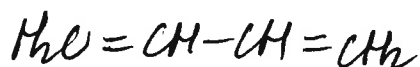
- 4) Special bonding situations w/ conj. Dienes. → heats of hydrogenation (ΔH_h°)



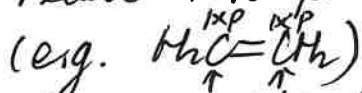
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-3.7 Kcal/mol stabilization associated w/ conjugation of π bonds
 Origin = π e^- delocalization that is not represented ~~in~~ in the standard graphical nomenclature.

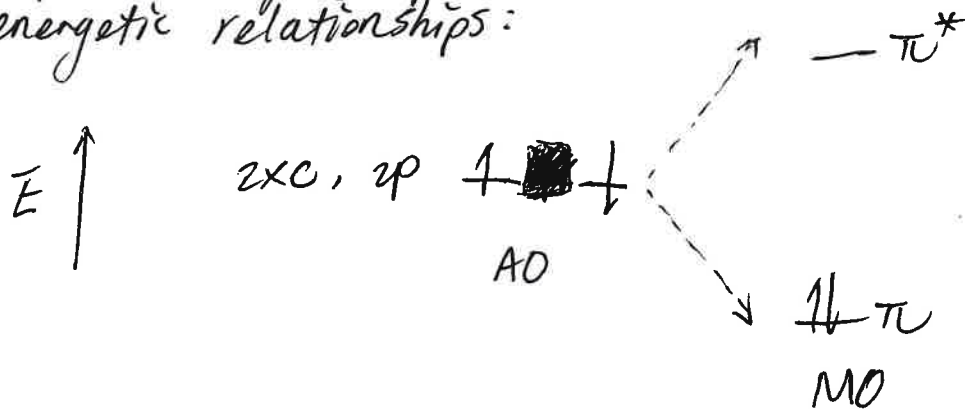


Prelude: recall MO pictures for an ~~isolated~~ isolated π bond.

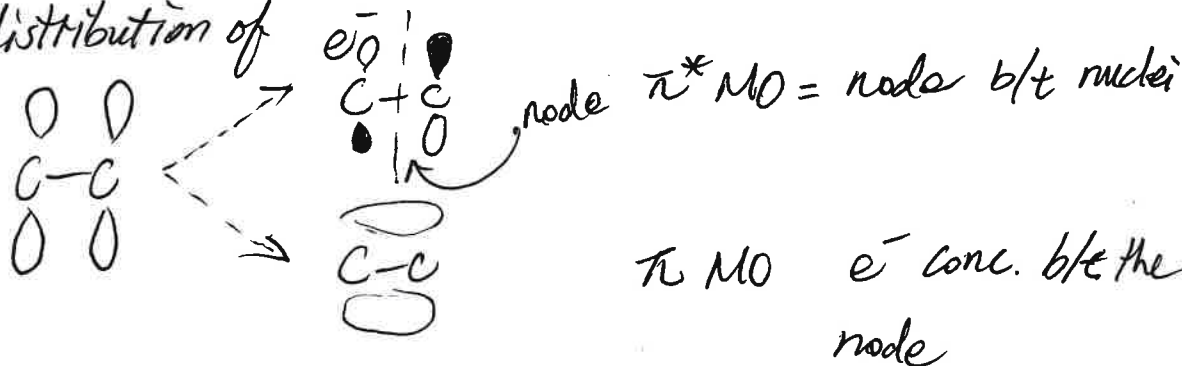


2 complementary graphical conventions.

1. energetic relationships:



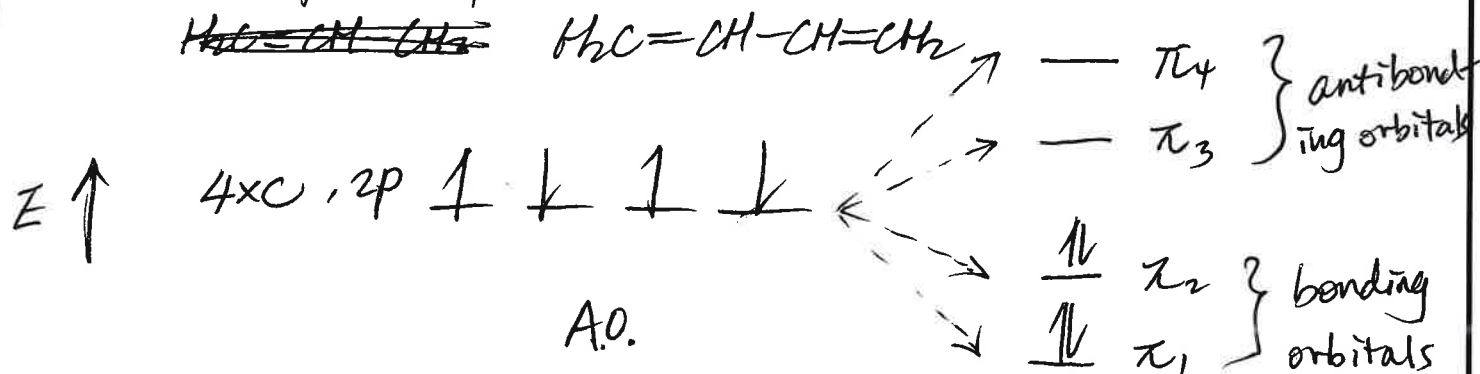
2. spatial distribution of



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π M.O. for conj. Diene.



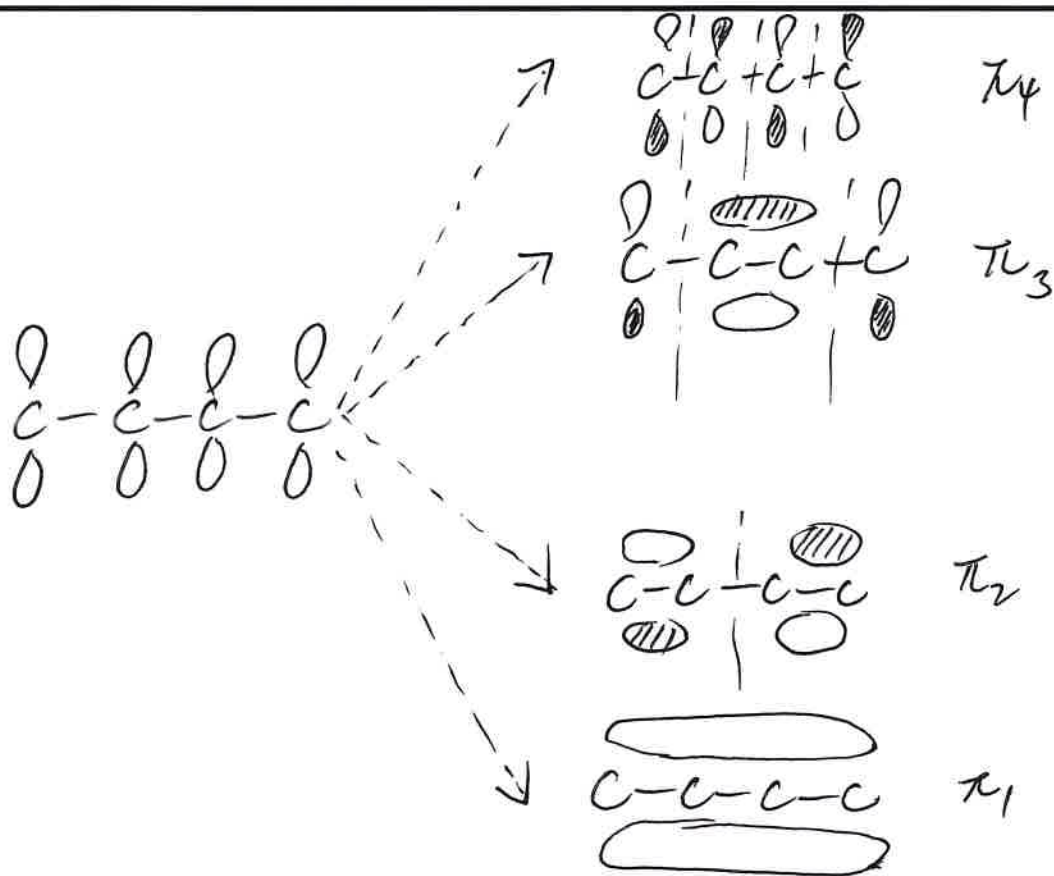
Comments:

- 1) # A.O. = # M.O.
 - 2) Some MO are better for e^- 's — ↓ E than A.O. (bonding)
- ↑ C = destabilizing



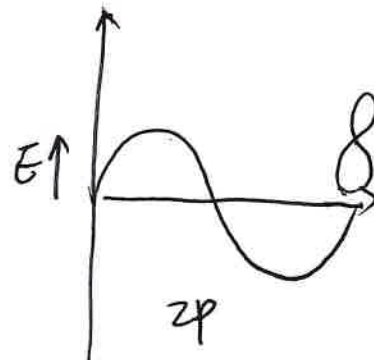
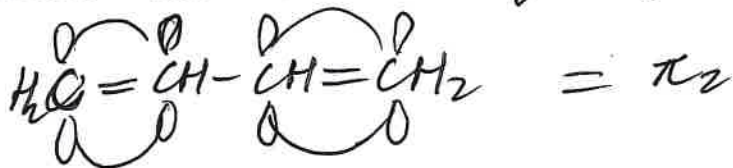
see next page
 for complete orbital diagram.

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Comments.

- 1) in π_1 , e^- are completely delocalized over all 4 C.
- 2) # vertical nodes \uparrow incrementally: \uparrow nodes = \uparrow energy
- 3) redraw diene in light of MO.



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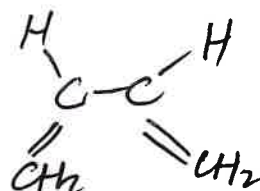
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Manifestation of delocalization

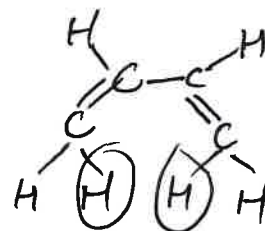
conj. diene prefers planar conformation



"s-trans"



"s-cis"



"s" - prefix indicates a bond that is formally single.
Twisted conf. unfavorable b/c overlap of "p₂+p₃" is disrupted.