Course Chem 343 11 AM Lecturer Gellman

Day Wednesday Date 12/7/11

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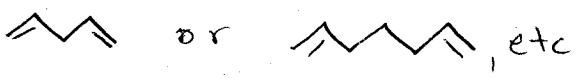
Recall: Classification of dienes...

1) Allenes ($H_2C=C=CH_2$)

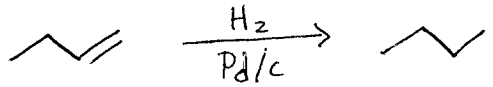
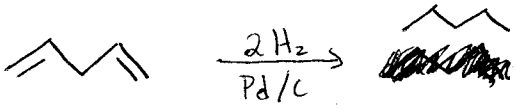
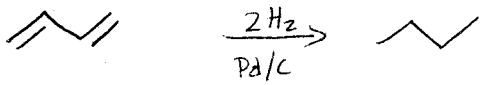
2) Conjugated dienes ($CH_2=CH-CH=CH_2$)

3) Others ($H_2C=CH-CH_2-CH=CH_2$) ⟶ a molecule that happens to have 2 C=C units


, etc

Special features of conjugated dienes - consider comparisons of

$\Delta H^\circ_H$

| | $\Delta H$ (kcal/mol) | |
|---|---|---|
|  | -30.3 | |
|  | -60.8 | (~2x alkene) |
|  | -57.1 | (~3.7 kcal/mol "missing") |

∴ conjugated diene has ~3.7 kcal/mol "extra" stability rel. to 2x isolated C=C units

Source of this stabilization?

"conjugation" ⟶ interaction between neighboring π bonds

Perspective: bonding phenomena in which e⁻s are shared by more than two atoms ("delocalization")

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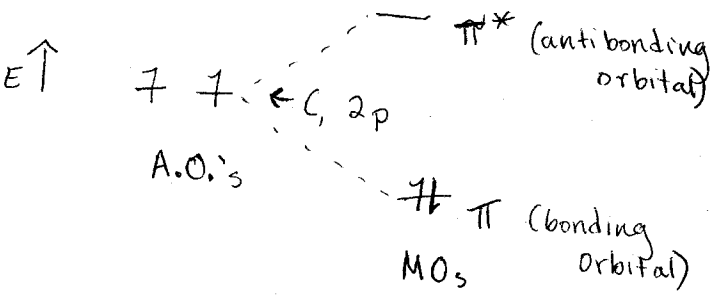
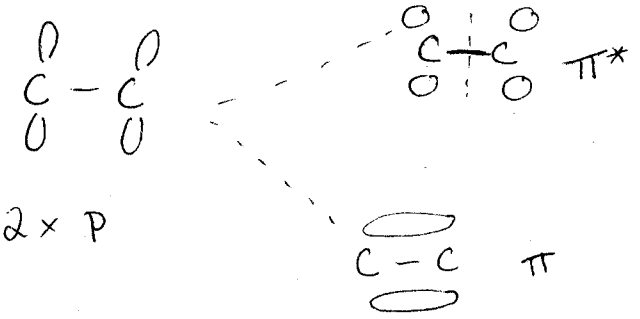
Prelude: recall M.O. analysis of an isolated $\pi$-bond (eg. $H_2C=CH_2$)

1) Energy info



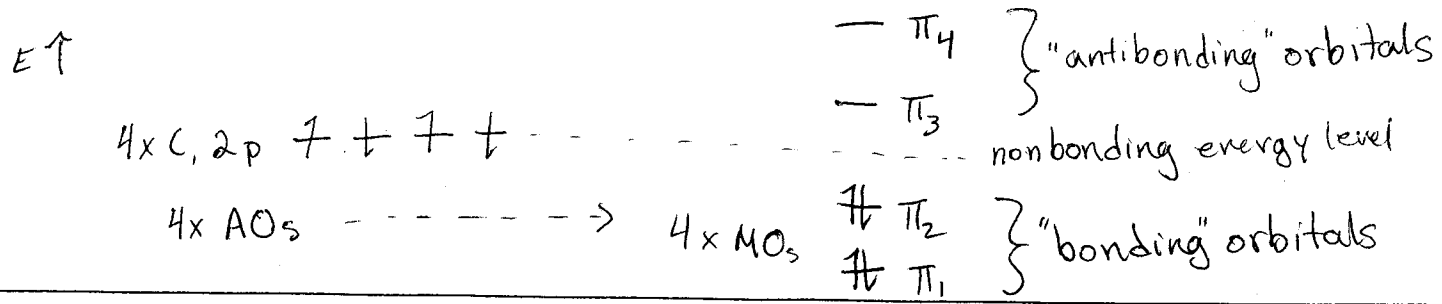

2) Spatial distribution of e⁻s in these MOs




Note: $\perp$ node in $\pi^*$ orbital (associated w/ high energy of this M.O.)

Extend MO analysis ($\pi$) to conjugated dieres:

$CH_2=CH-CH=CH_2$, for example



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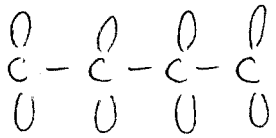
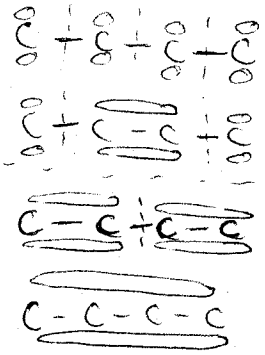
Spatial distribution:



(Note: ignore "β" analysis in text)




Full delocalization

Note: as * ⊥ nodes increases, energy increases (e's more confined)

Re-examine:

$H_2C = CH - CH = CH_2$

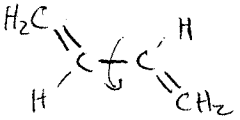
↑ now we recognize that there is some π bonding between $C_2$ + $C_3$

($H_2C = CH \cdots CH = CH_2$)

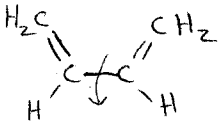
Thus, conventional drawing corresponds to $\pi_2$.

Structural manifestation of the delocalization implied by $\pi_1$:

Conjugated dienes prefer planar conformations.

$H_2C = CH - CH = CH_2$ ---> 

(all 4 C's in 1 plane) s-trans

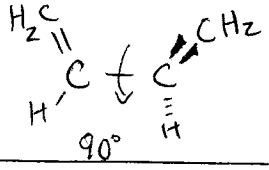
vs. 

s-cis

3.7 kcal/mol to interconvert

S - ~~simular~~ "single bond"

but not stable:



90°

conjugation not possible!

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15.2 - skip.