Conjugated Systems I

General / Prep.

MO Theory

UV Spectroscopy

Practice

Ref 13: (1 - 9); 1, 2B, 7, 9 (both ed^{ns})

Prob HMWK #4

Adv Rdg 13: 10, 11 (both ed^{ns})

General / Terminology

- traditional:

  alternating single/ multiple bonds

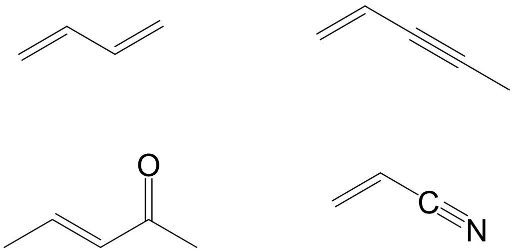
  (incl. heteroatoms such as O, S, N ...)

- modern:

  "continuous sideways overlap of p orbitals" =

  "extended π system"

Examples:

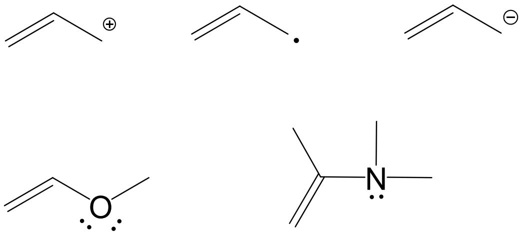


General ...

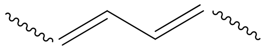
also:

"π bond interacting with single p orbital",

such as



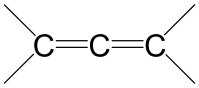
Emphasis will be on 1, 3 dienes: i.e.



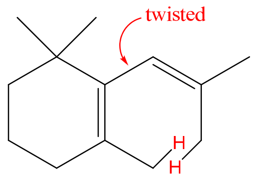
General ..

In contrast, here are some **non-conjugated** systems:

- cumulenes, which have perpendicular π bonds:



- steric strain may prevent parallel line–up, e.g.

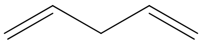


red H's interfere

steric strain between indicated methyl groups results in twisting

"no parallel overlap" = not conjugated

- isolated π bonds, such as

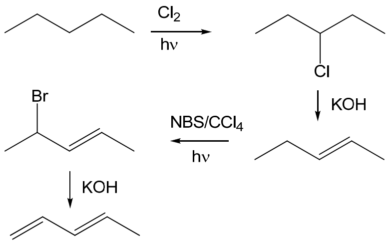


Preparation of 1,3 Dienes

Retrosynthetic Analysis

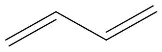
diene
⇑ *E1*
allyl halide
⇑ *“allylic halogenation”*
alkene
⇑ *E1 or E2*
haloalkane
⇑ *radical halogenation*
alkane

Ex. Prep. of 1,3-pentadiene



Bonding in 1,3 Dienes

(*MO Theory*)

simplest example: 

σ-bond MO network:

is built up by “head-on” overlap of

sp^2 / sp^2 orbitals (C – C bonds), and

sp^2 / s orbitals (C – H bonds)

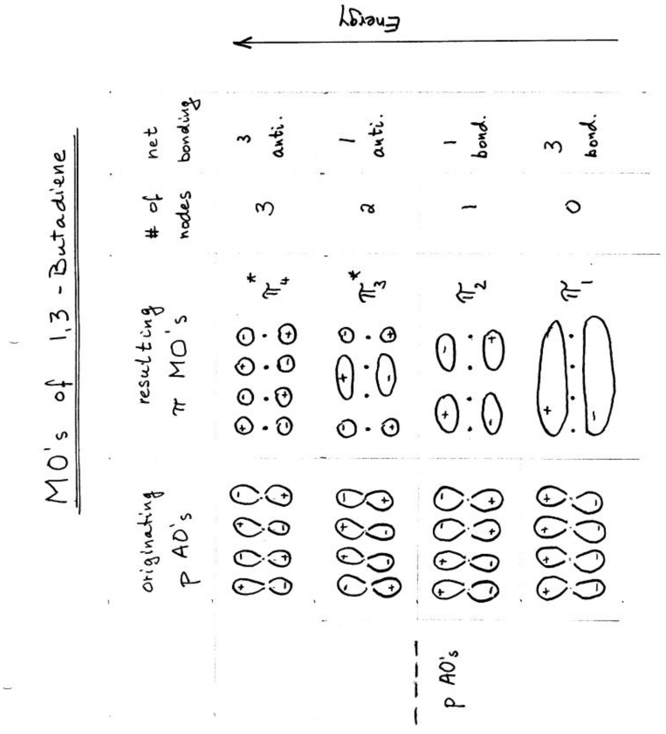
π-bond MO network:

is the result of the “sideways” combination of 4 p AO’s

Recall

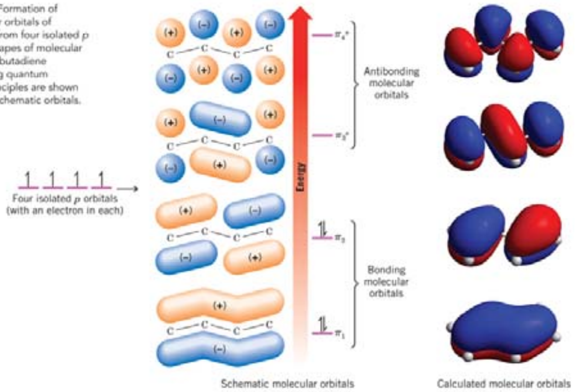
- # of MO’s = # of originating AO’s
- in-phase combination → bonding
- out-of-phase comb. → antibonding, results in nodes
- less nodes = more bonding; lower energy ...
- location of nodes: generally symmetric

π MO’s of 1,3 Butadiene



Solomons Fig 13.5

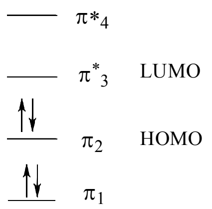
FIGURE 13.5 Formation of the π molecular orbitals of 1,3-butadiene from four isolated *p* orbitals. The shapes of molecular orbitals for 1,3-butadiene calculated using quantum mechanical principles are shown alongside the schematic orbitals.



Filling of MO’s with e^-’s

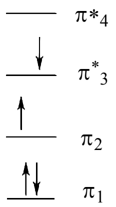
- 4 e^-’s available for π system;
- go into lowest energy MO’s

- **ground state**



all e^-’s in bonding orbitals

- **1st excited state**



much less stable

UV (VIS) Spectroscopy

(in organic chemistry)

range for UV: ~ 200 – 360 nm

VIS ~ 360 – 800 nm

generally,

due to transition of e^-’s

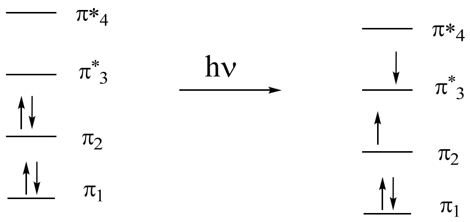
from $\pi \rightarrow \pi^*$ (also $n \rightarrow \pi^*$)

relates to e^- transition with lowest energy

most common: HOMO → LUMO

(highest occupied → lowest unoccupied)

Ex. 1,3 – butadiene (light absorption process)



UV Trends

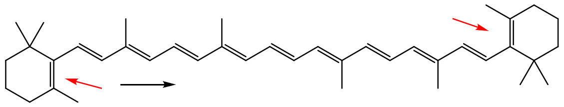
- the greater the extent of conjugation, the smaller the ΔE between HOMO & LUMO
- transition between HOMO and LUMO can be caused by absorption of EMR
- acc. to Planck: $\Delta E = h\nu$ and $\nu = \Delta E/h$
- therefore:

$$\text{smaller } \Delta E \\ \downarrow \\ \text{smaller frequency} \\ \downarrow \\ \text{larger wavelength }, \lambda$$

∴ highly conjugated systems absorb at larger λ, ultimately in the UV region e.g., vitamin A, β - carotene

UV Trends

Structure of β - carotene:



β-carotene

has 9 double bonds in conjugation,

→ double bonds not in conjugation (twisted out of plane, because of steric strain

recall process of light absorption:

white light hits surface,
green light is taken out
reddish light is reflected

vitamin A is chemically related to β - carotene;
involved in physiology of vision,
for more details see Biochem courses

UV Correlation

system	UV peak at
isolated -ene	< 200 nm
conj. diene	~ 220 nm
conj. triene	~ 260 nm
conj. tetraene	~ 290 nm

$\therefore$ can be used for structure analysis
(similar to IR, NMR, ..)

Practice

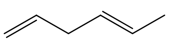
An unknown with MF C_6H_{10}
has no observable UV above 200 nm,
no rings , no triple bonds.
Possible structure?

Ans.

D of U = 2
$\therefore$ 2 double bonds

no UV above 200 nm
$\therefore$ no conjugation

Possible structures:



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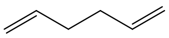

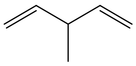

, or ....