Hybridization

Part 2

Reading: Gray: (4-7)
OGN: (16.2)

The Story so far:

MO-LCAO works great for diatomic molecules!

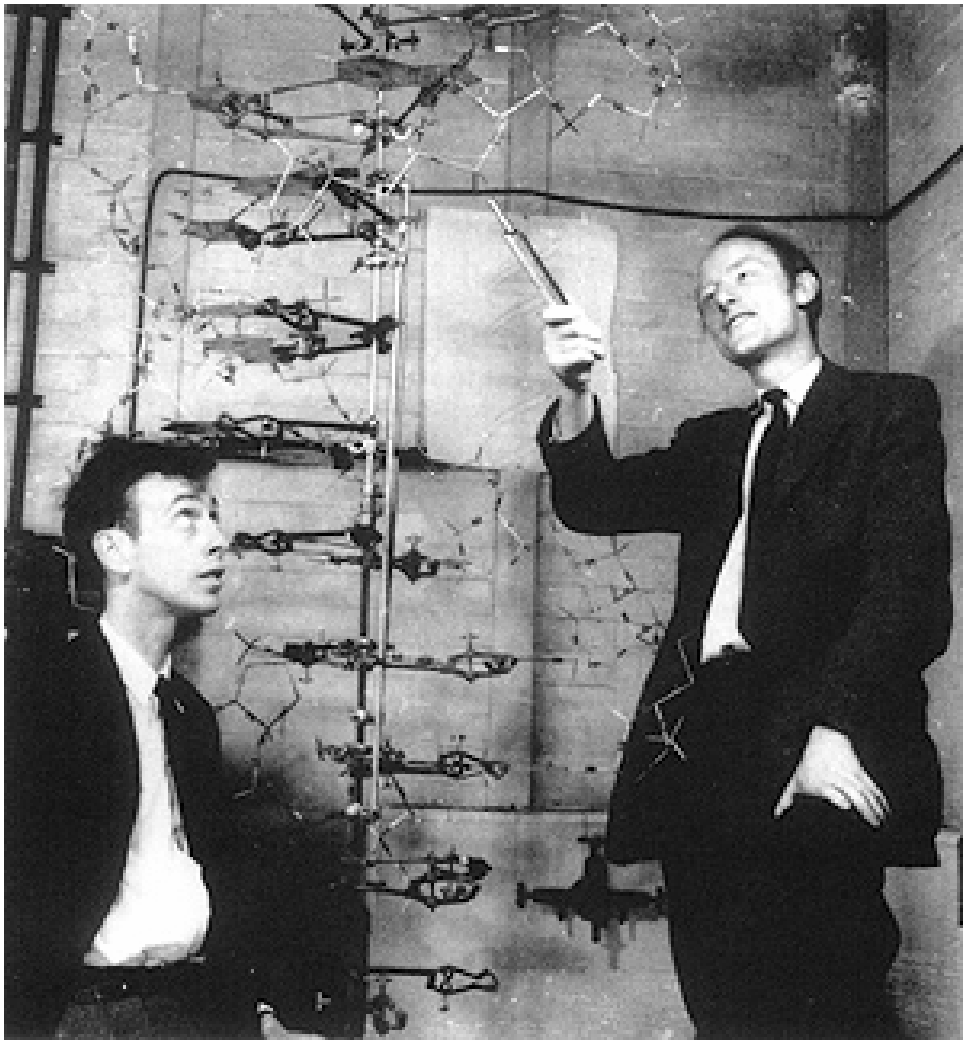
We can use hybridization of the central atom and MO-LCAO together to describe small polyatomic molecules.

But...

What about **larger** molecules?

Does hybridization / MO-LCAO enable us to describe more complicated molecules?

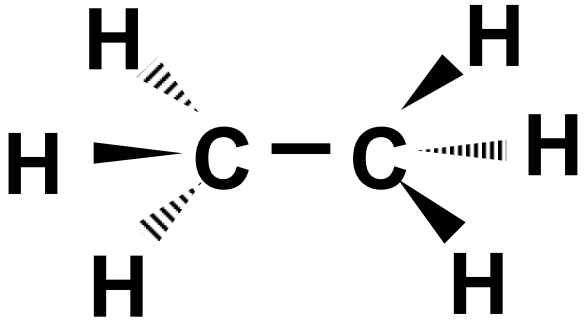
Watson and Crick's Original DNA Model

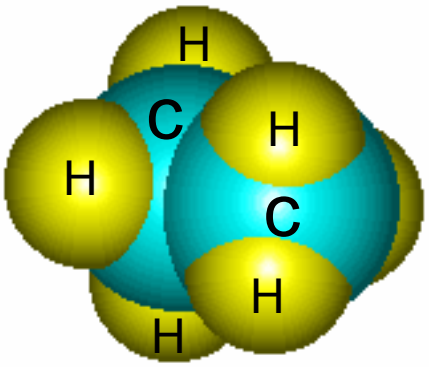


We'll take the challenge:

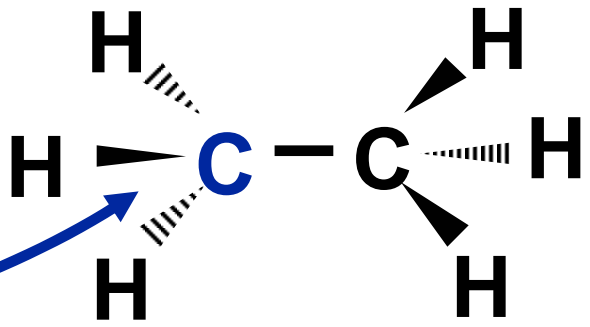
$$C_2H_6$$

From VSEPR and Lewis dot structures, we know it looks like this:





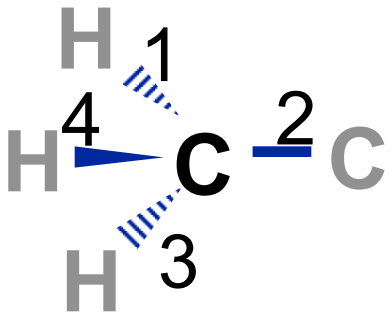
C_2H_6



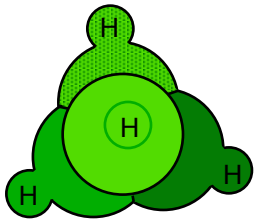
Let's analyze one **C** at a time.

Look at the left **C**.

Notice it has a steric number of four:

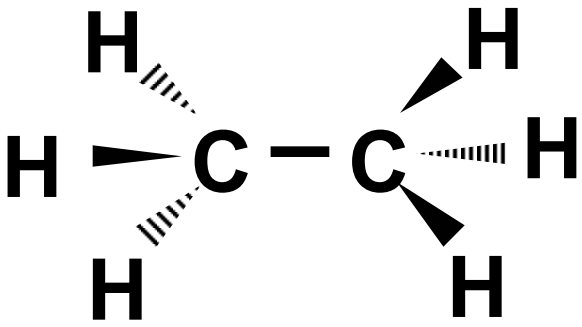


What other molecule had a steric number of four? **CH_4**

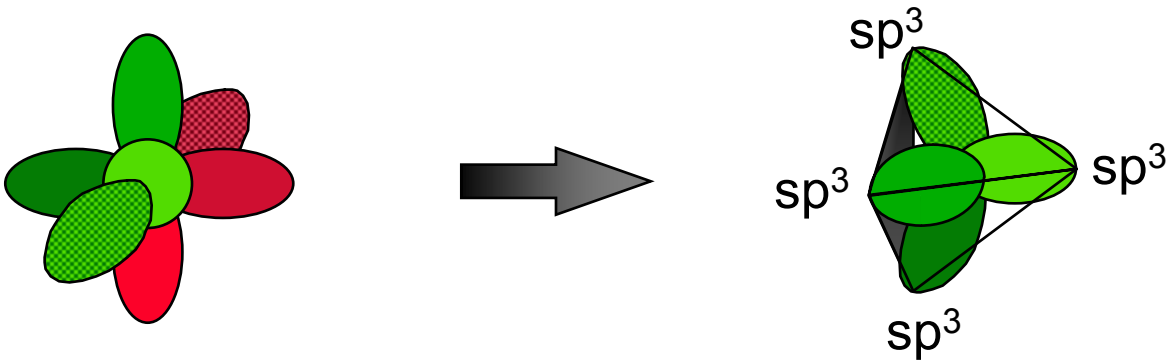


This suggests we should hybridize our current **C** the same way.

C_2H_6

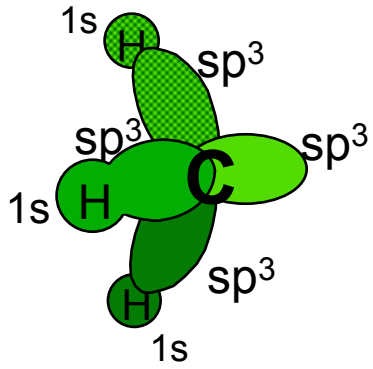


sp^3 hybridize the carbon:

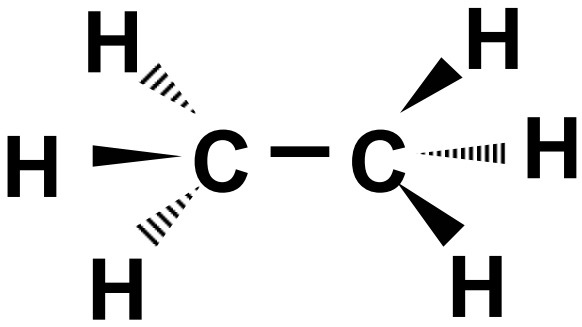


Notice the tetrahedral shape.

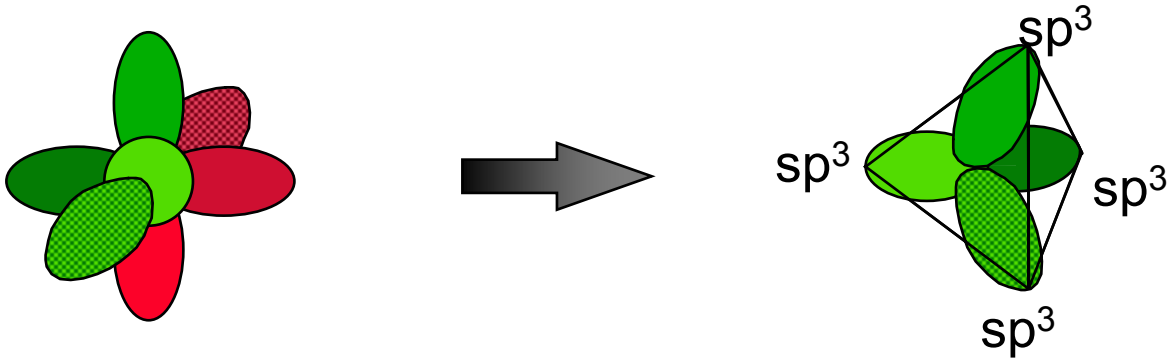
Add 3 hydrogens (using MO-LCAO)



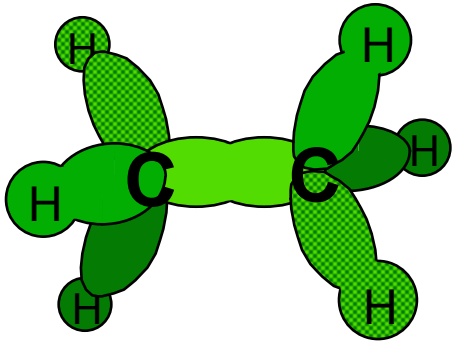
C_2H_6



Do the same to the other side:

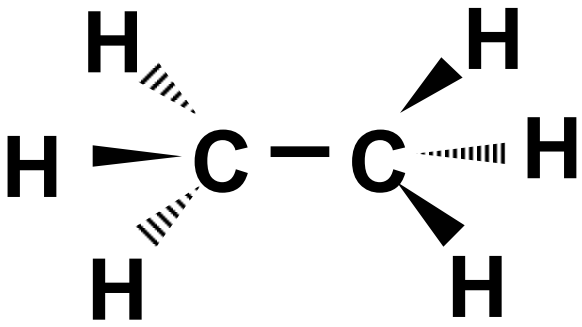


Bring the two halves together:

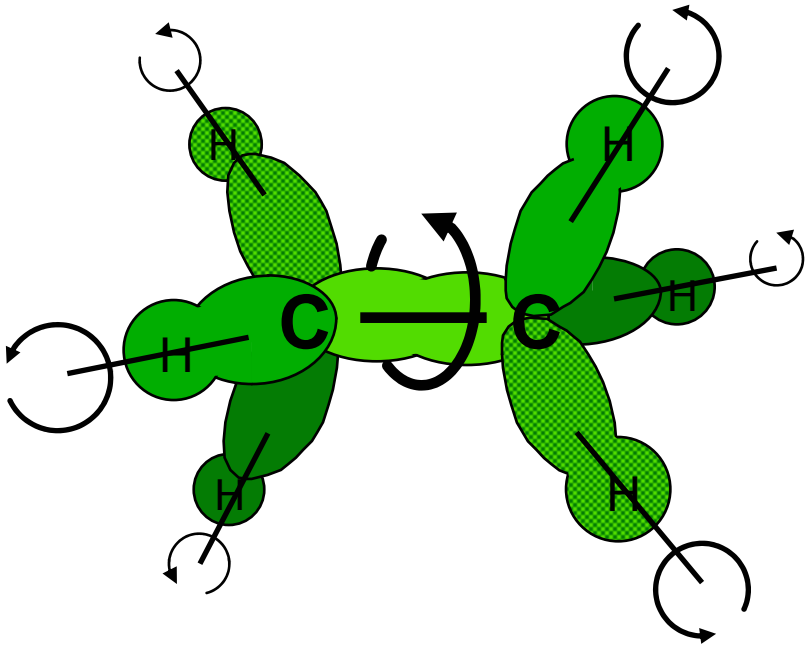


Success!

C_2H_6



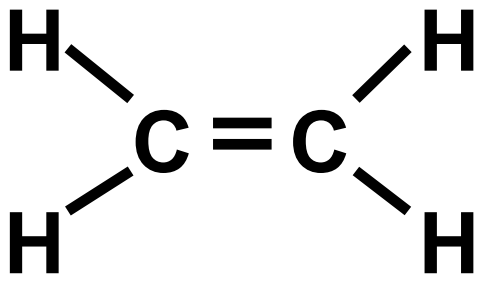
Notice that all the bonds formed are σ bonds.
Each is rotationally symmetrical about its axis.

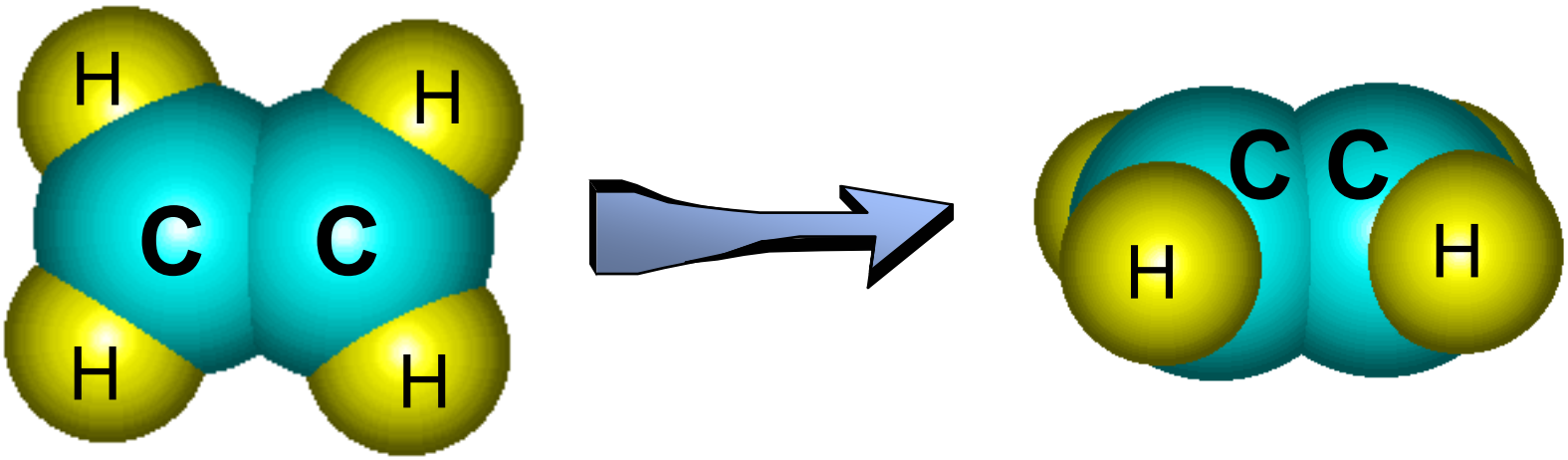


Let's try another:

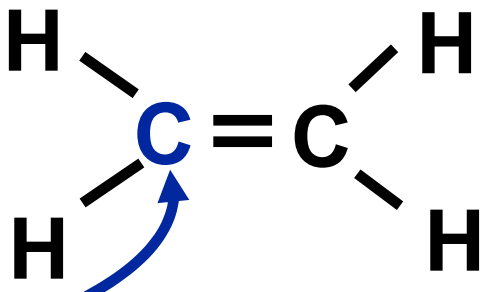
$$C_2H_4$$

From VSEPR and Lewis dot structures, we know it looks like this:





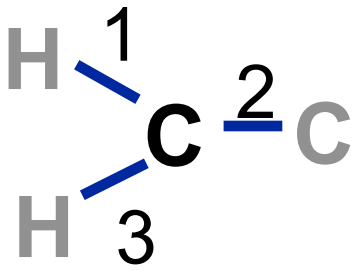
C_2H_4



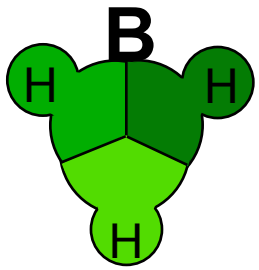
Let's analyze one **C** at a time.

Look at the left **C**.

Notice it has a steric number of three:

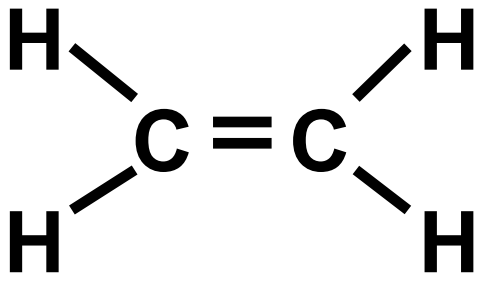


What other molecule had a steric number of three? **BH_3**

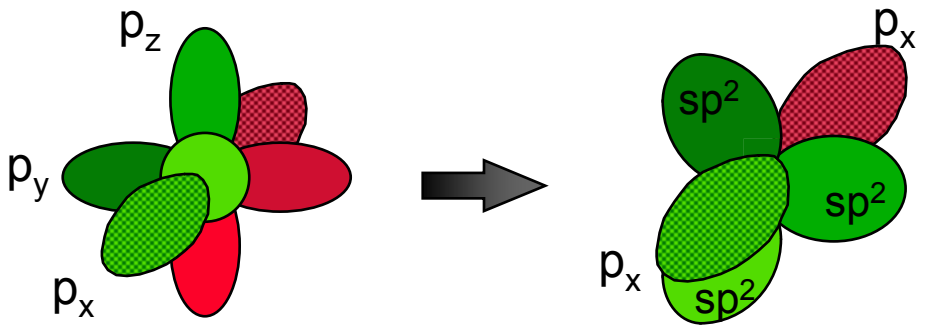


This suggests we should hybridize our current **C** the same way.

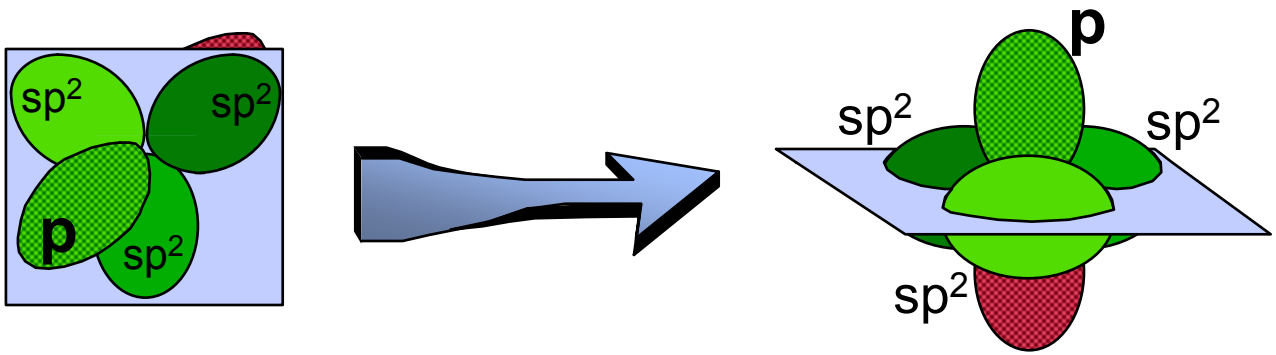
C_2H_4



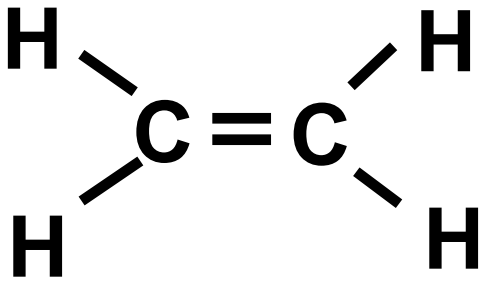
sp^2 hybridize the carbon:



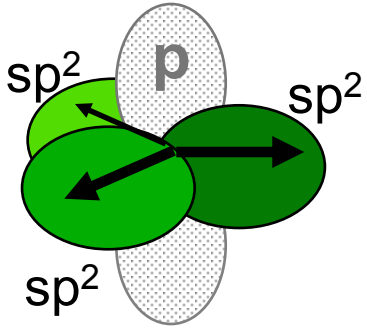
Notice there is an extra **p** orbital that is not involved in hybridization:



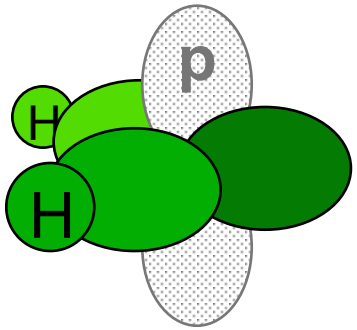
C_2H_4



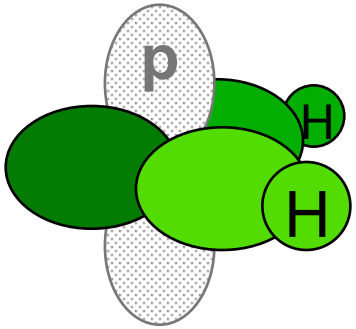
For now, we will de-emphasize the p orbital.



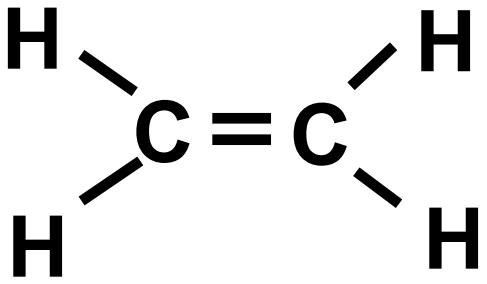
Add hydrogen:



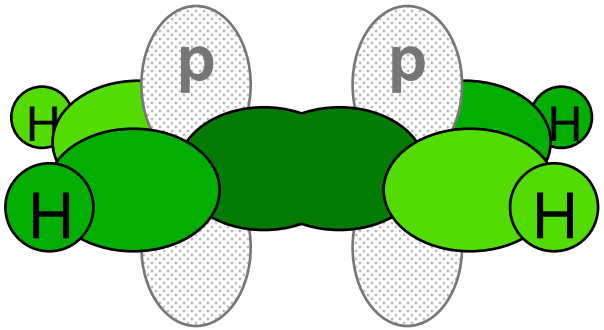
Do the same for the other C:



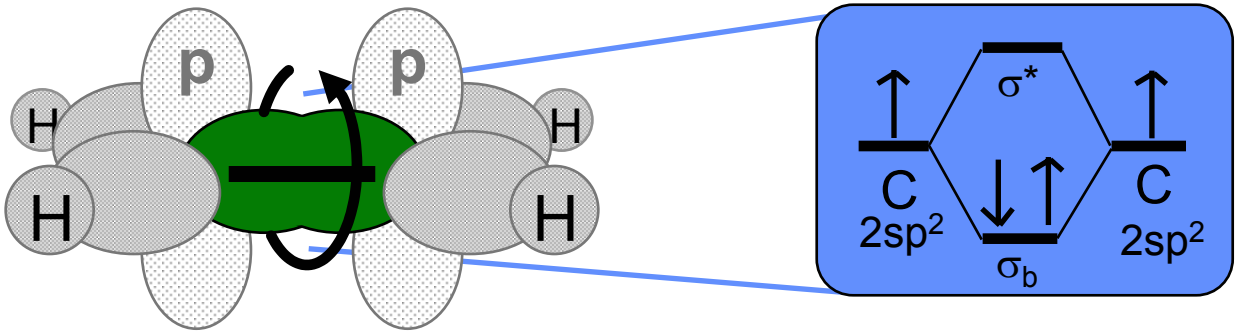
C_2H_4



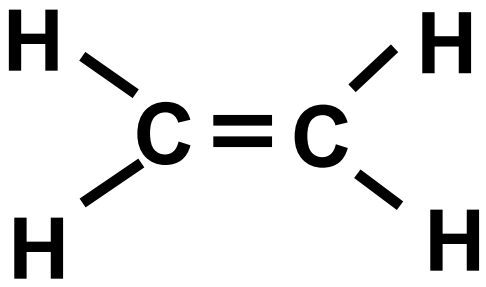
Now bond the two **C** together:



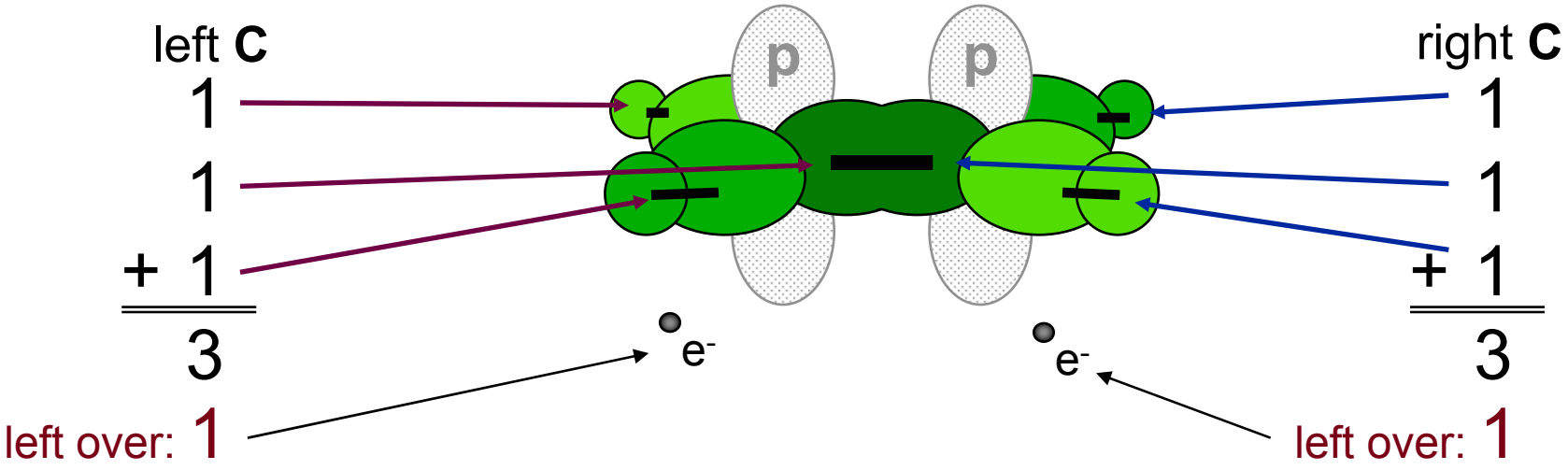
Notice that the two sp^2 orbitals form a σ orbital that is rotationally symmetric.



C_2H_4

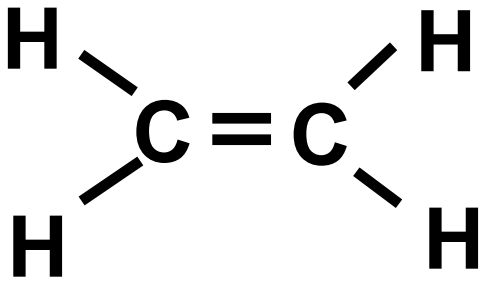


Count the bonding e^- around each carbon:

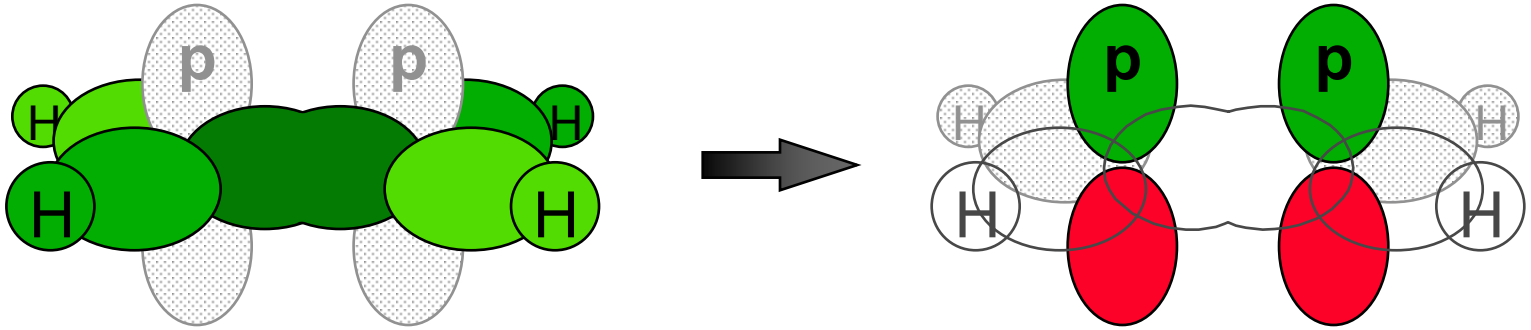


But each C has 4 e^-! What do we do with the extras?

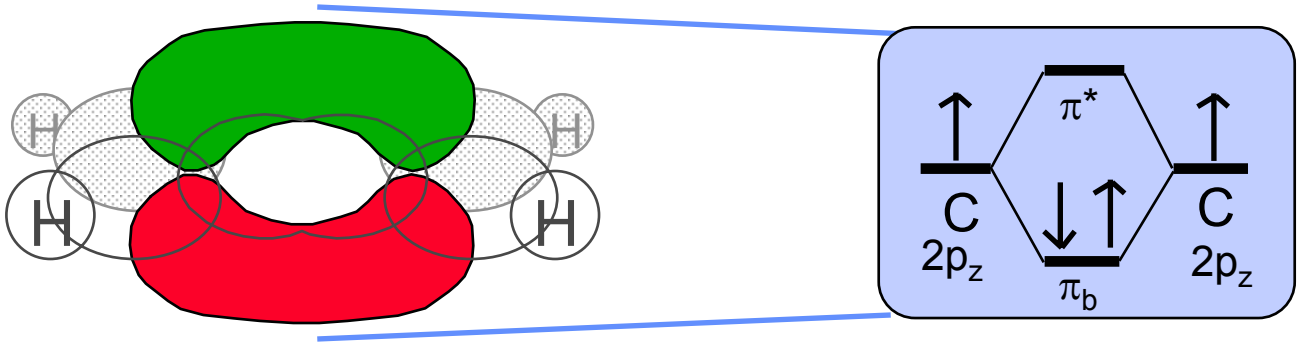
C_2H_4



Let's re-emphasize the **p** orbitals:



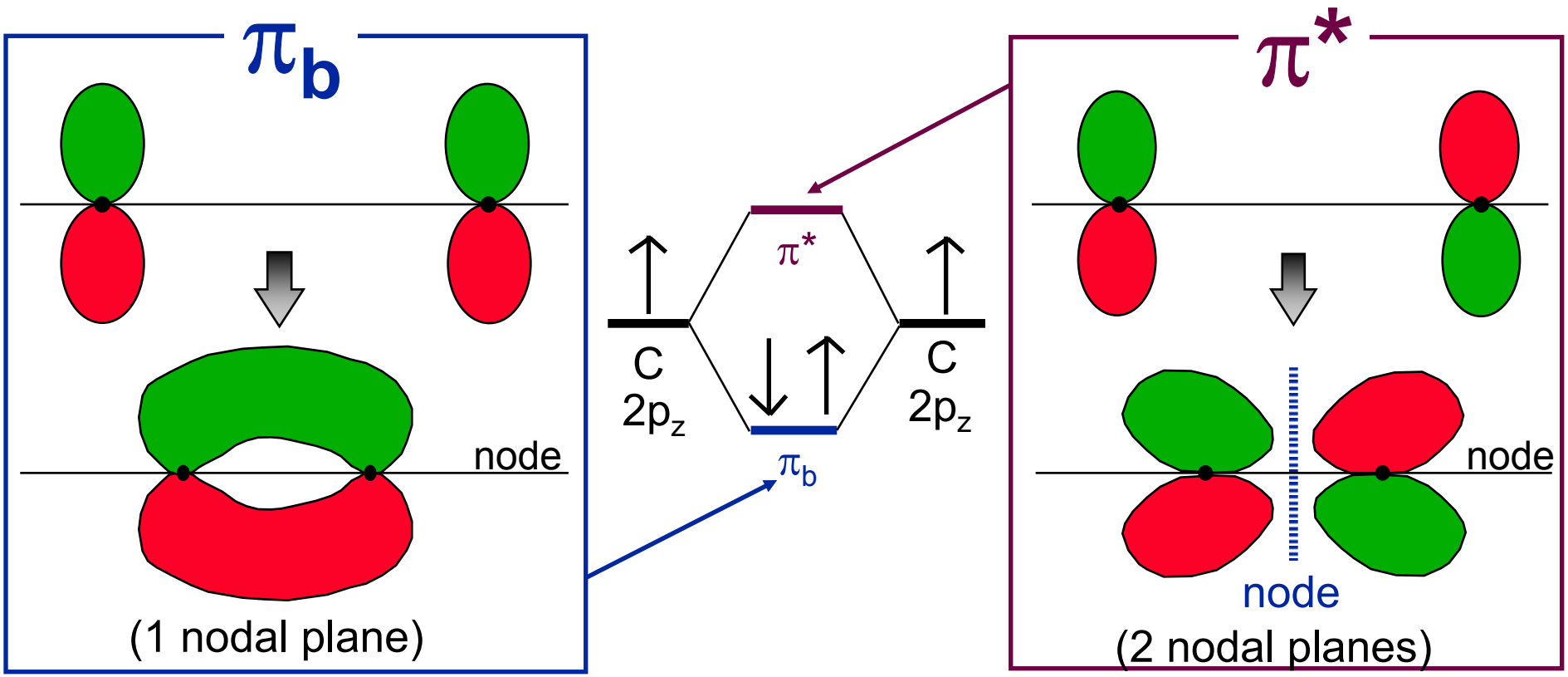
The **p** orbitals can combine, forming a π bond:



π bonds

Notice that π bonds are **not** rotationally symmetric.

The orbital changes sign every 180°

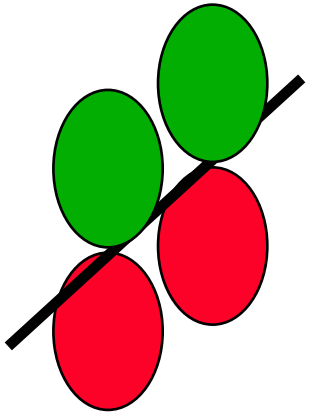


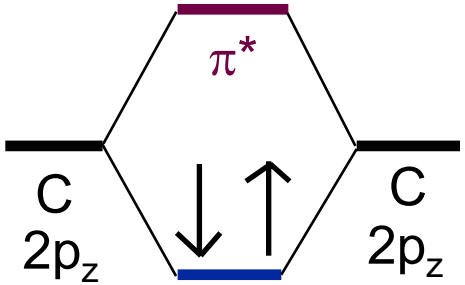
π bonds

Notice that π bonds do **not** allow rotation.

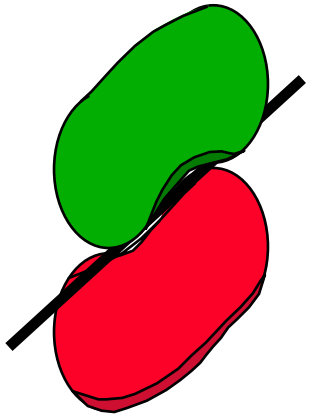
When rotated around the axis, the bond is broken:

Orientation of orbitals





π_b



Bond

π bonds

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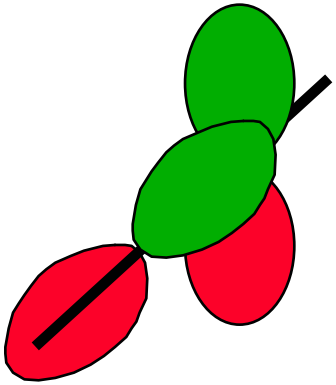
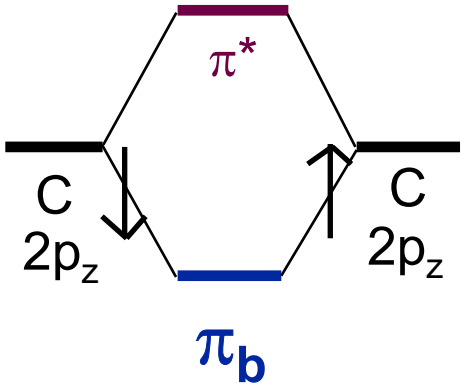
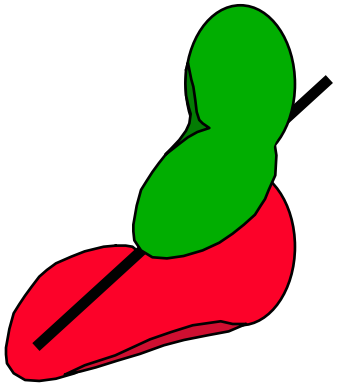
Orientation of orbitals





π_b



No Bond

π bonds

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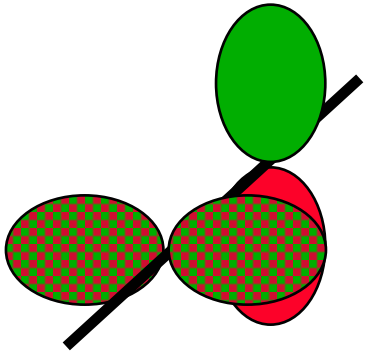
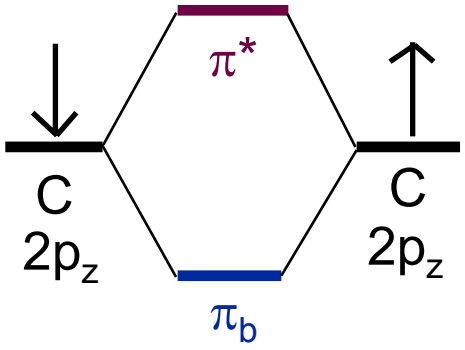
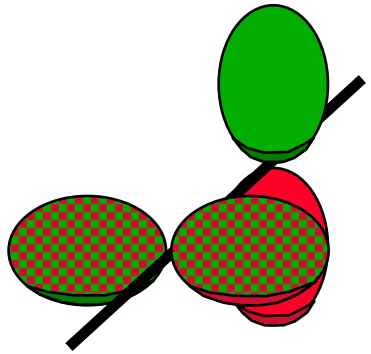
Orientation of orbitals







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π bonds

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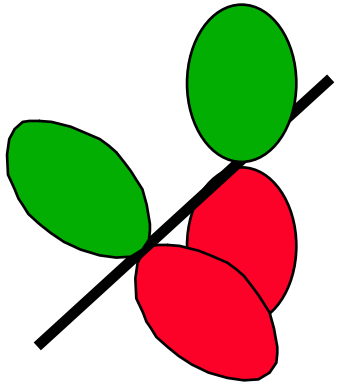
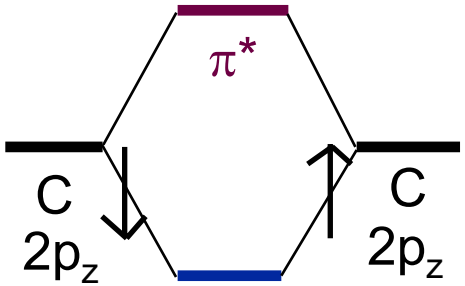
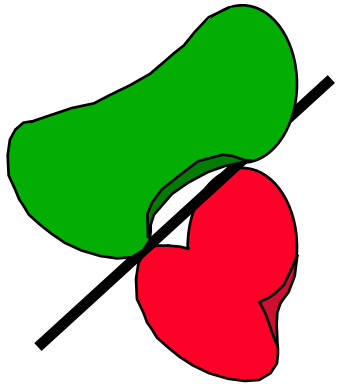
Orientation of orbitals





π_b



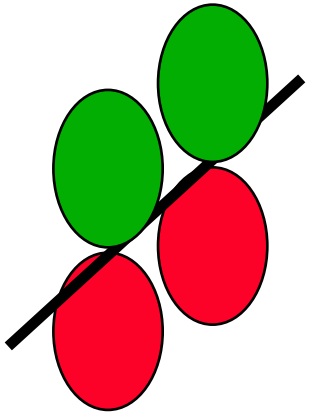
No Bond

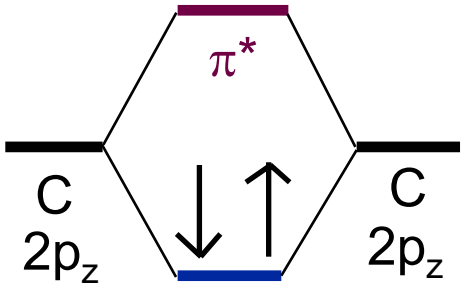
π bonds

Notice that π bonds do **not** allow rotation.

When rotated around the axis, the bond is broken:

Orientation of orbitals





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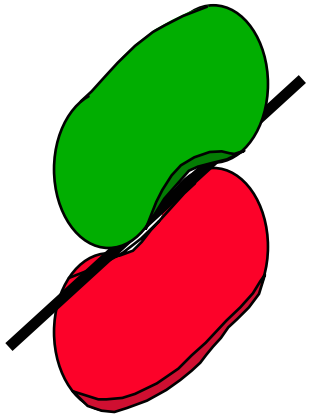

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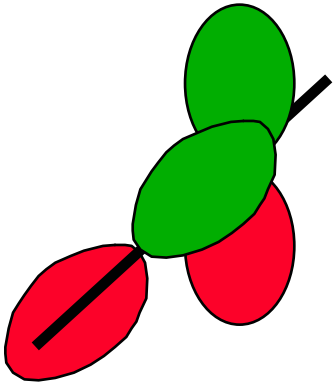
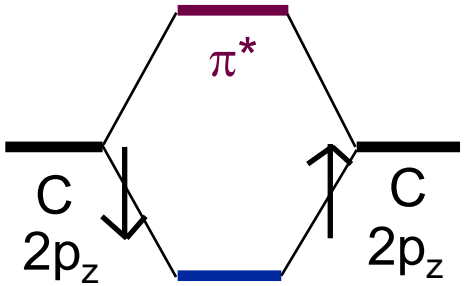
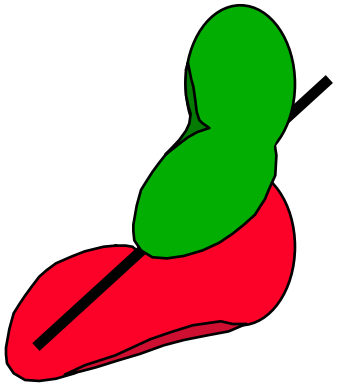
Orientation of orbitals





π_b



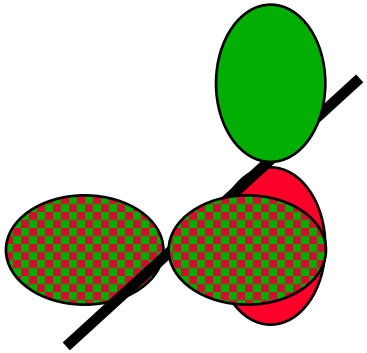
No Bond

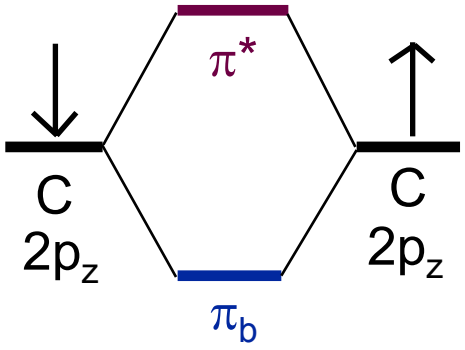
π bonds

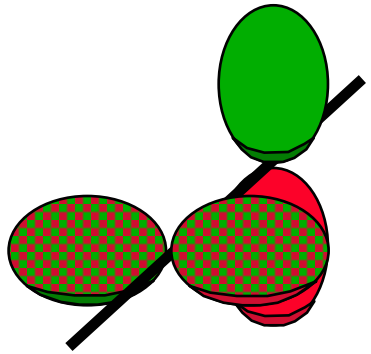
Notice that π bonds do **not** allow rotation.

When rotated around the axis, the bond is broken:

Orientation of orbitals







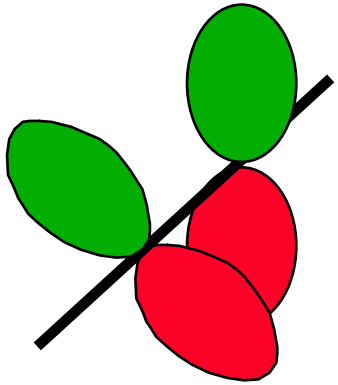
No Bond

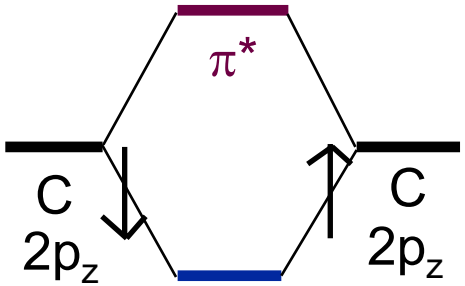
π bonds

Notice that π bonds do **not** allow rotation.

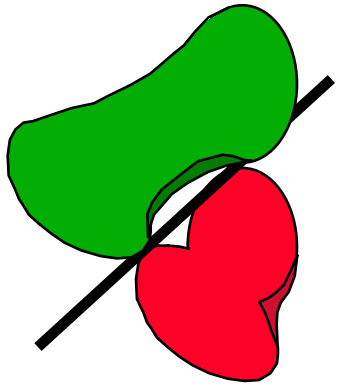
When rotated around the axis, the bond is broken:

Orientation of orbitals





π_b



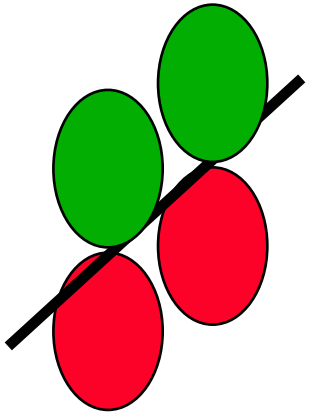
No Bond

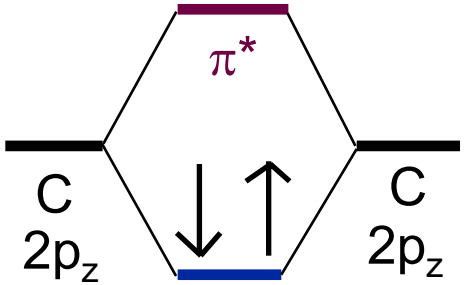
π bonds

Notice that π bonds do **not** allow rotation.

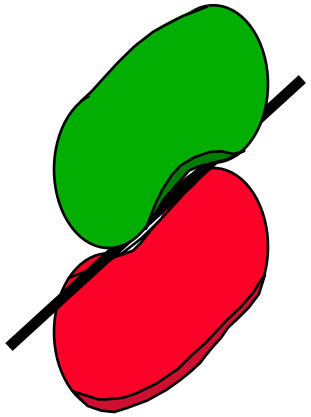
When rotated around the axis, the bond is broken:

Orientation of orbitals



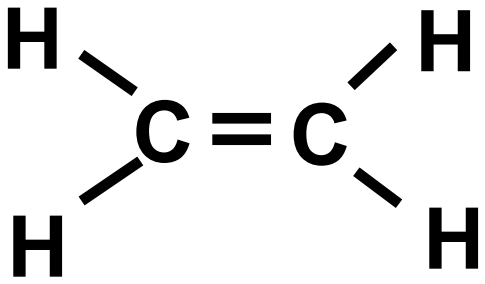


π_b

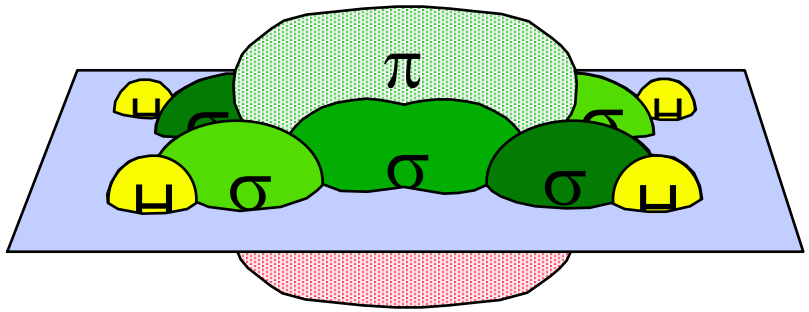


Bond

C_2H_4



Because of the extra energy required to rotate the π bond, the **H**'s are constrained to lie in a plane.

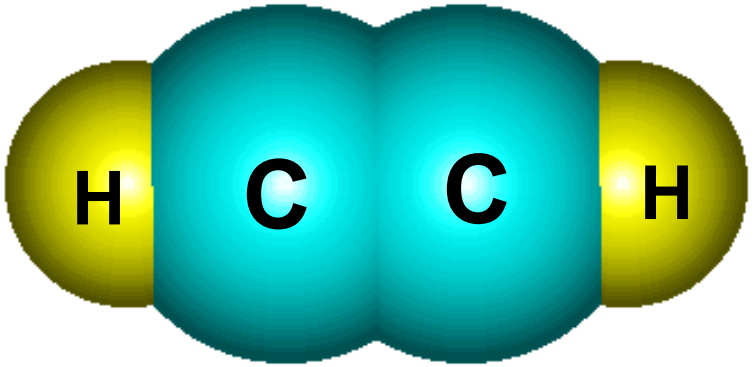


Let's try another:

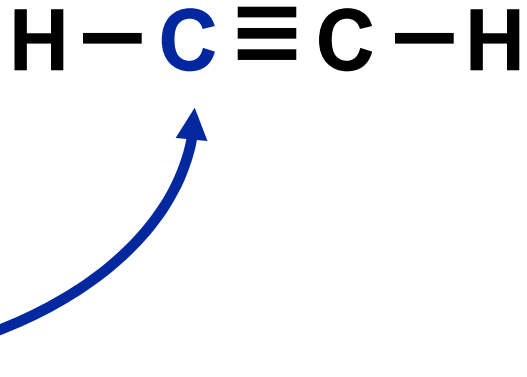
$$C_2H_2$$

From VSEPR and Lewis dot structures, we know it looks like this:

$$H-C\equiv C-H$$



C_2H_2

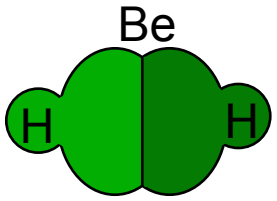


Let's analyze one **C** at a time.

Look at the left **C**.

Notice it has a steric number of two:

What other molecule had a steric number of two? **BeH_2**

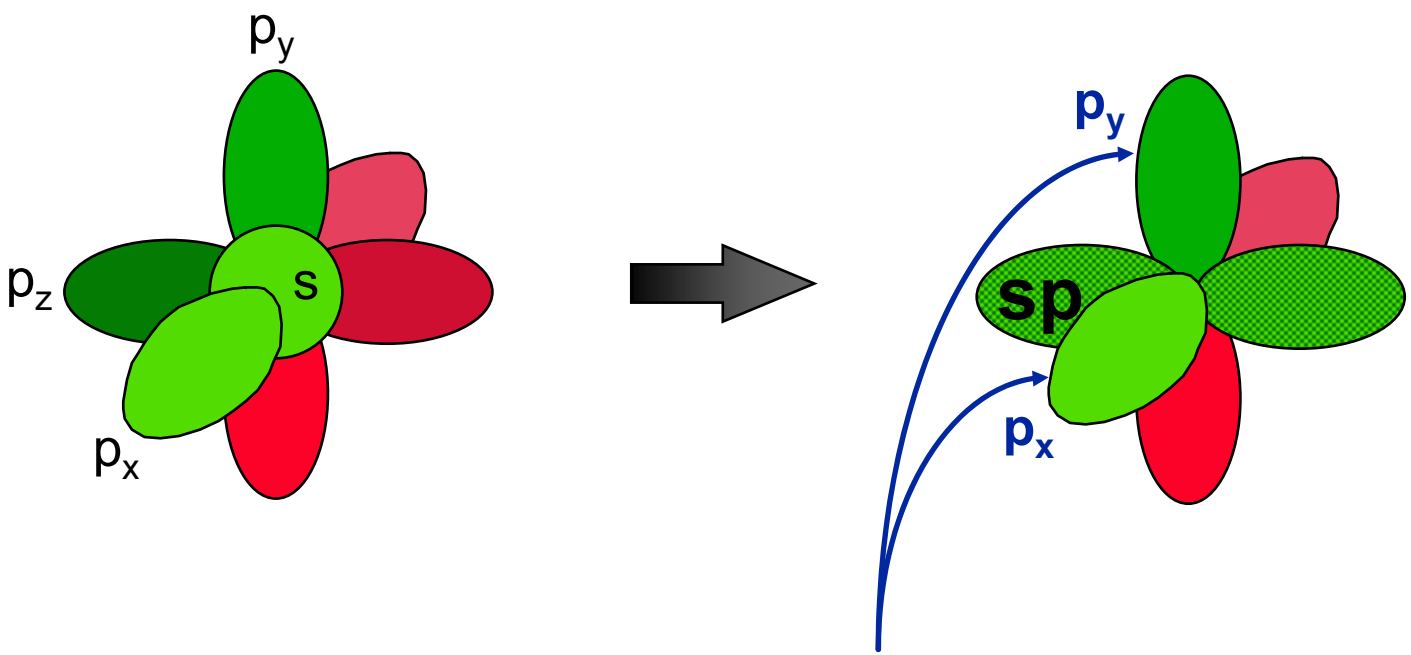


This suggests we should hybridize our current **C** the same way.

C_2H_2

H—C≡C—H

sp hybridize the carbon:

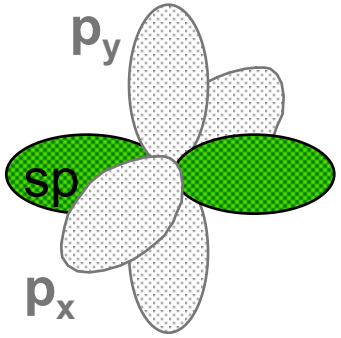


Notice there are two extra **p** orbitals that are not involved in hybridization.

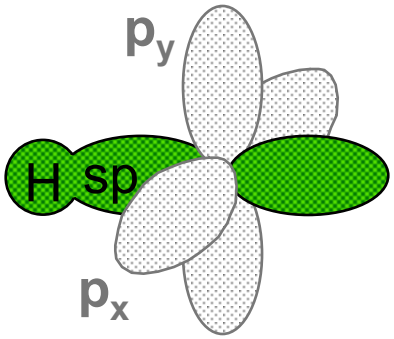
C_2H_2

H–C≡C–H

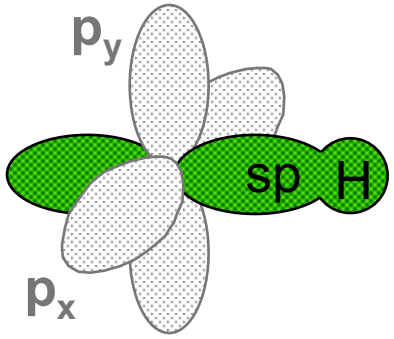
For now, we will de-emphasize the p orbitals.



Add hydrogen:



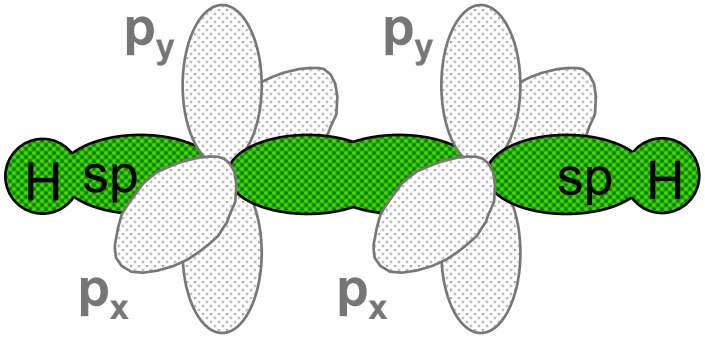
Do the same for the other C:



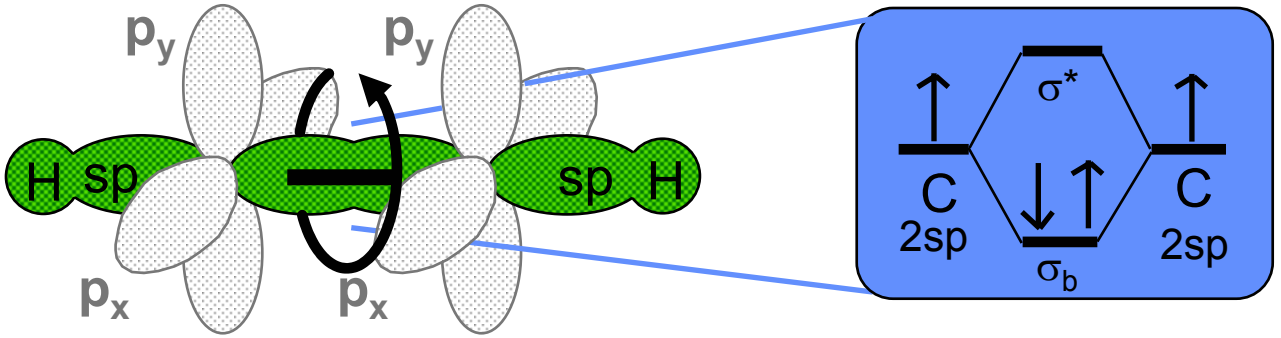
C_2H_2

H–C≡C–H

Bond the two **C** together:



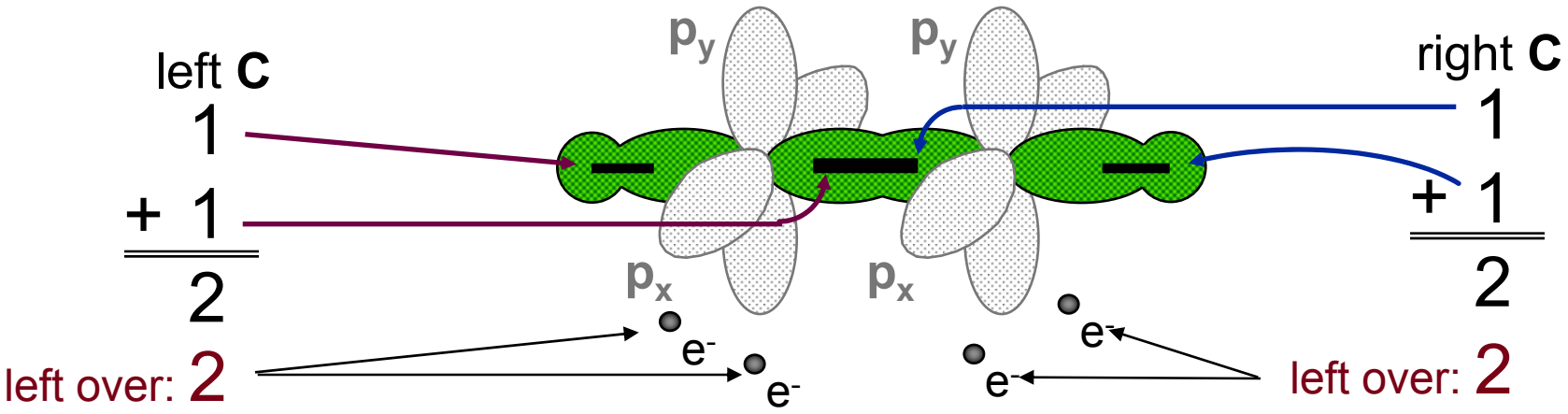
Notice that the two sp orbitals form a σ orbital that is rotationally symmetric.



C_2H_2

H–C≡C–H

Count the e^- around each carbon:

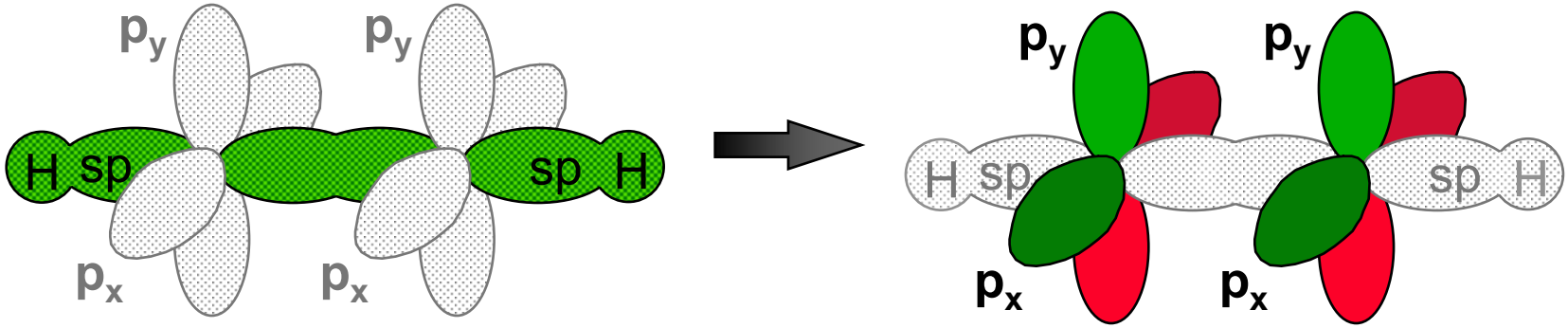


But each C has 4 e^-! What do we do with the extras?

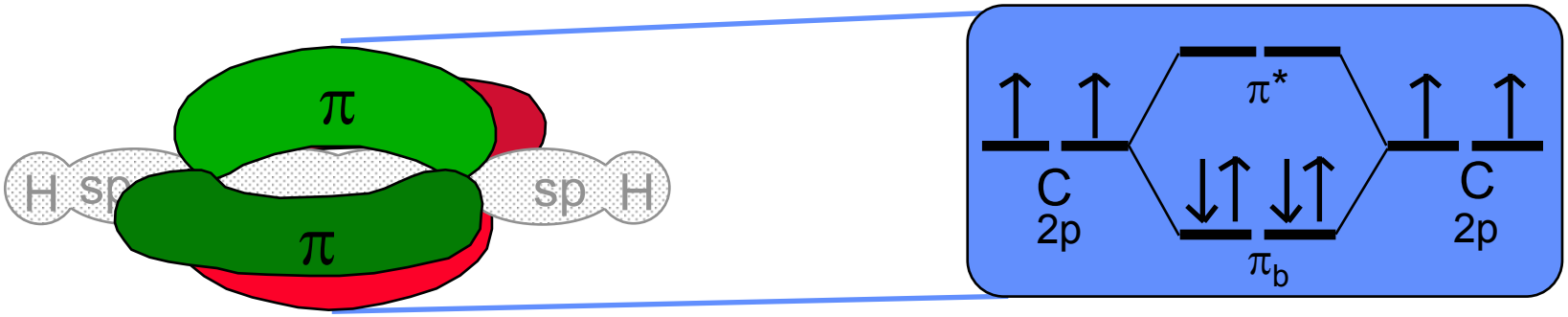
C_2H_2

$H-C\equiv C-H$

Let's re-emphasize the **p** orbitals:



The **p** orbitals combine, forming π bonds:

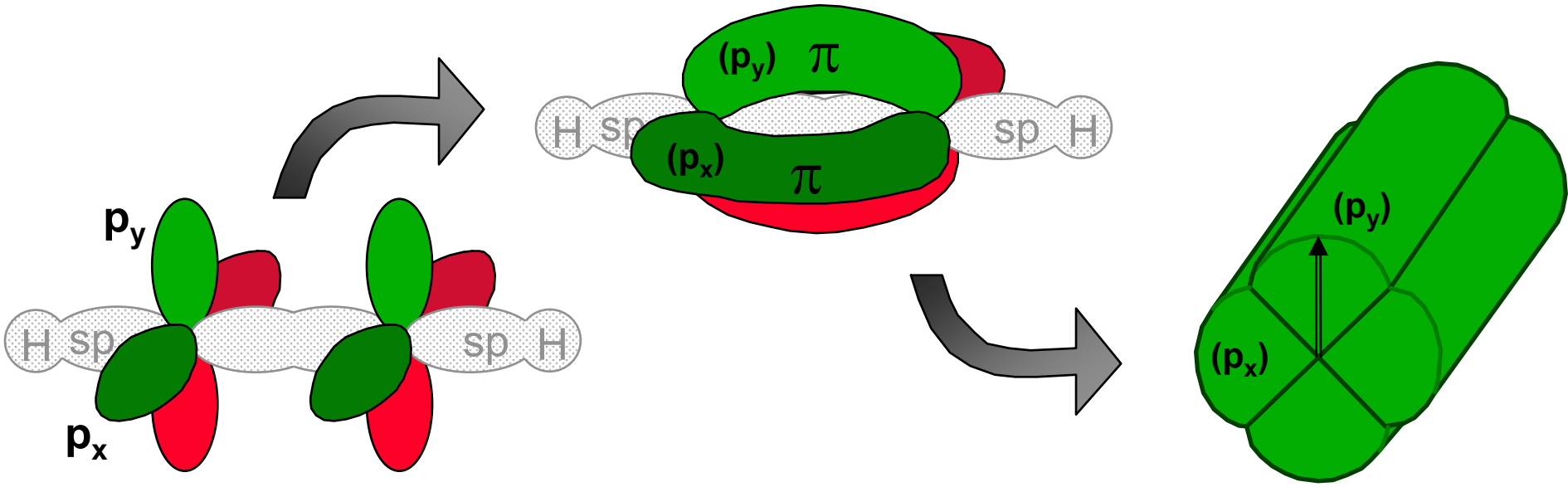


C_2H_2

H—C≡C—H

Unlike a double bond (one π), a triple bond (two π) allows rotation.

Because the π bonds occupy almost all the space around the carbons, the transition between a p_y-p_y π bond and a p_y-p_x π bond is fairly smooth.



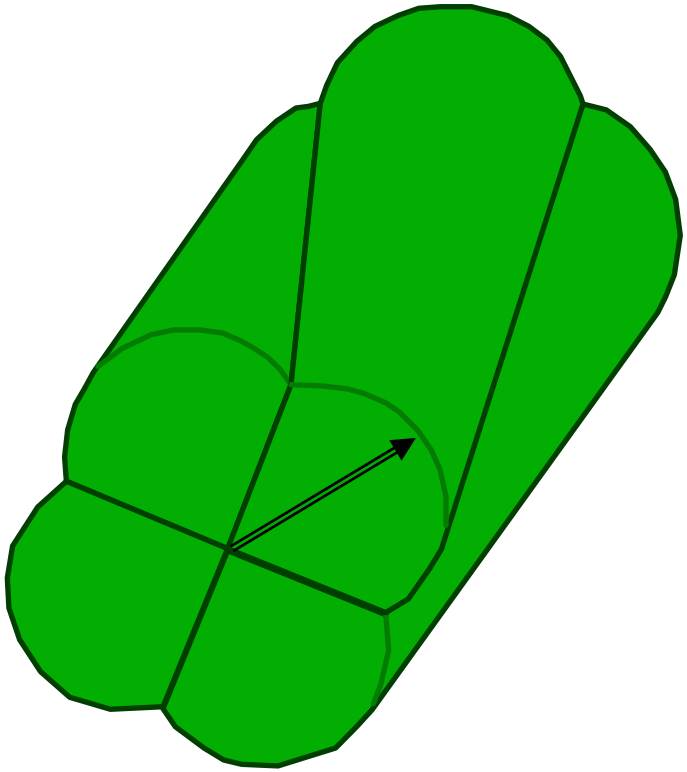
Orbital view

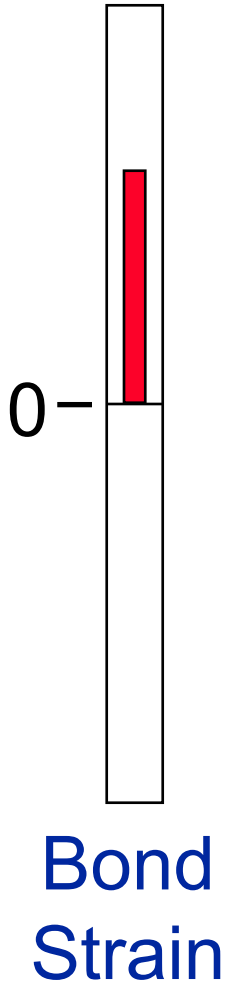
Space filling view

C_2H_2

$H-C\equiv C-H$

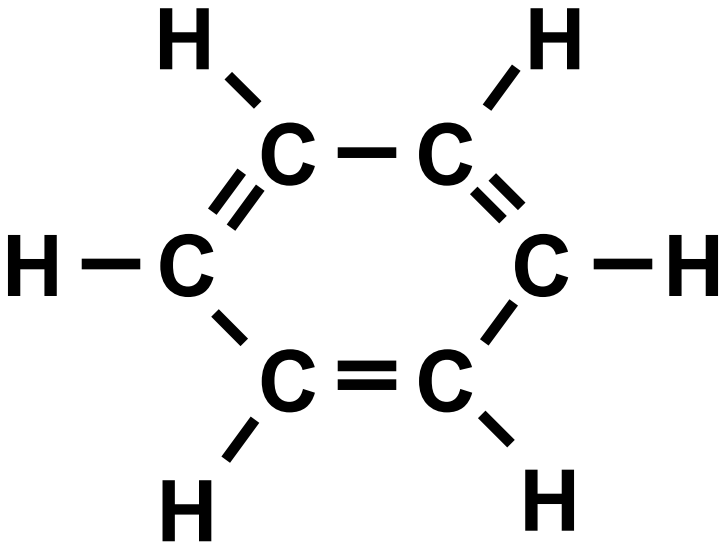
Unlike a double bond (one π), a triple bond (two π) allows rotation.

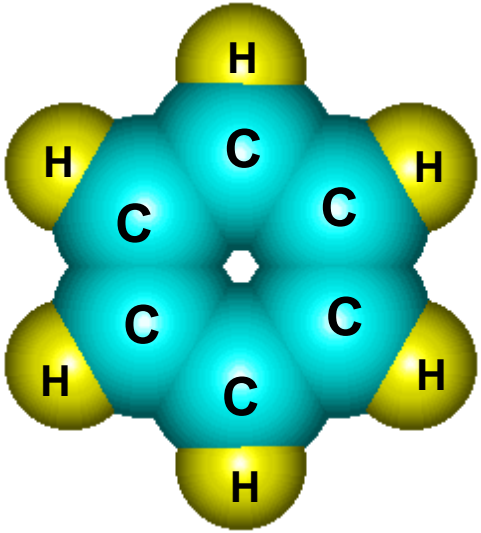


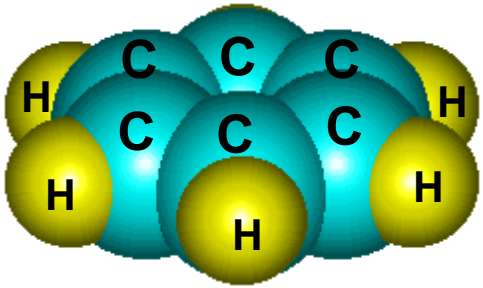


Let's try another: C_6H_6

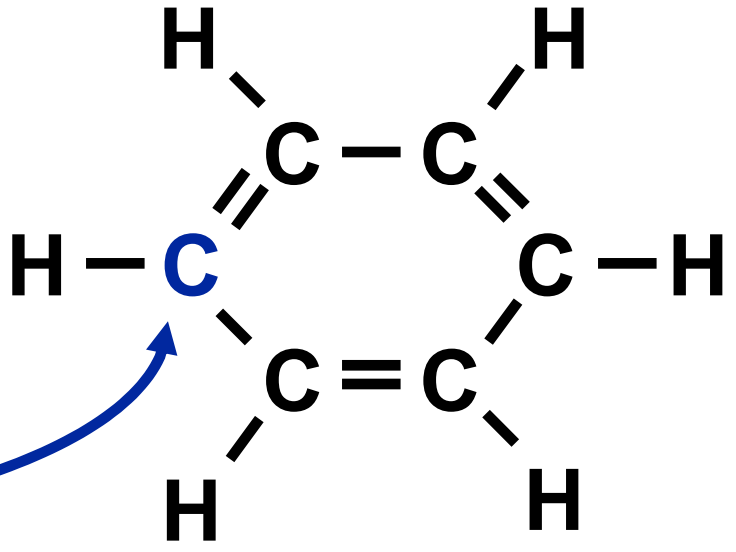
From VSEPR and Lewis dot structures, we know it looks like this:







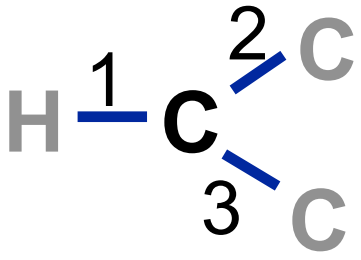
C_6H_6



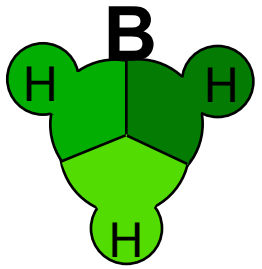
Let's analyze one **C** at a time.

Since they are all the same, pick any **C**.

Notice it has a steric number of three:

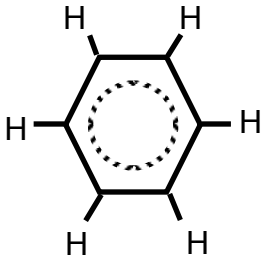


What other molecule had a steric number of three? **BH_3**

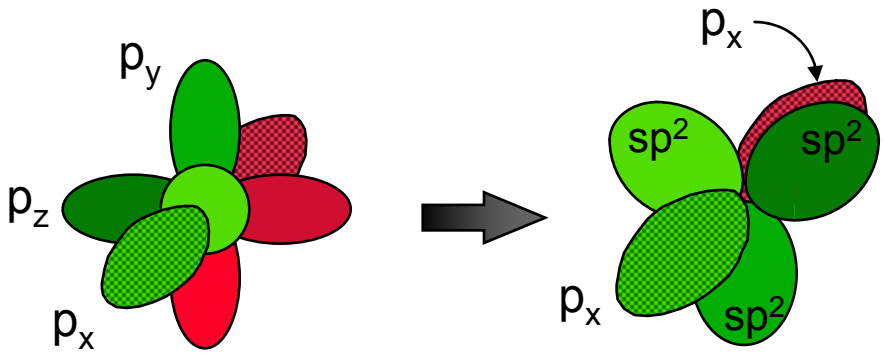


This suggests we should hybridize our current **C** the same way.

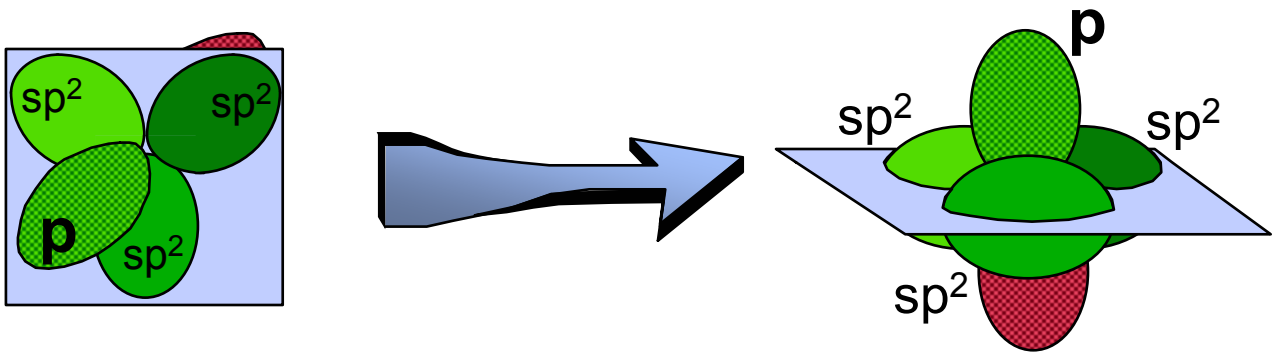
C_6H_6



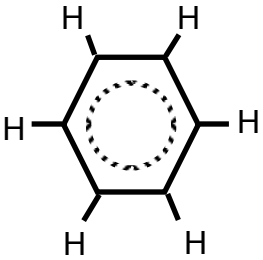
sp^2 hybridize the carbon:



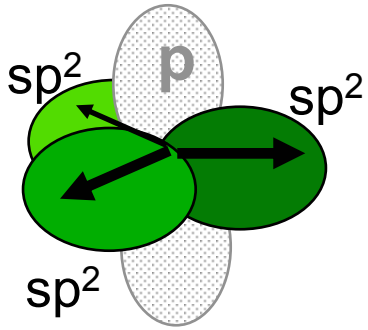
Just as in C_2H_4, there is an extra **p** orbital that is not involved in hybridization:



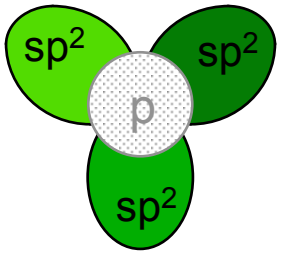
C_6H_6



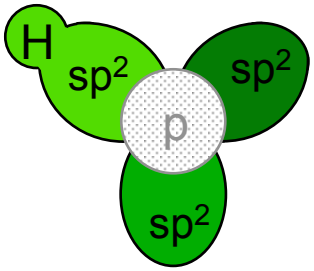
For now, we will de-emphasize the p orbital.



Since all the C's are in the same plane, we will switch to a top view:

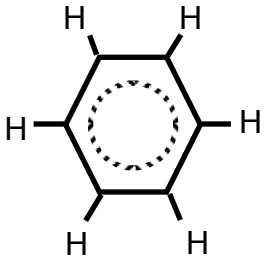


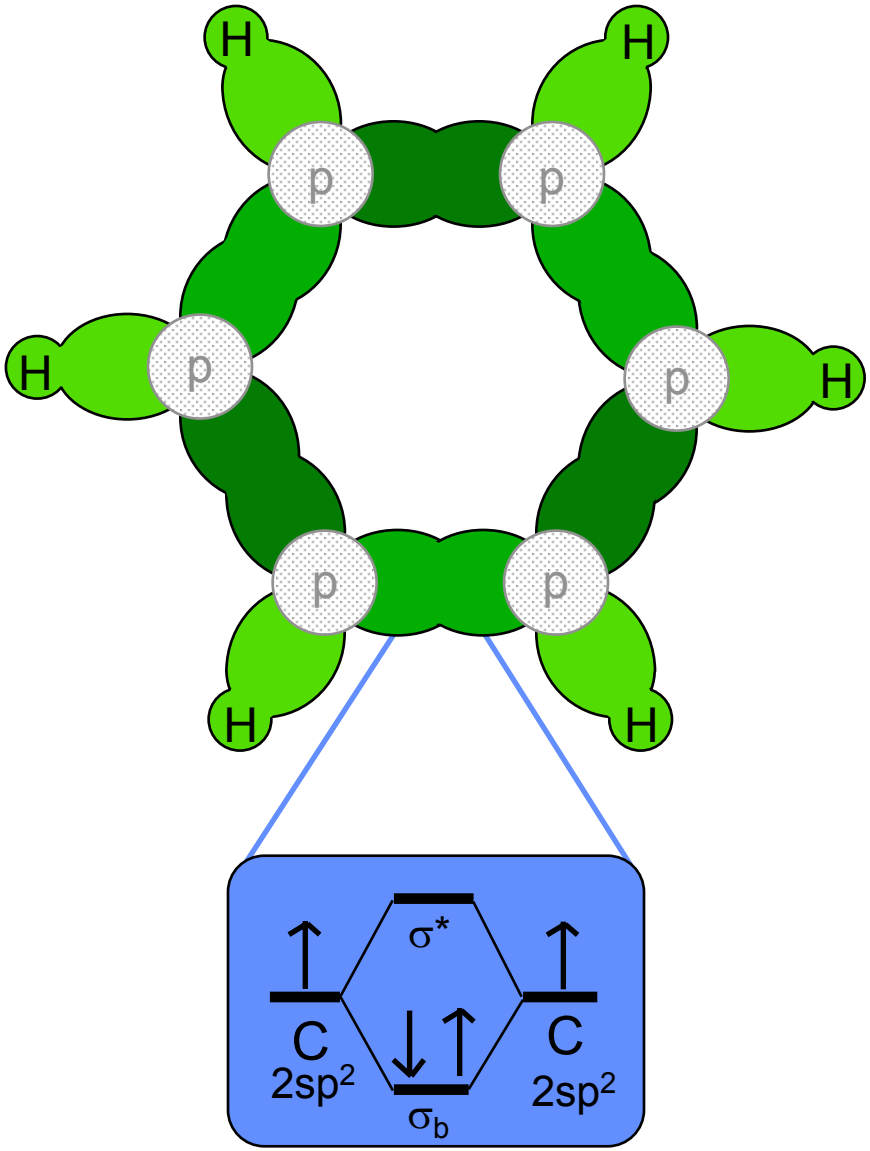
Add hydrogen:



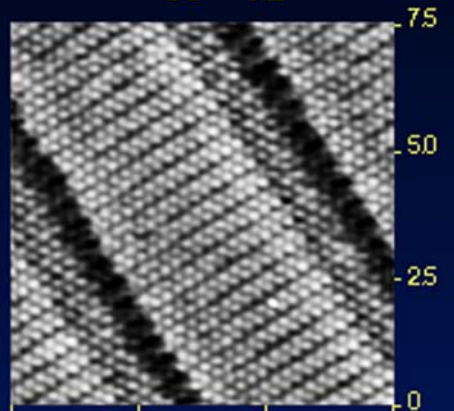
C_6H_6

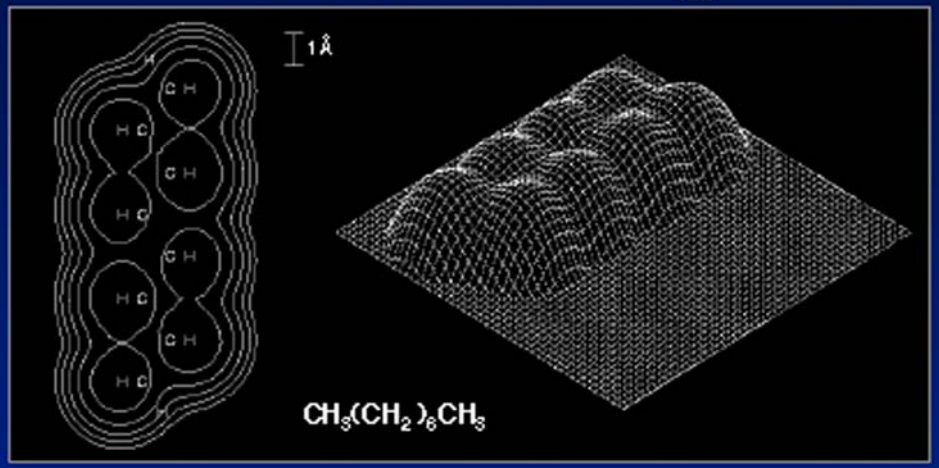
Bond the six **C** together:

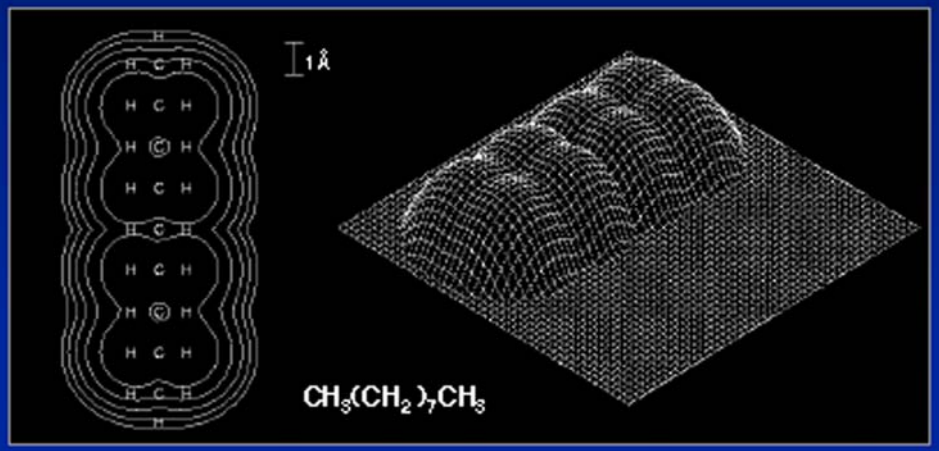




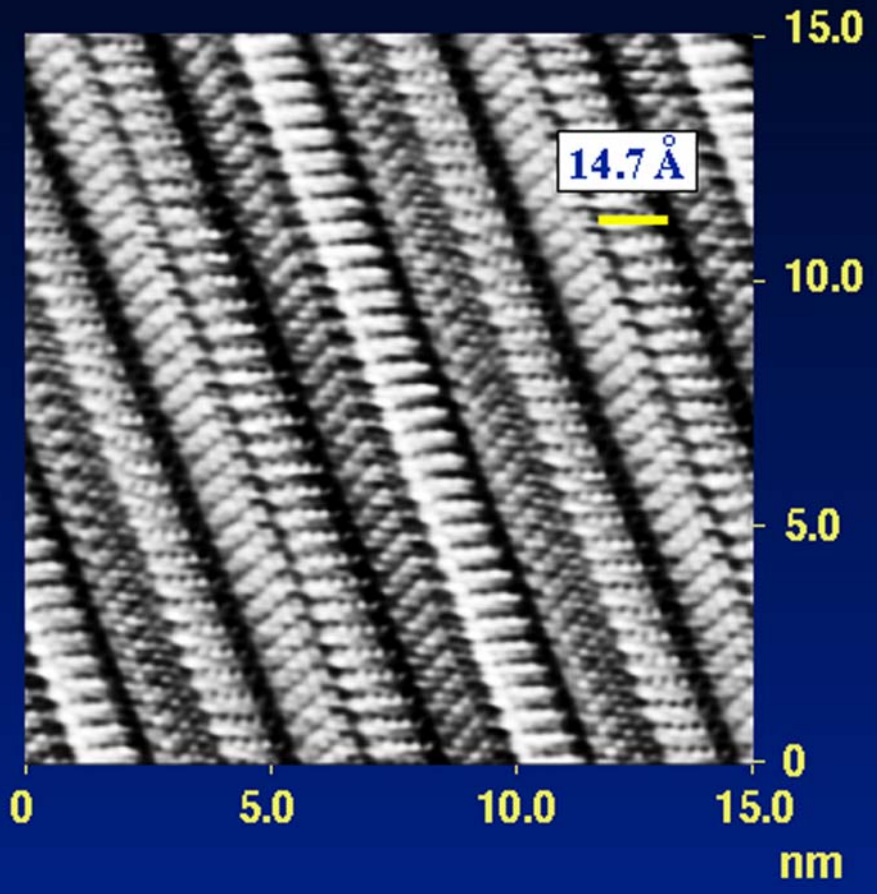
$C_{35}H_{72}$

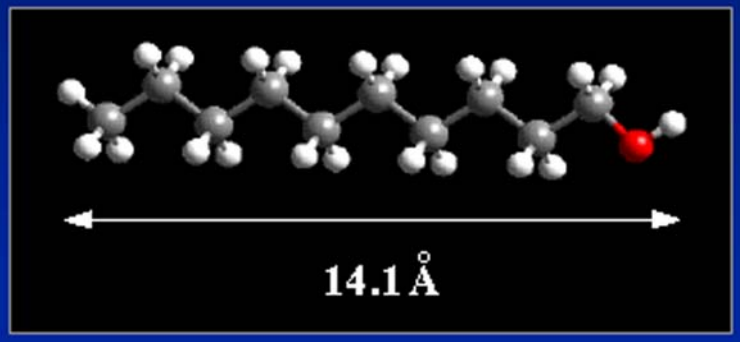




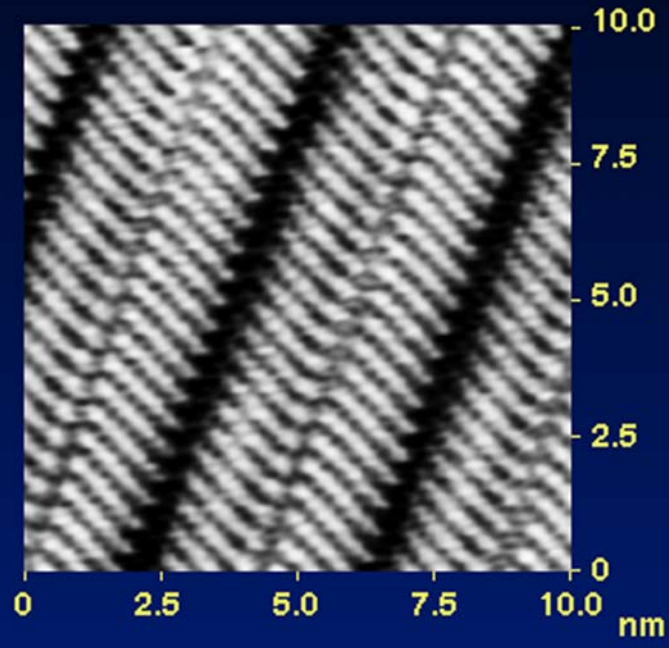


$C_{10}H_{21}OH$

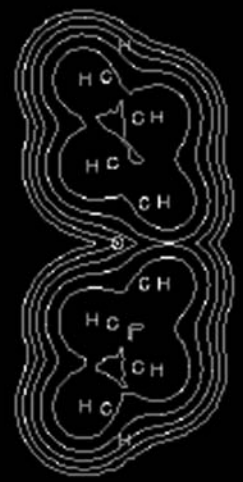


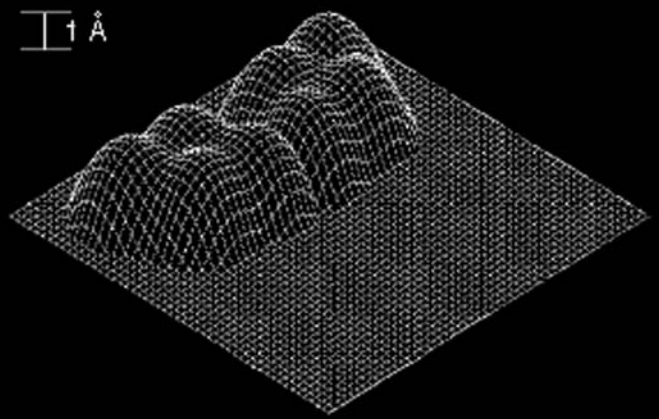


$(C_{16}H_{33})_2O$

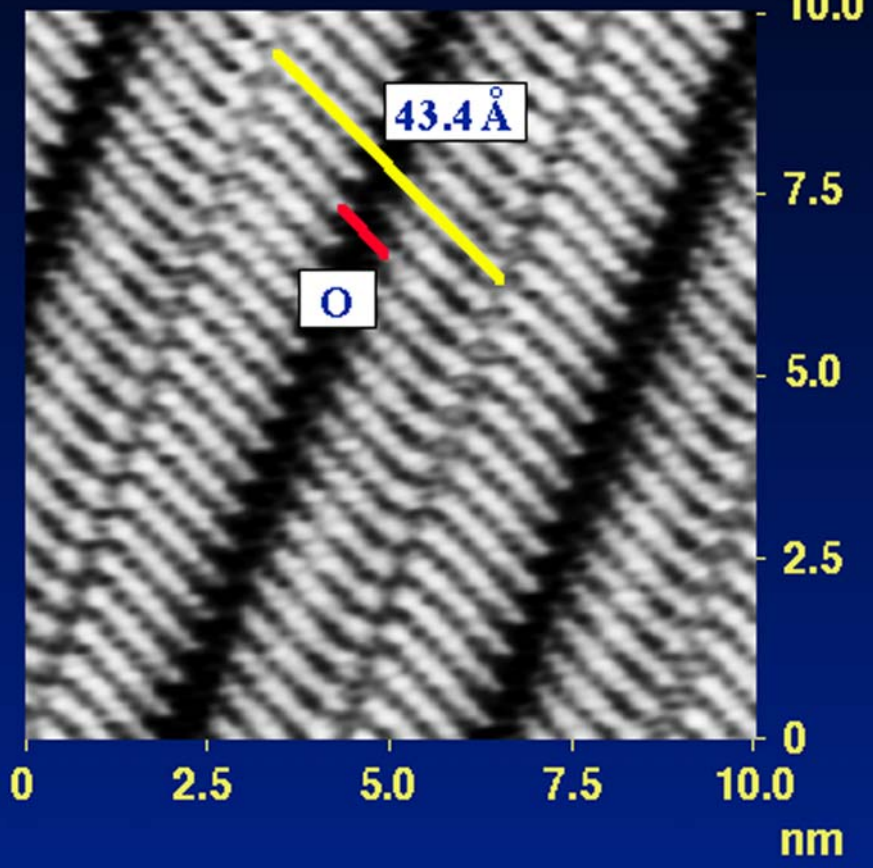


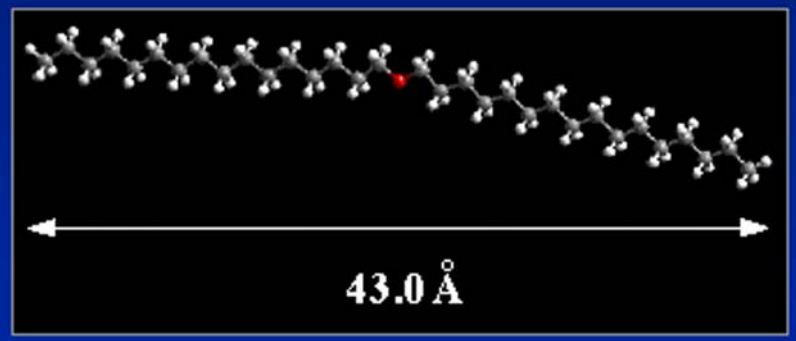
$CH_3(CH_2)_3O(CH_2)_3CH_3$



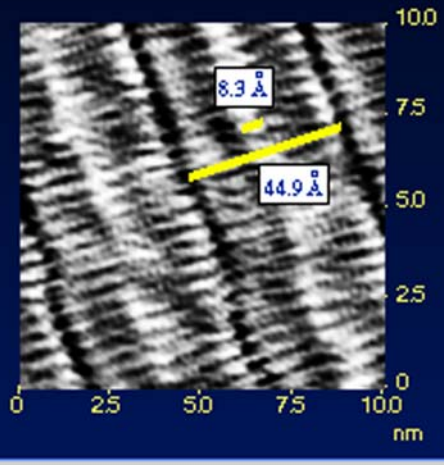


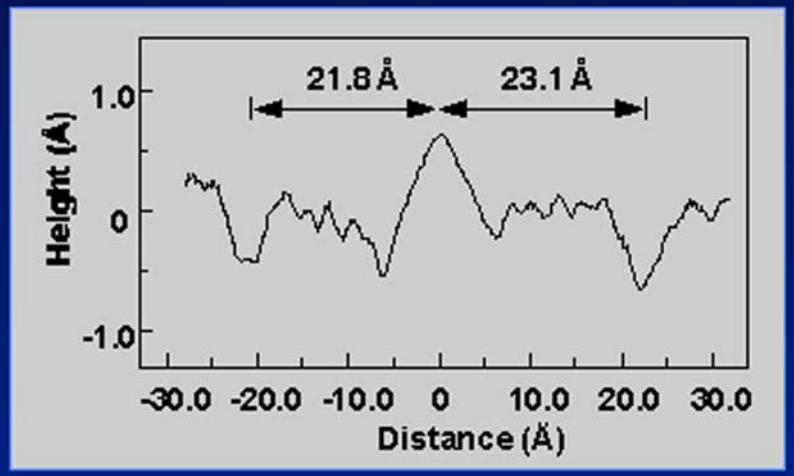
$(C_{16}H_{33})_2O$

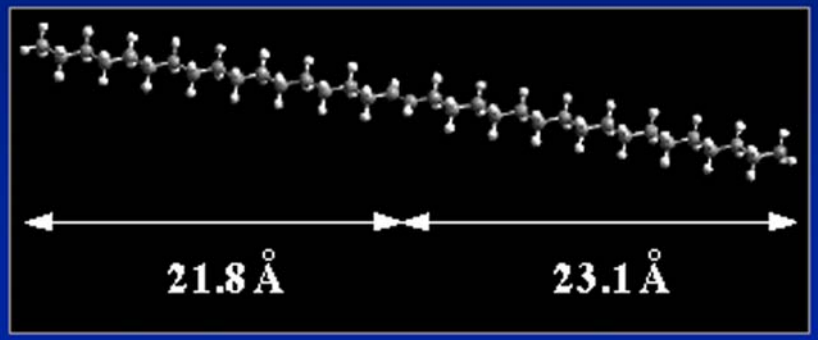




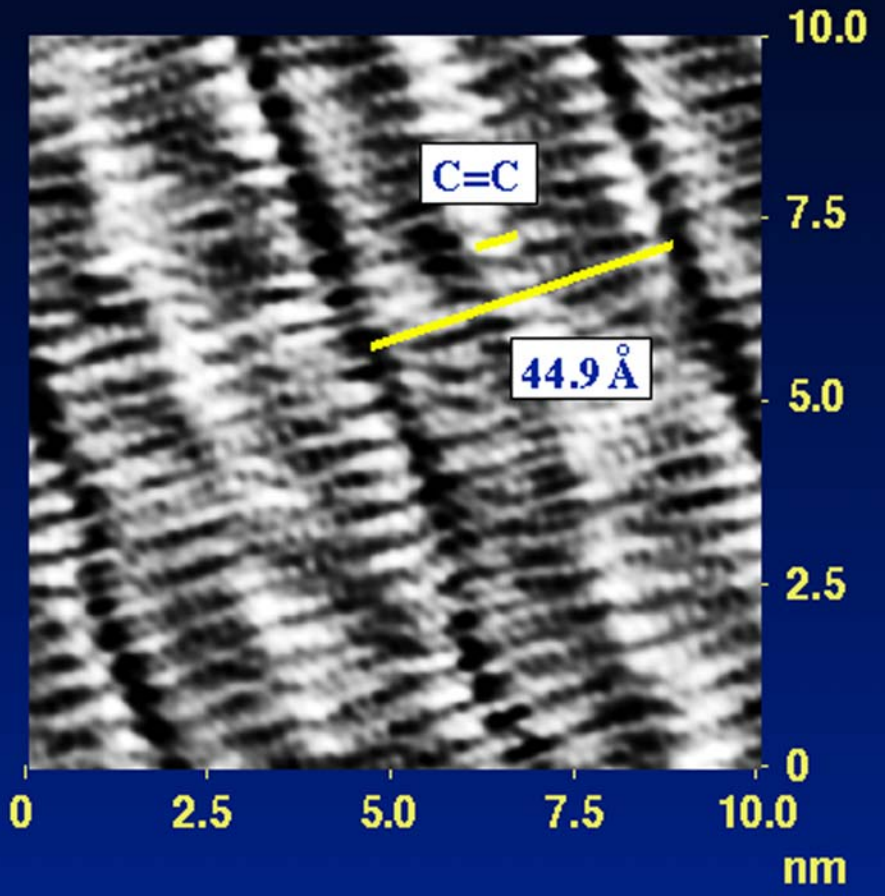
$C_{16}H_{33}HC{=}CHC_{17}H_{35}$

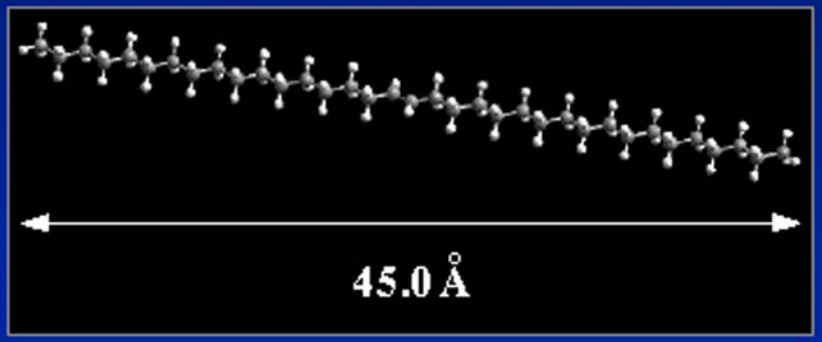




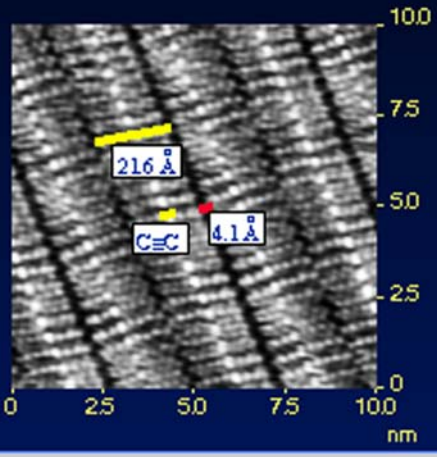


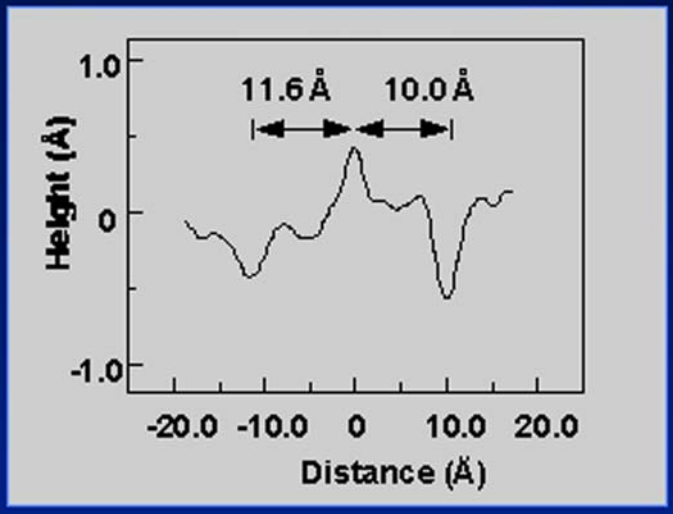
$C_{16}H_{33}HC{=}CHC_{17}H_{35}$

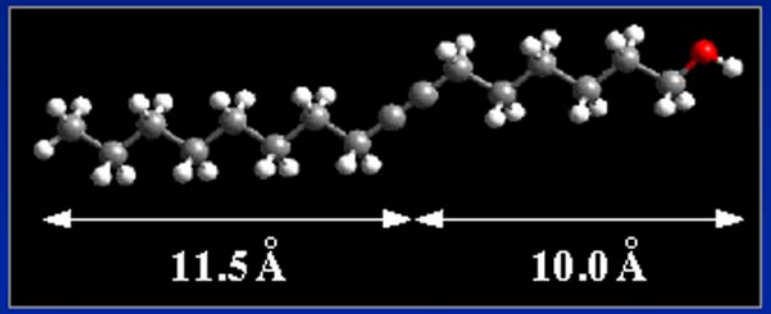




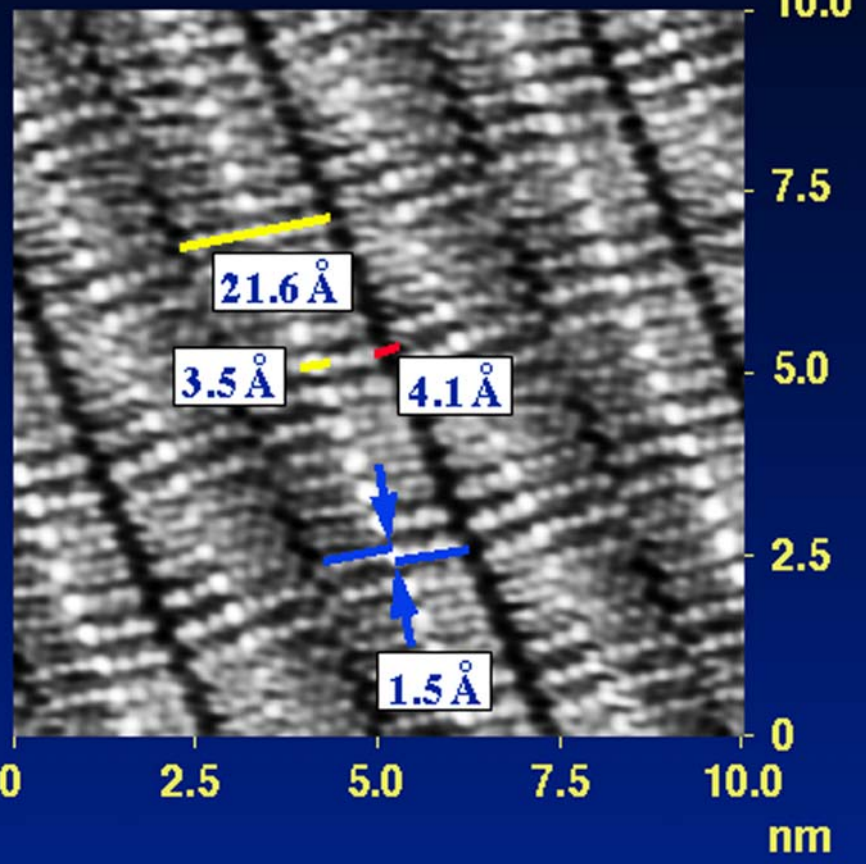
$H_3C(CH_2)_7C{\equiv}C(CH_2)_6OH$

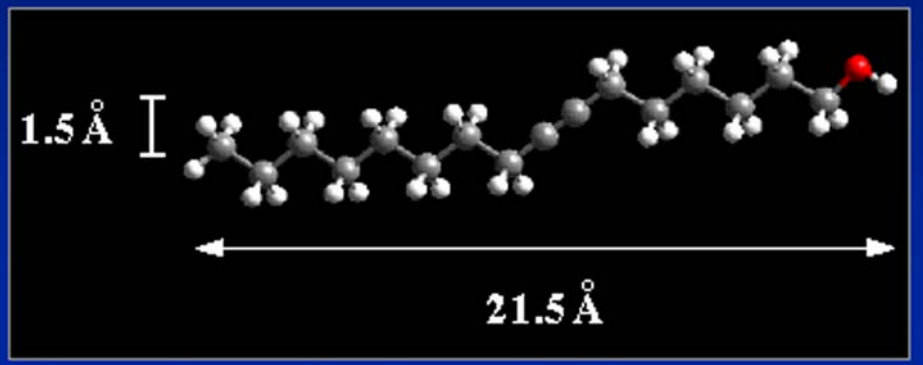




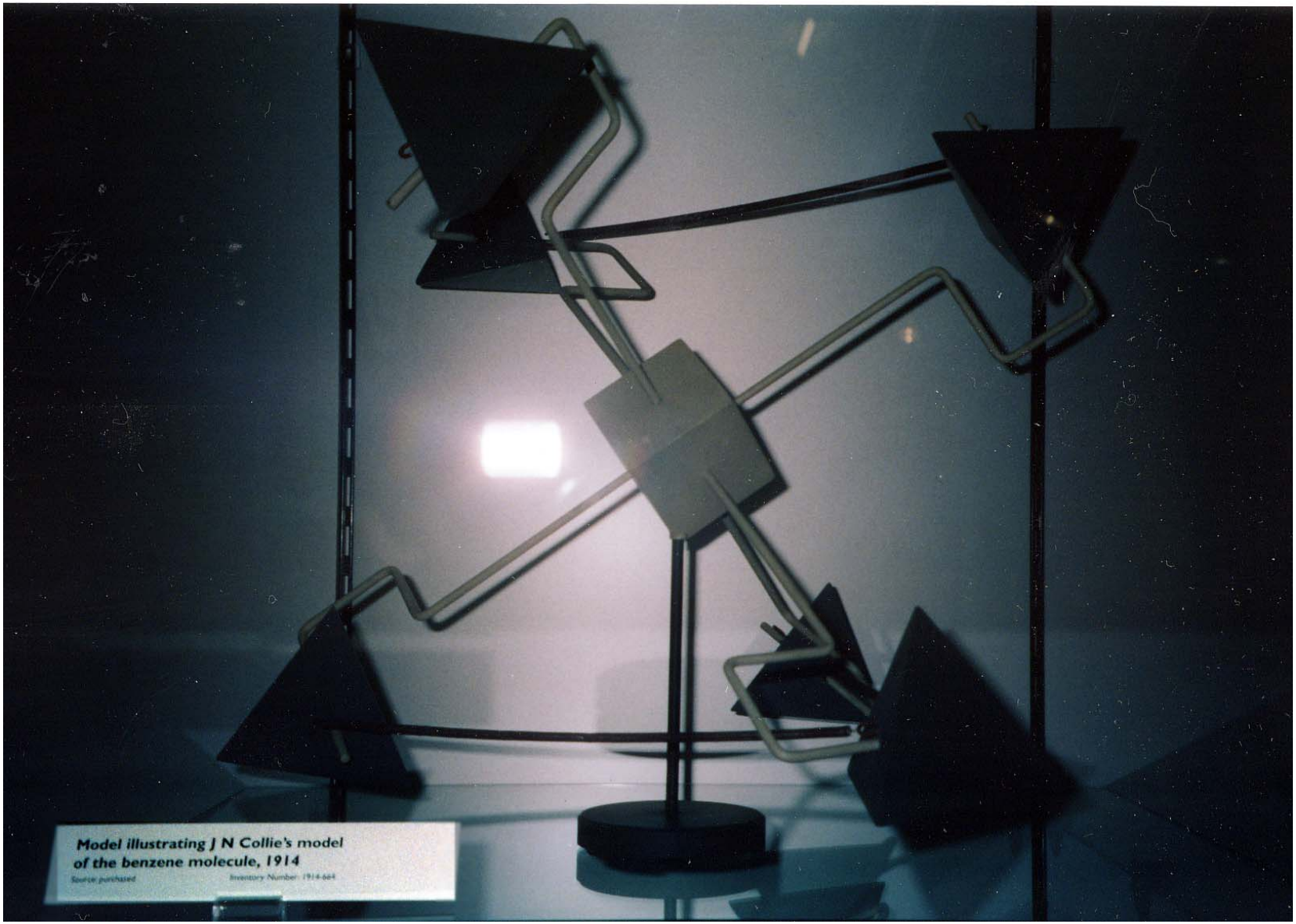


$H_3C(CH_2)_7C{\equiv}C\ (CH_2)_6OH$



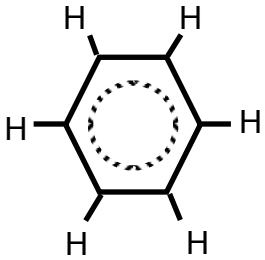


Benzene in 1914

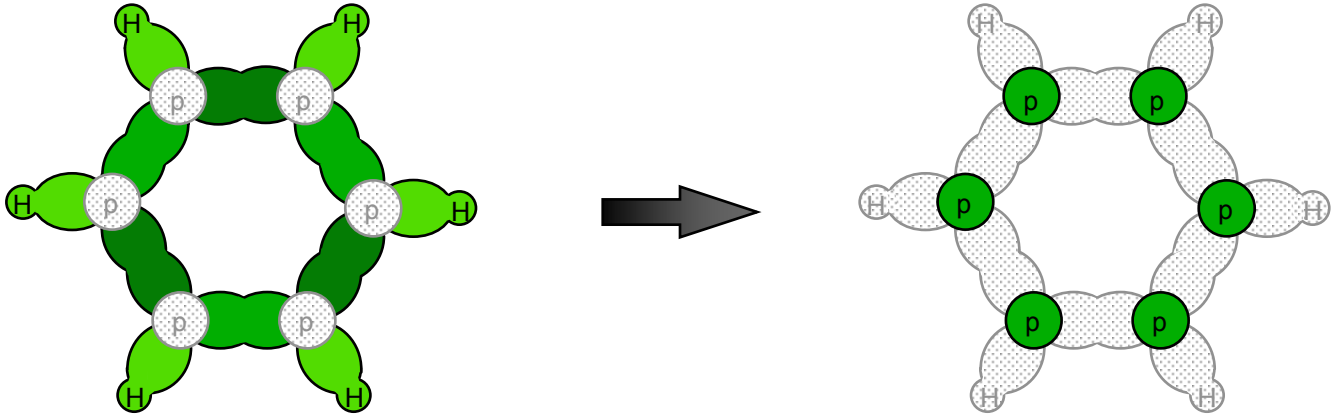


Faraday's sample of benzene

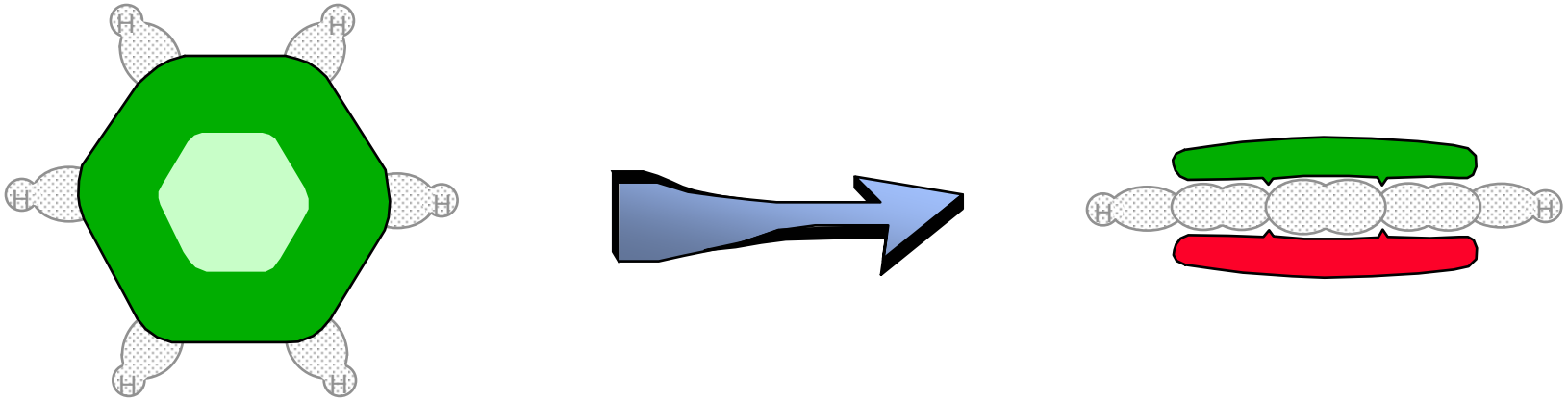
C_6H_6



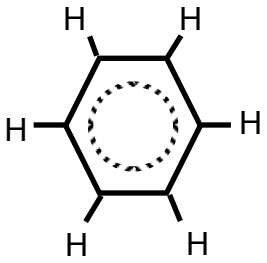
Let's re-emphasize the **p** orbitals:



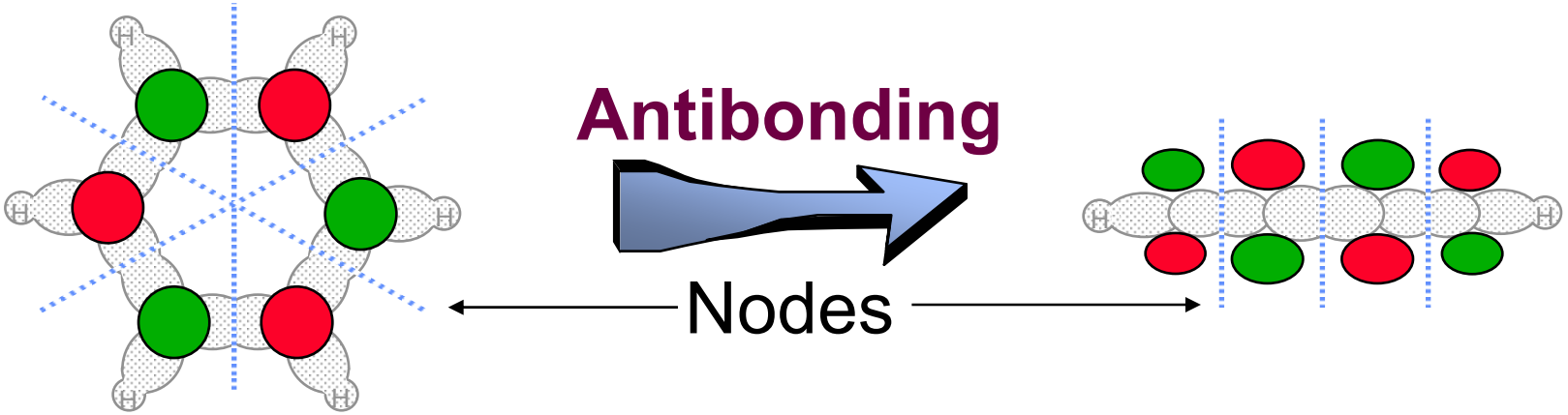
<u>The **p** orbitals act as a single, delocalized π bond.</u>

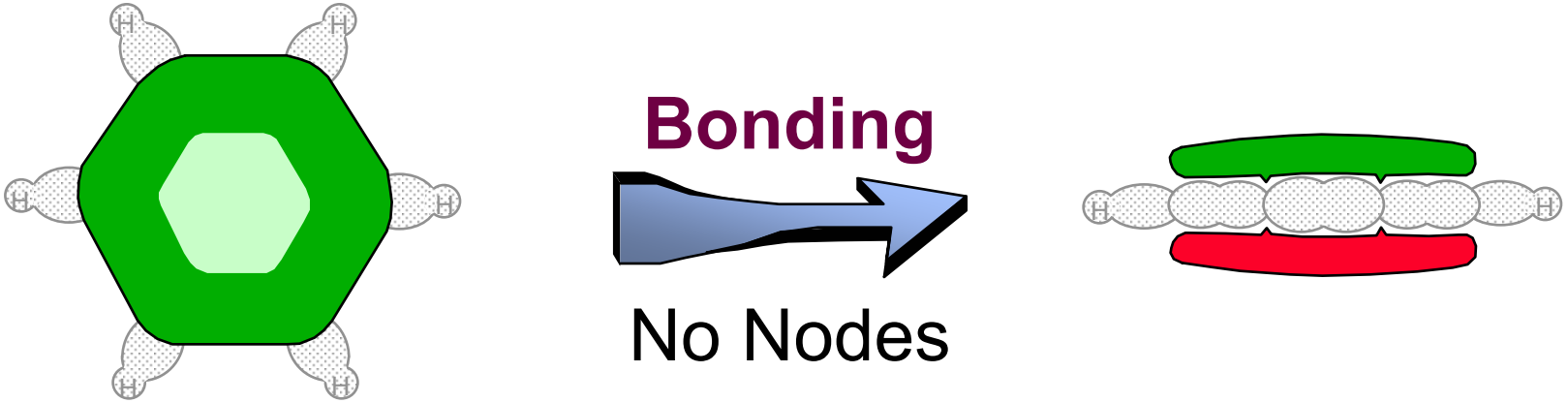


C_6H_6

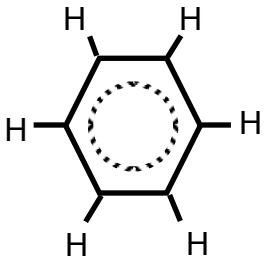


The **p** orbitals act as a single, delocalized π bond. Thus, the nodes in the antibonding orbitals also act over the entire molecule.

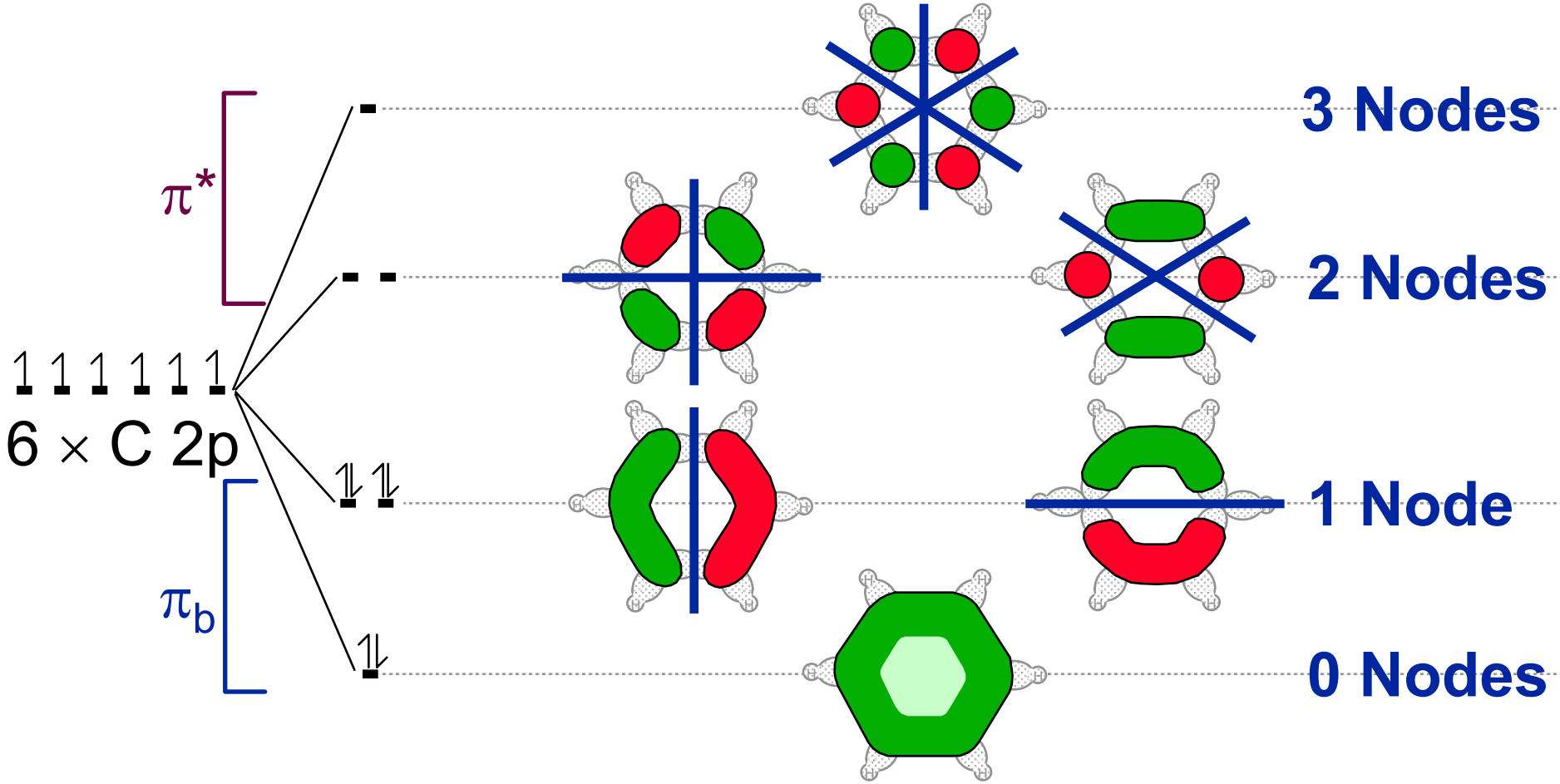


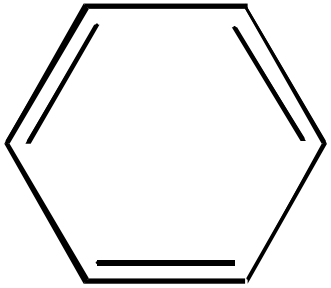


C_6H_6

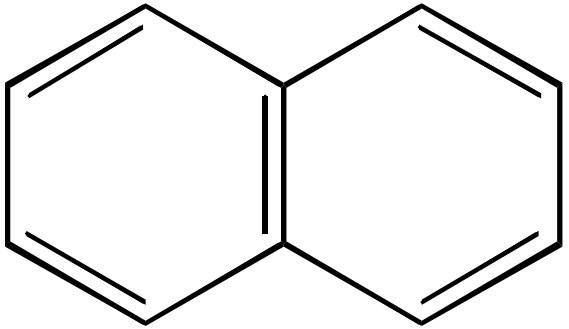


Instead of 2 atomic orbitals combining to form 2 MO's, we have 6 atomic orbitals combining to form 6 MO's.

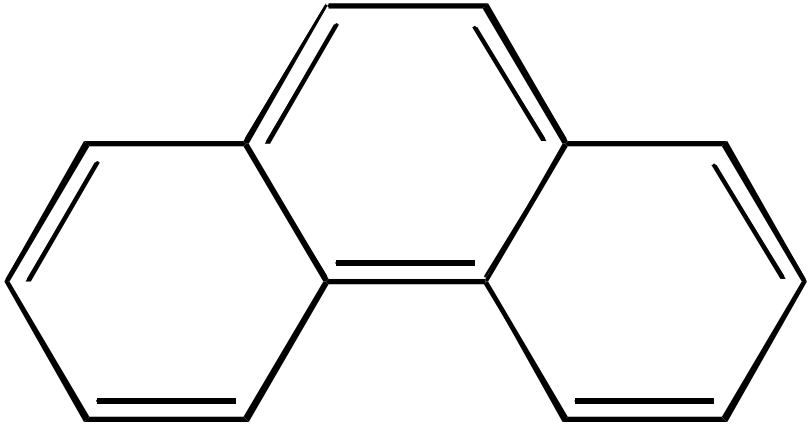




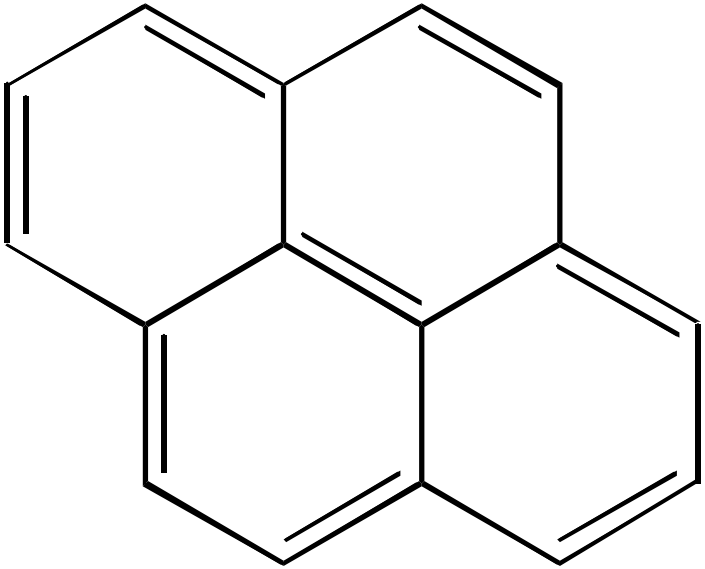
Benzene



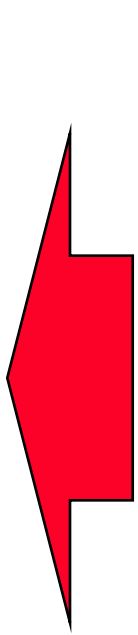
Napthalene

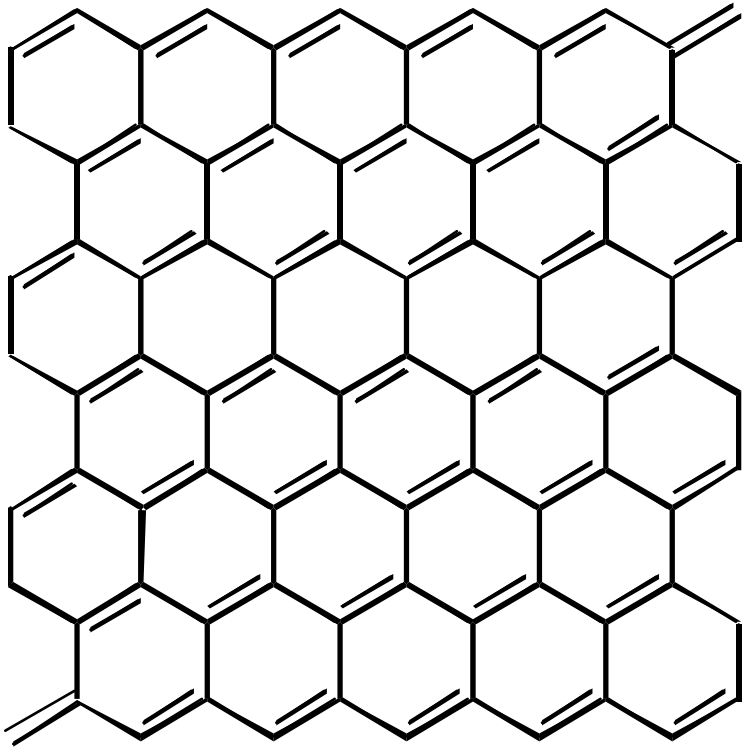


Phenanthrene

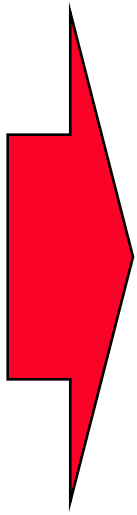


Benzo(a)pyrene (tar)

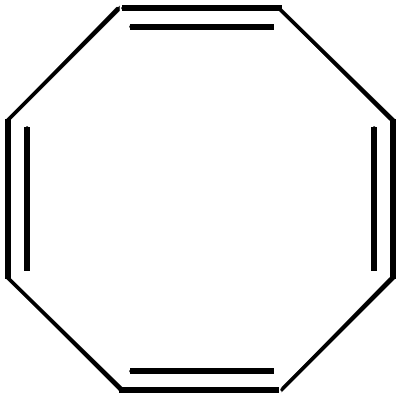




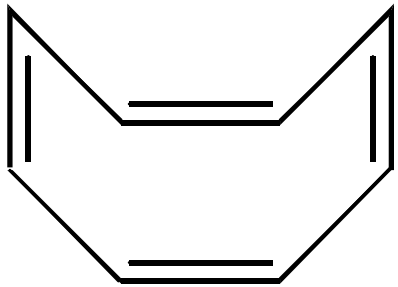
Graphite (all sp^2)

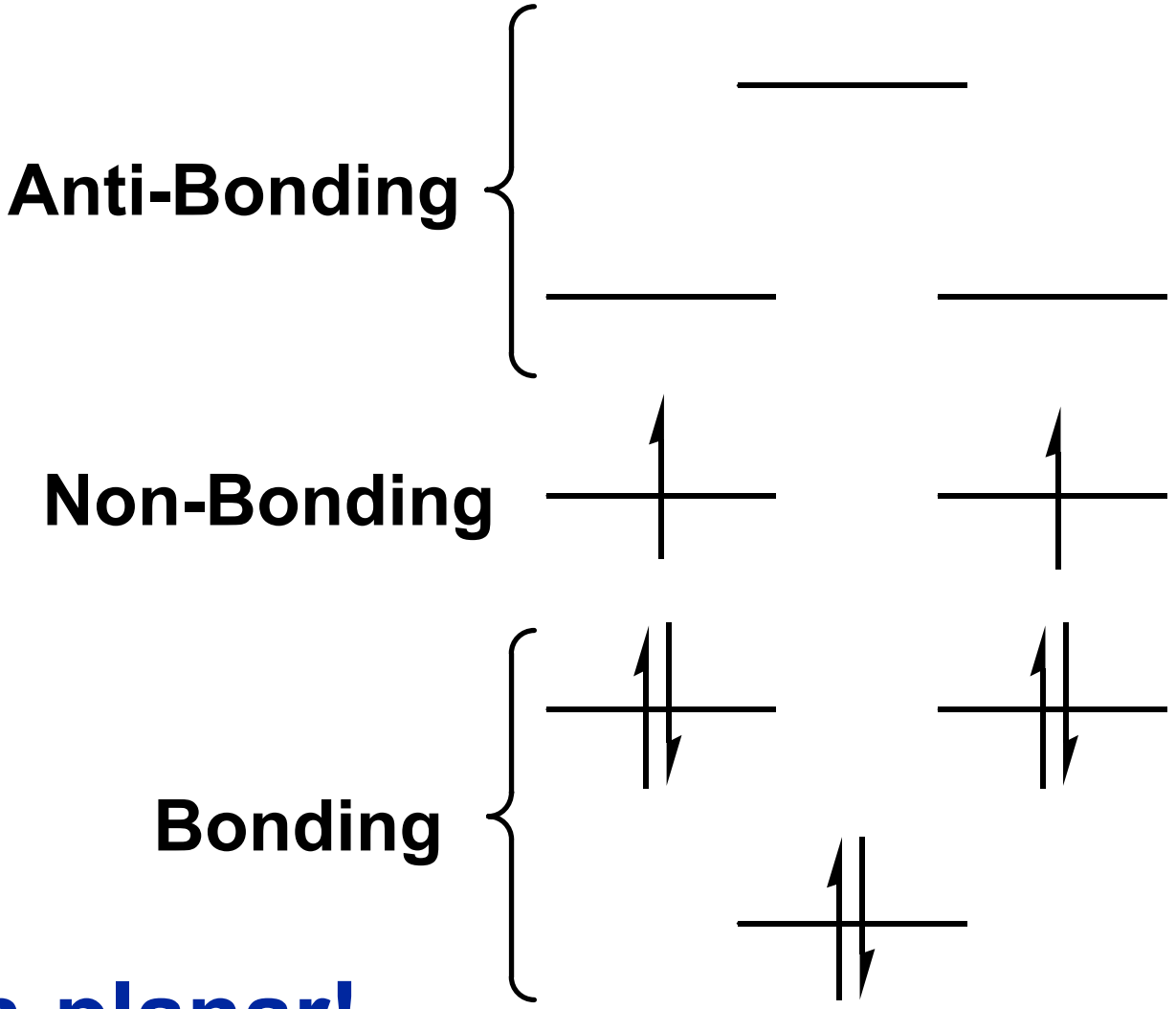


Non-Resonance in Cycloctatetrene



"COT"

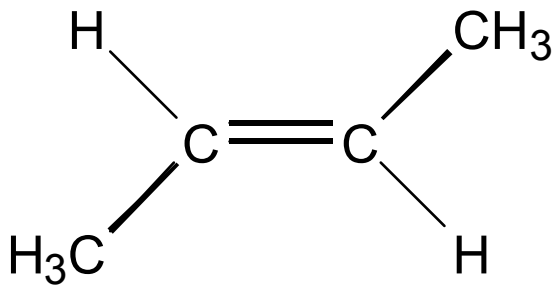




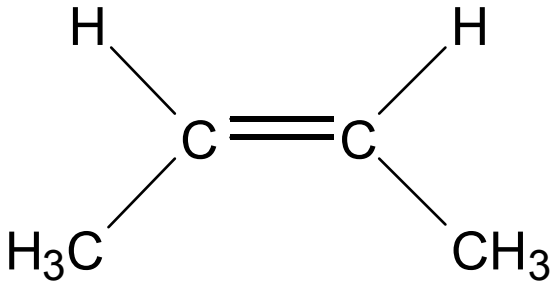
COT goes non-planar!

but...COT^{2-} and COT^{2+} are planar!

Another Look at Ethylene

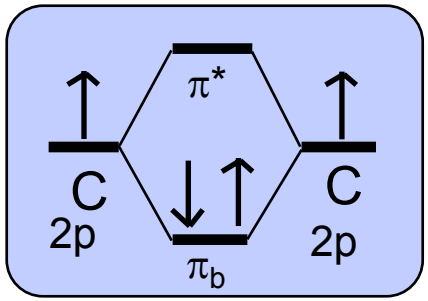


vs.



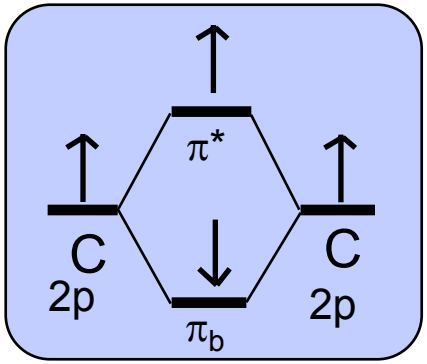
These are non-identical *isomers*

Light can promote interconversion



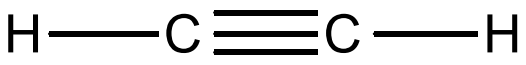
light

hν

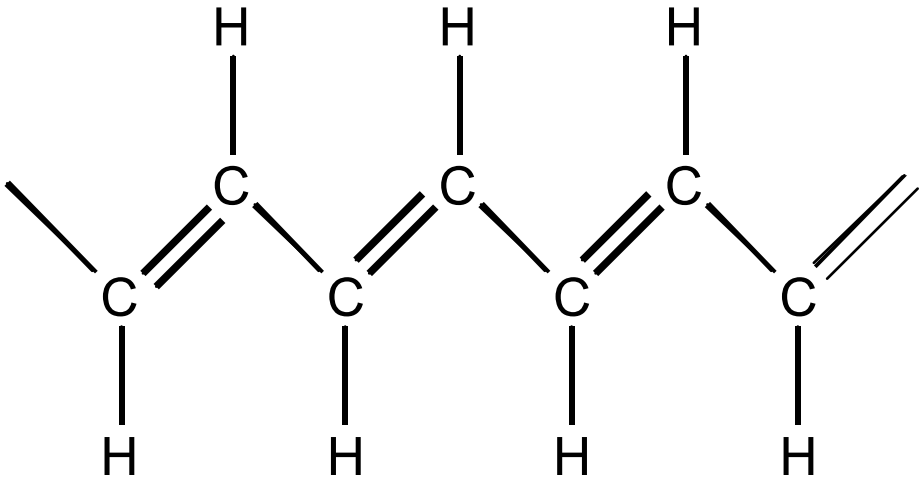


Excited State is Free to Rotate

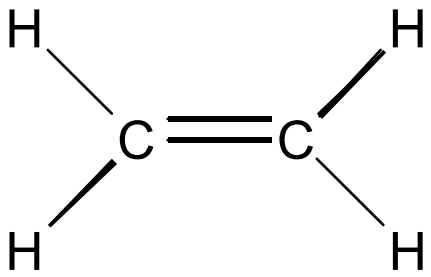
Bonding and Polymer Properties



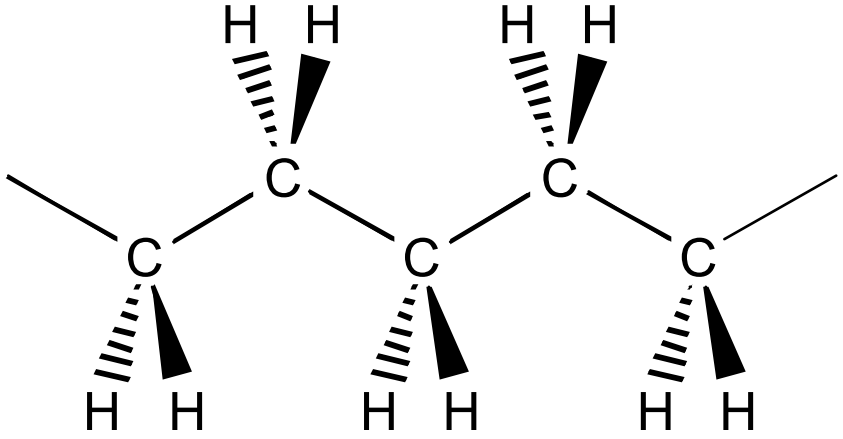
Acetylene



A Conducting Polymer

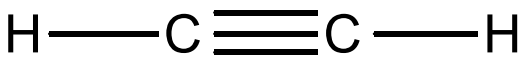


Ethylene

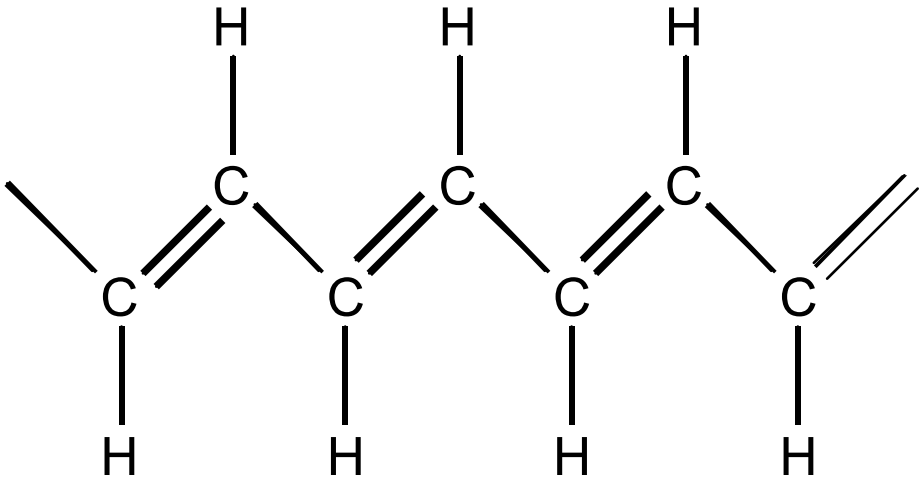


An Insulating Polymer

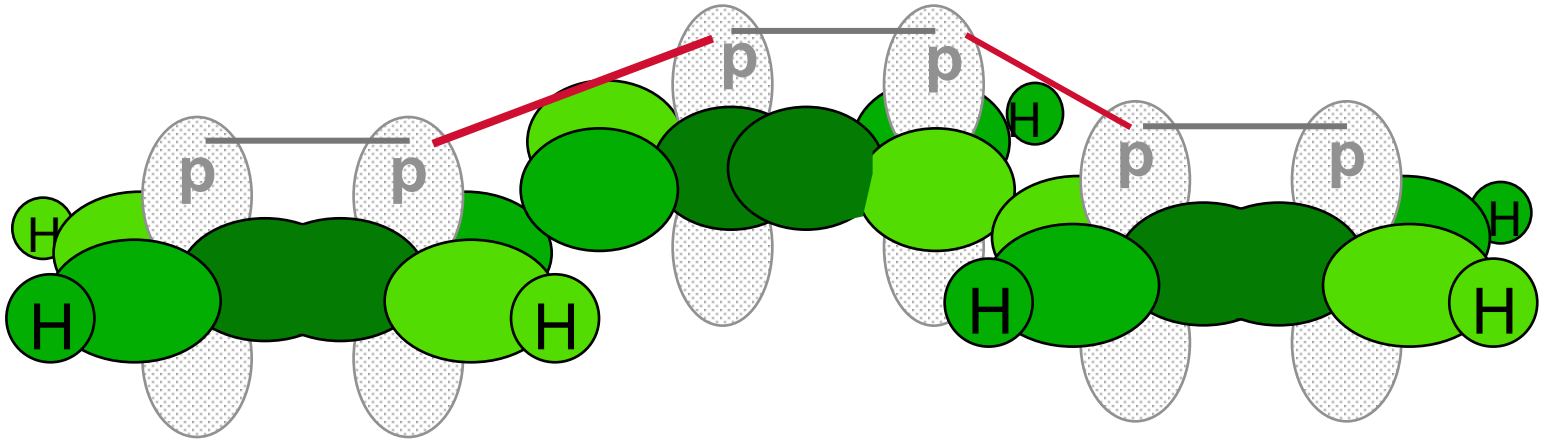
Bonding and Polymer Properties



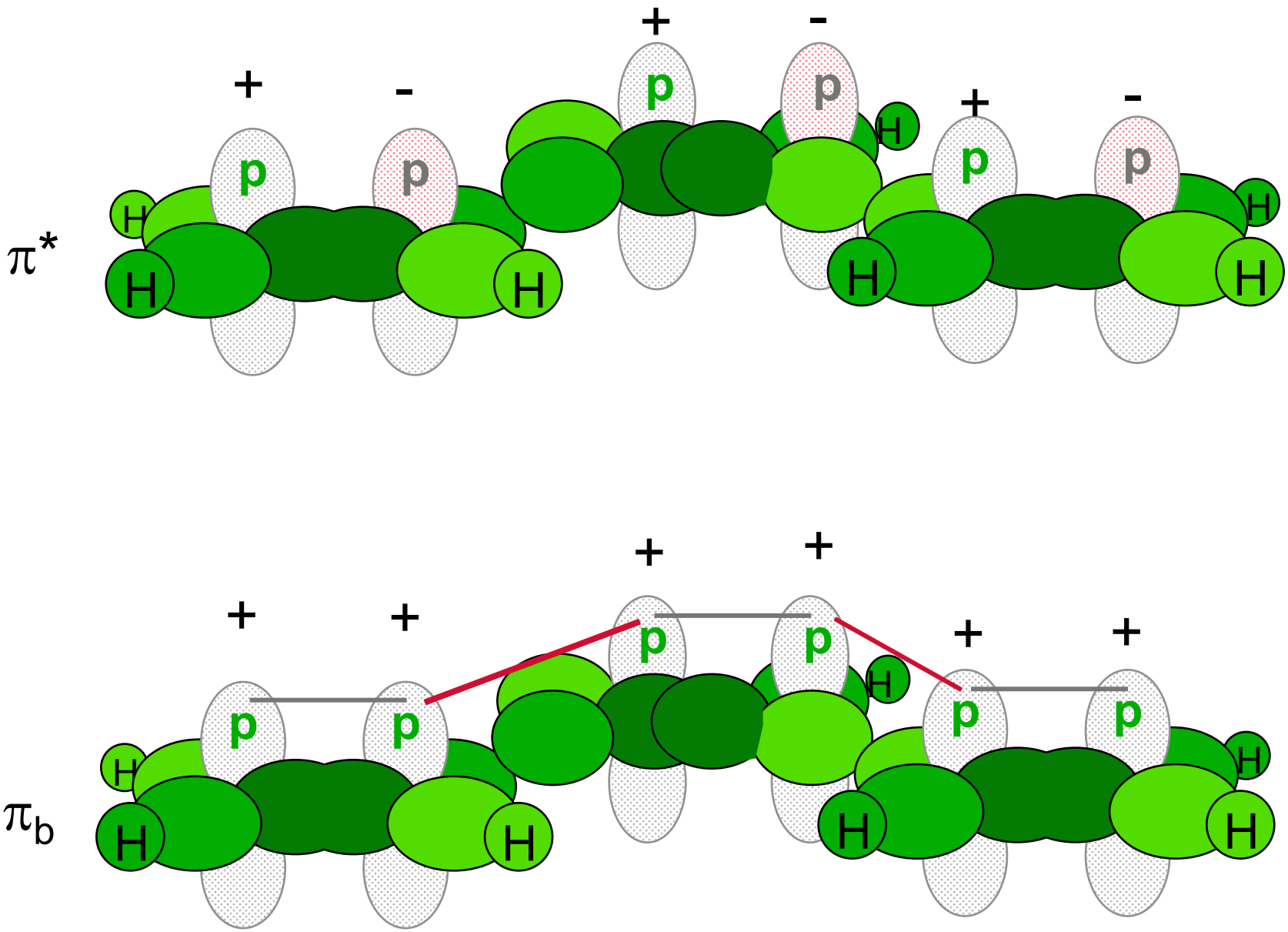
Acetylene



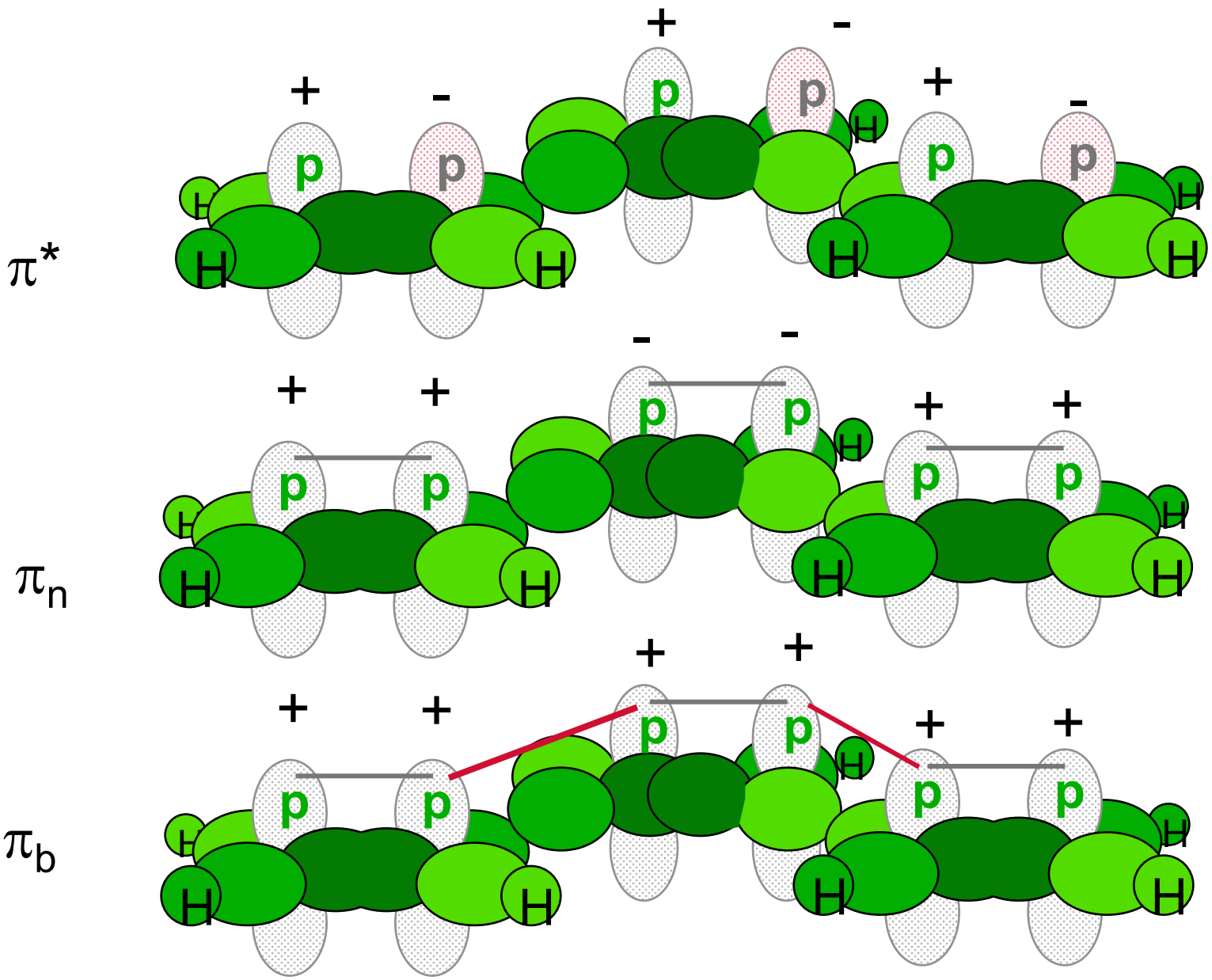
A Conducting Polymer



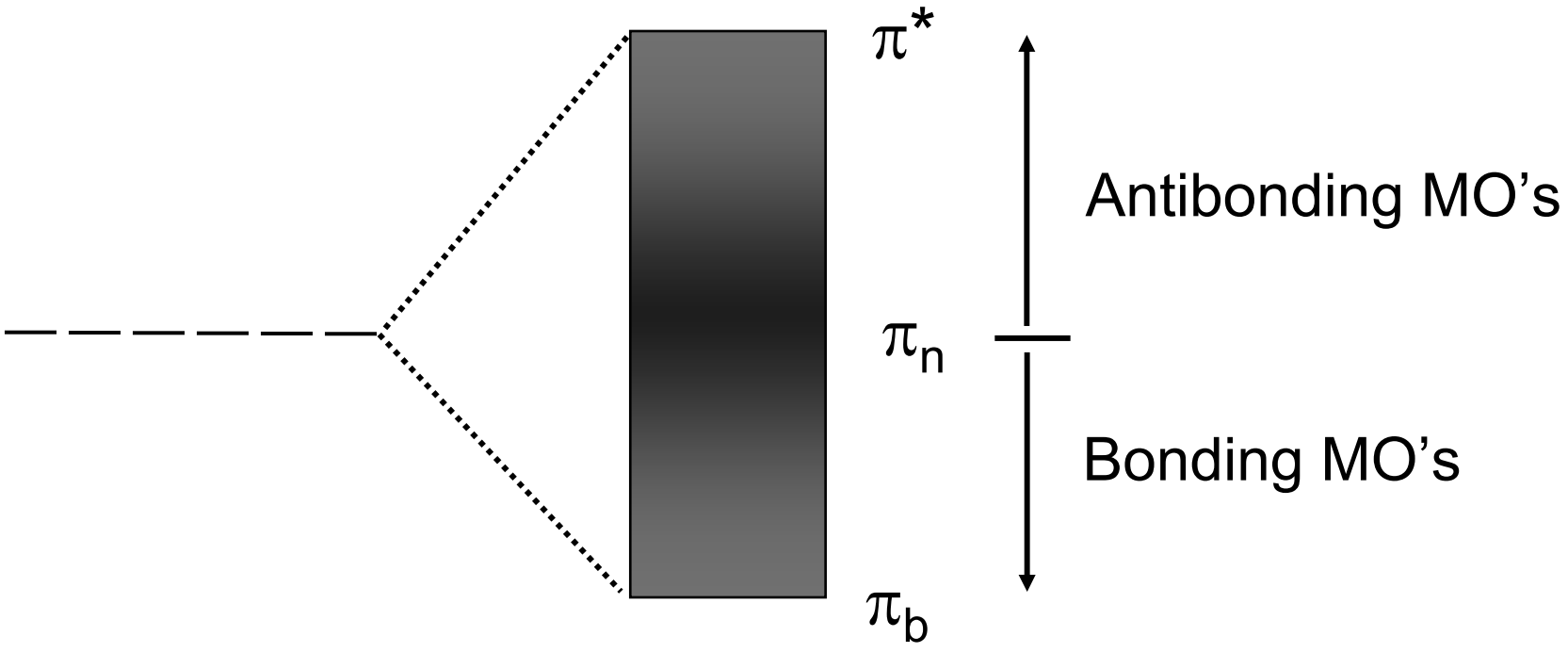
Bonding and Polymer Properties



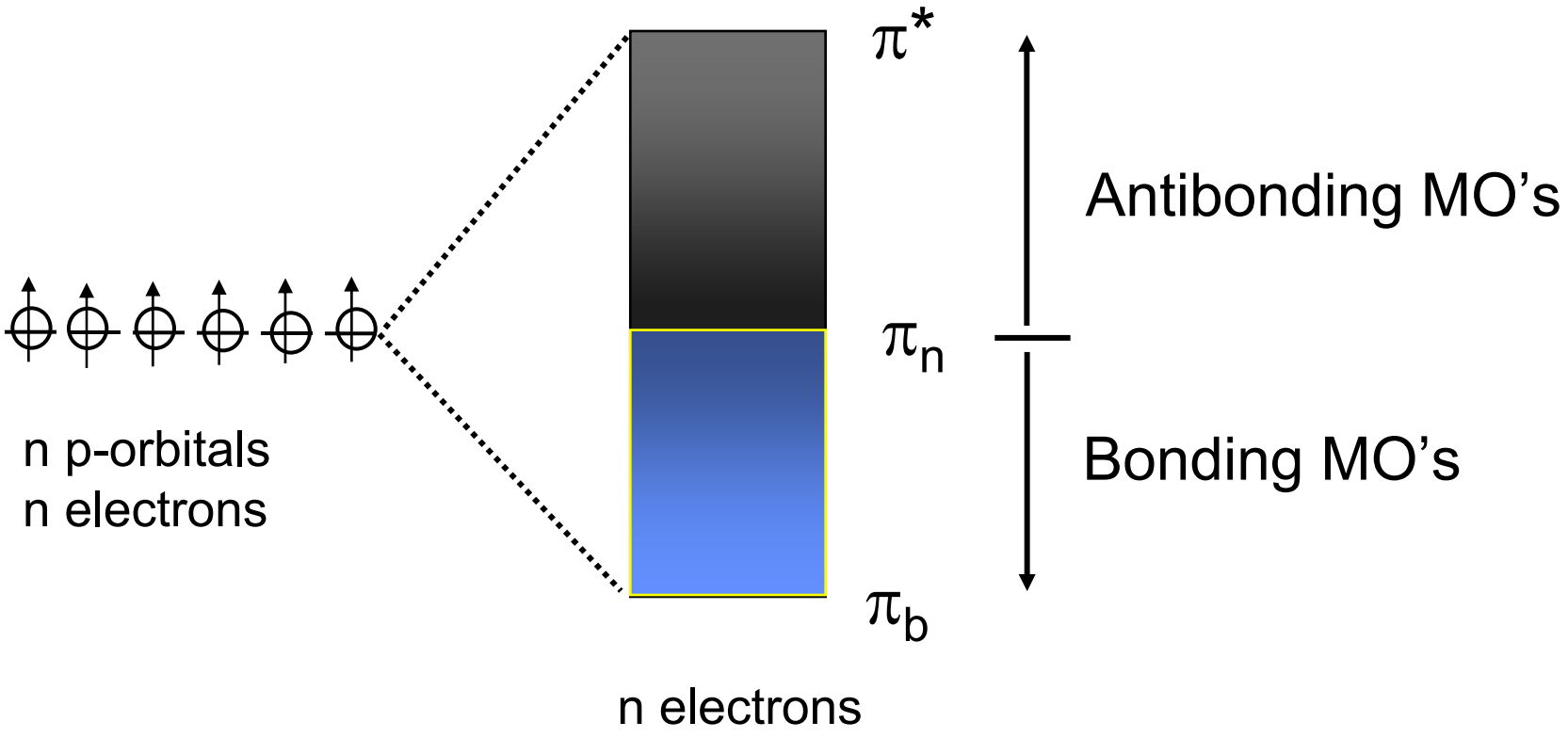
Bonding and Polymer Properties



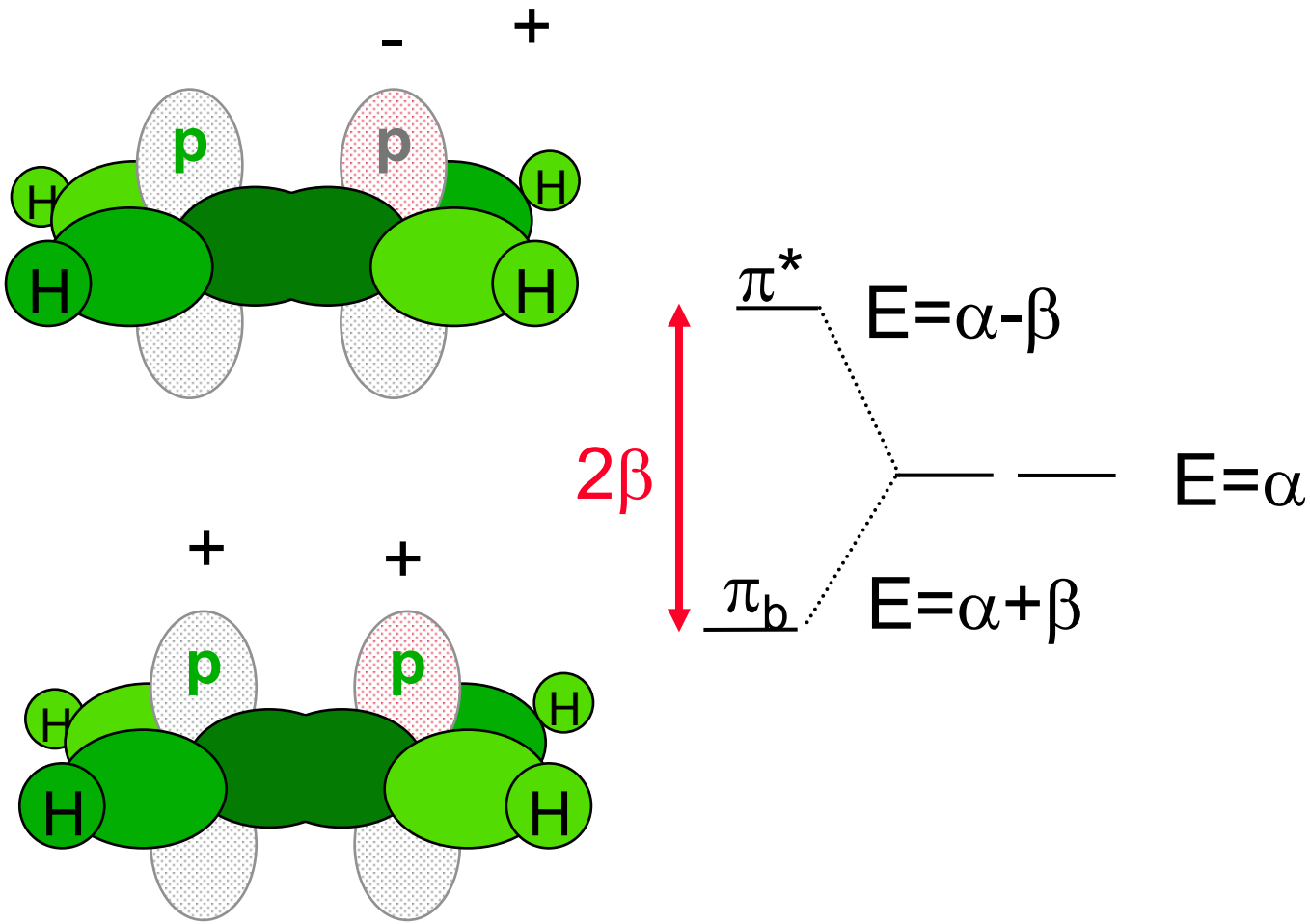
Band Structure of Conducting Polymers



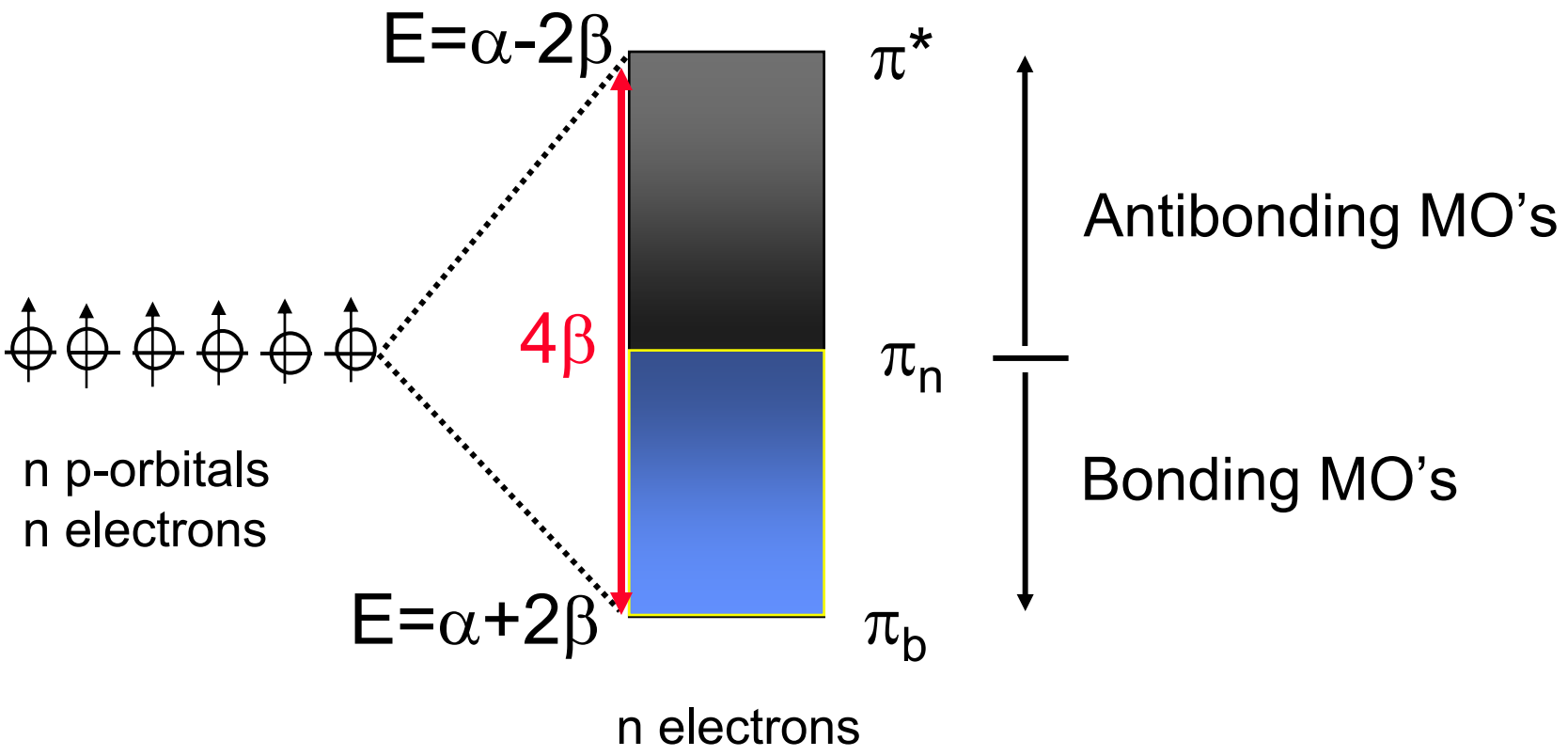
Band Structure of Conducting Polymers



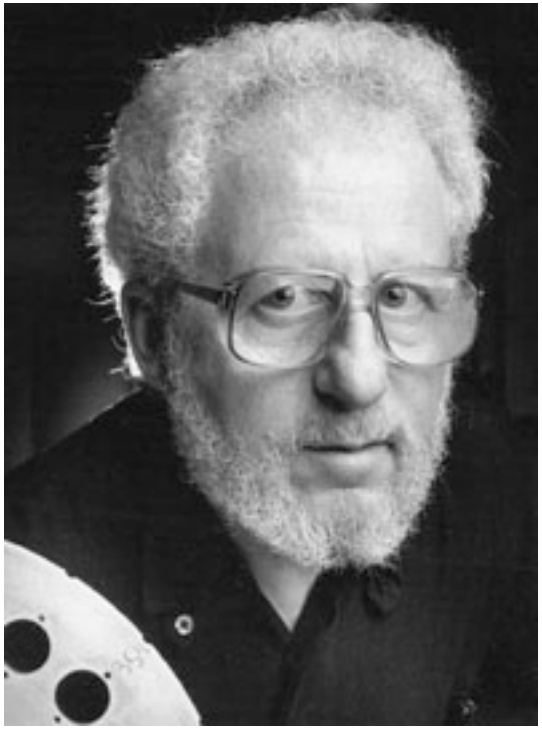
Energy Difference in Ethylene



Bandwidth of Infinite Conjugated π System



2000 Nobel Prize



Alan MacDiarmid Alan Heegar

"For the Discovery of Conducting Organic Polymers", 1977

Aspects of Chemical Bonds
⇨ Bonding in Chem 1a ⇦

- Atomic Structure
- Explain Atomic Line Spectra, Galaxies, etc.
- Shapes of Orbitals in Atoms for Bonding
- Ionization Energies and Trends in Chemical Reactivity (e.g., Li^+ vs Li)
- Which Molecules are Likely to Exist and Their Shapes and Reactivities (Ozone, Glo. Warm.)
- Magnetic and Bonding Properties of Molecules (Magnetic Tapes, Disks, etc.)
- Special Properties of Resonance Stabilization
- Directionality of Covalent Chemical Bonds
- Hydrogen Bonds

Nobel Prize in Physiology/Medicine, 1962

Francis Crick
Cambridge

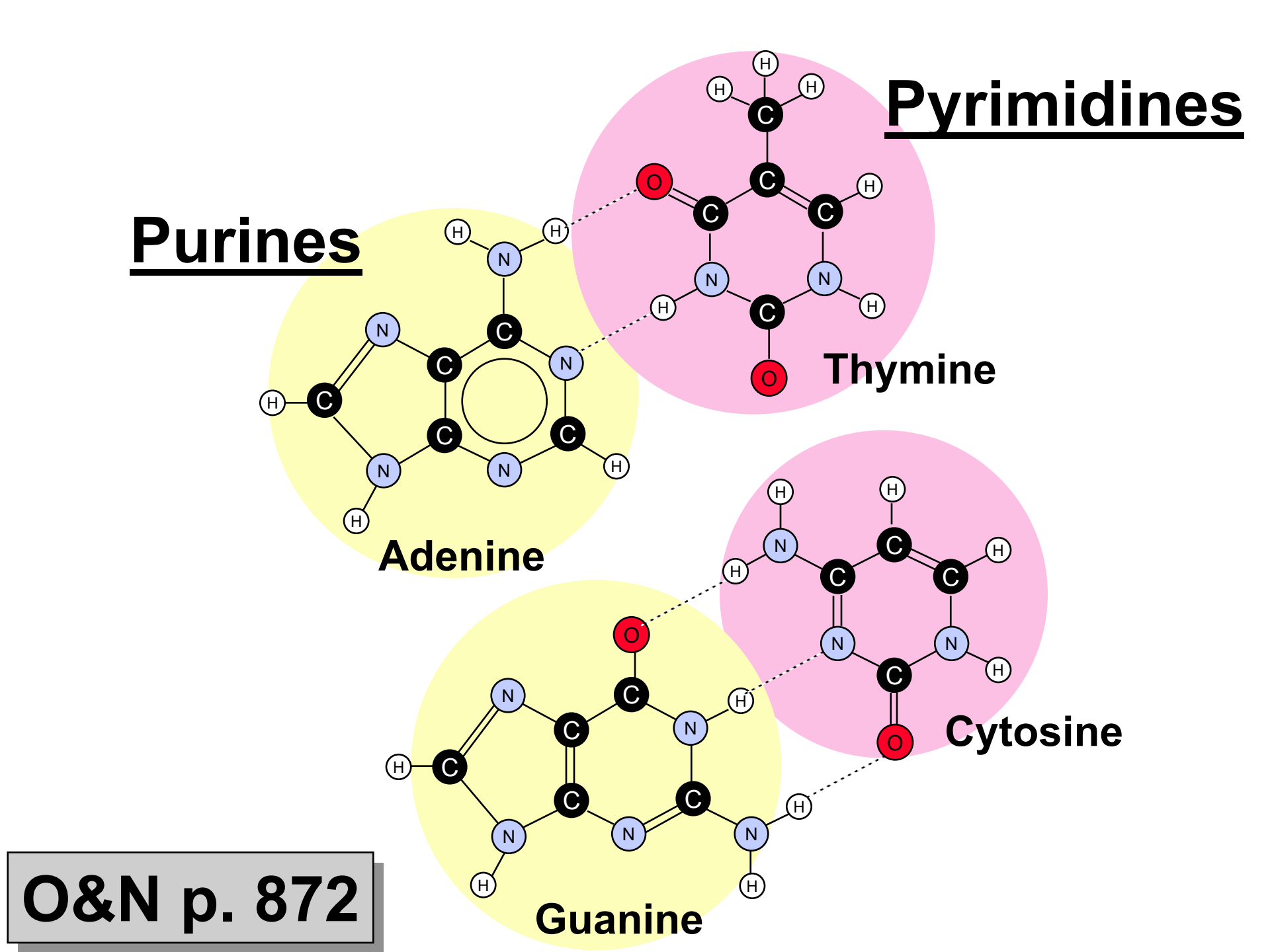
Competed with Pauling and Corey for alpha-helix structure of peptides

James Watson
Harvard

1951-1953 Proposes double helix Of DNA
1954-1956 Caltech with A. Rich Structure of RNA

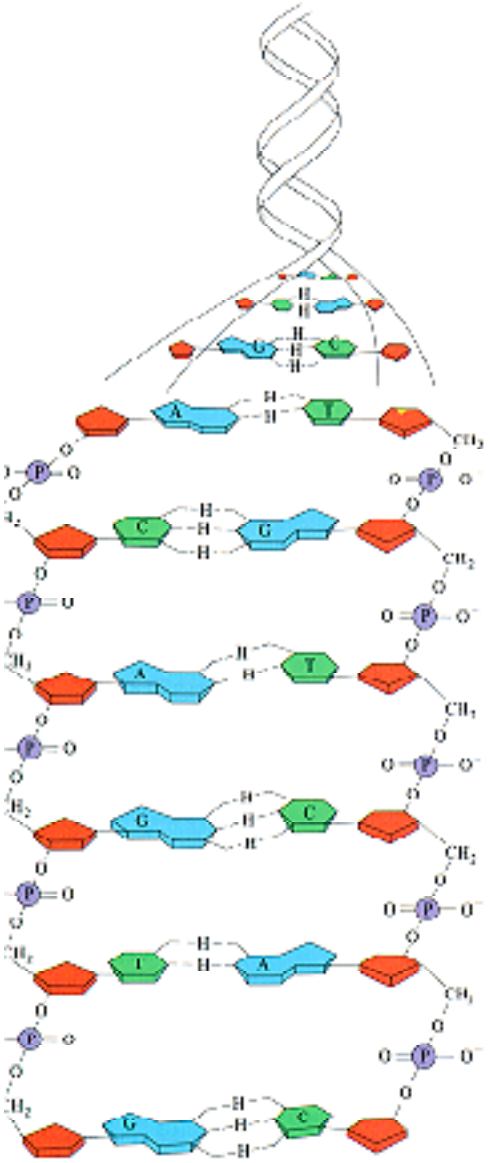
Maurice Wilkins
King's College London

Demonstrates X-ray Diffraction Of DNA



O&N p. 872

OGN
p. 873



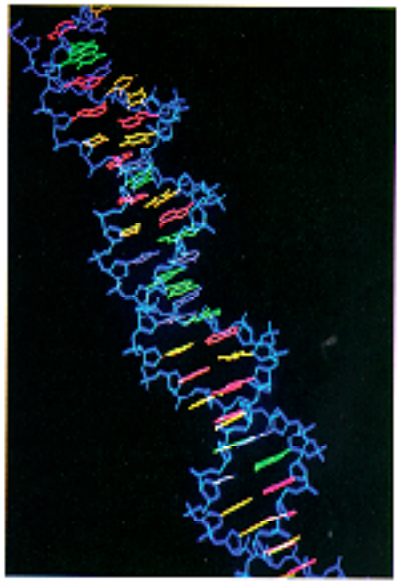
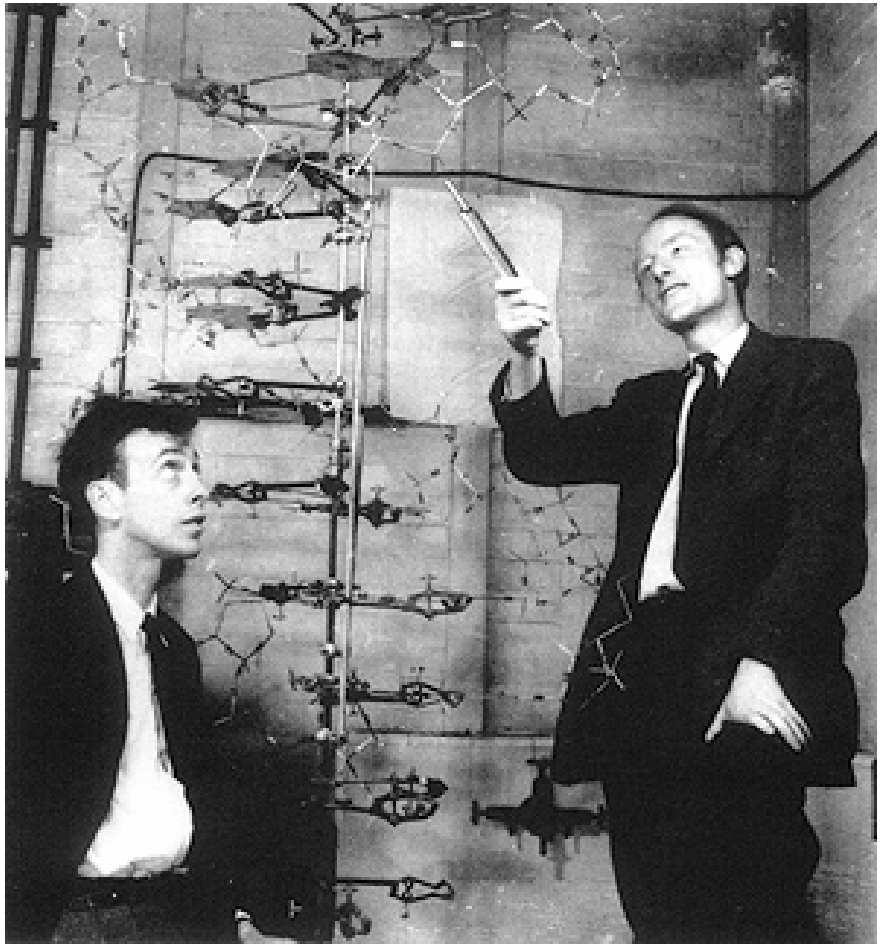


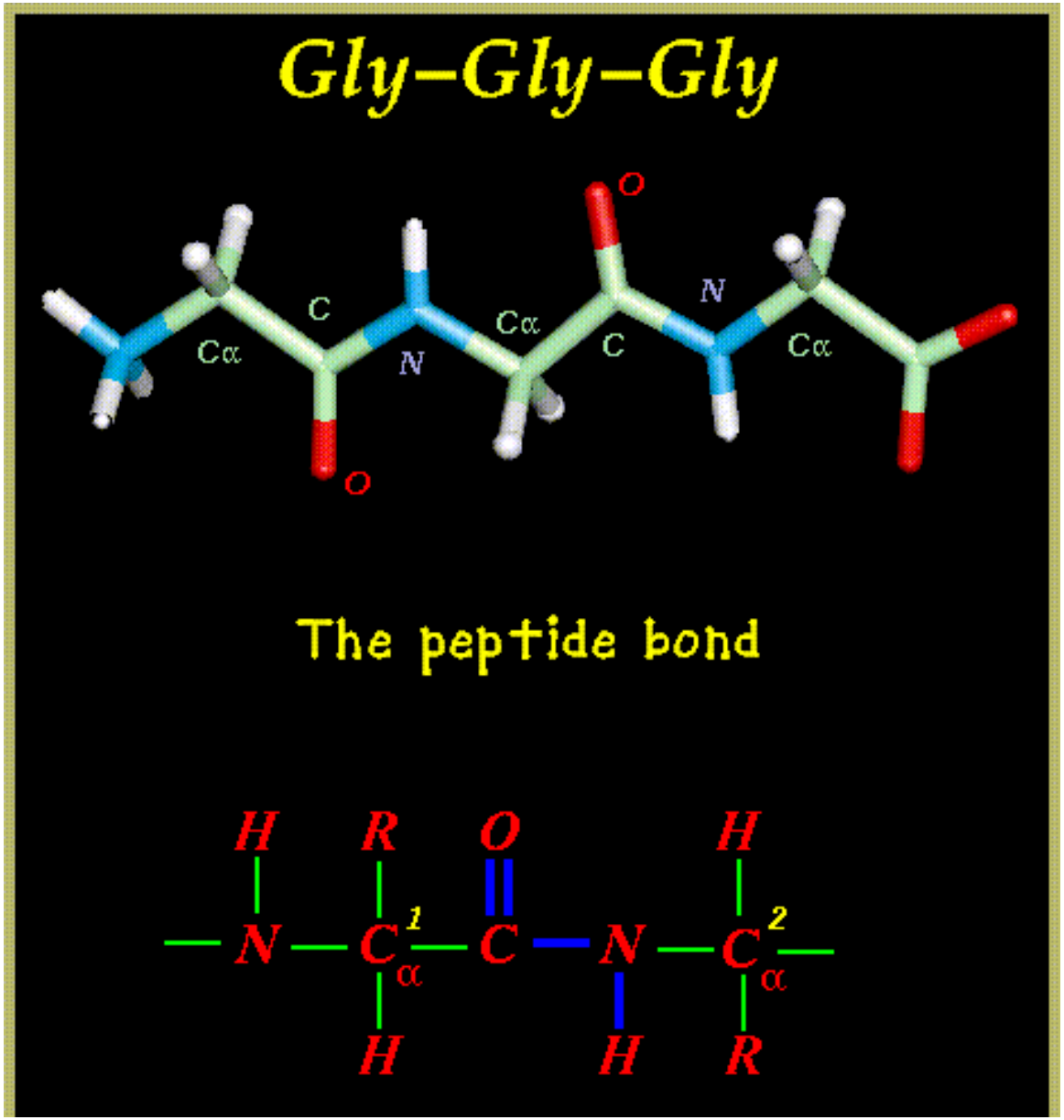
Figure 23-33

The double-helix structure of DNA. (©Jeff Dan McCoy/R. Langridge/Rainbow)

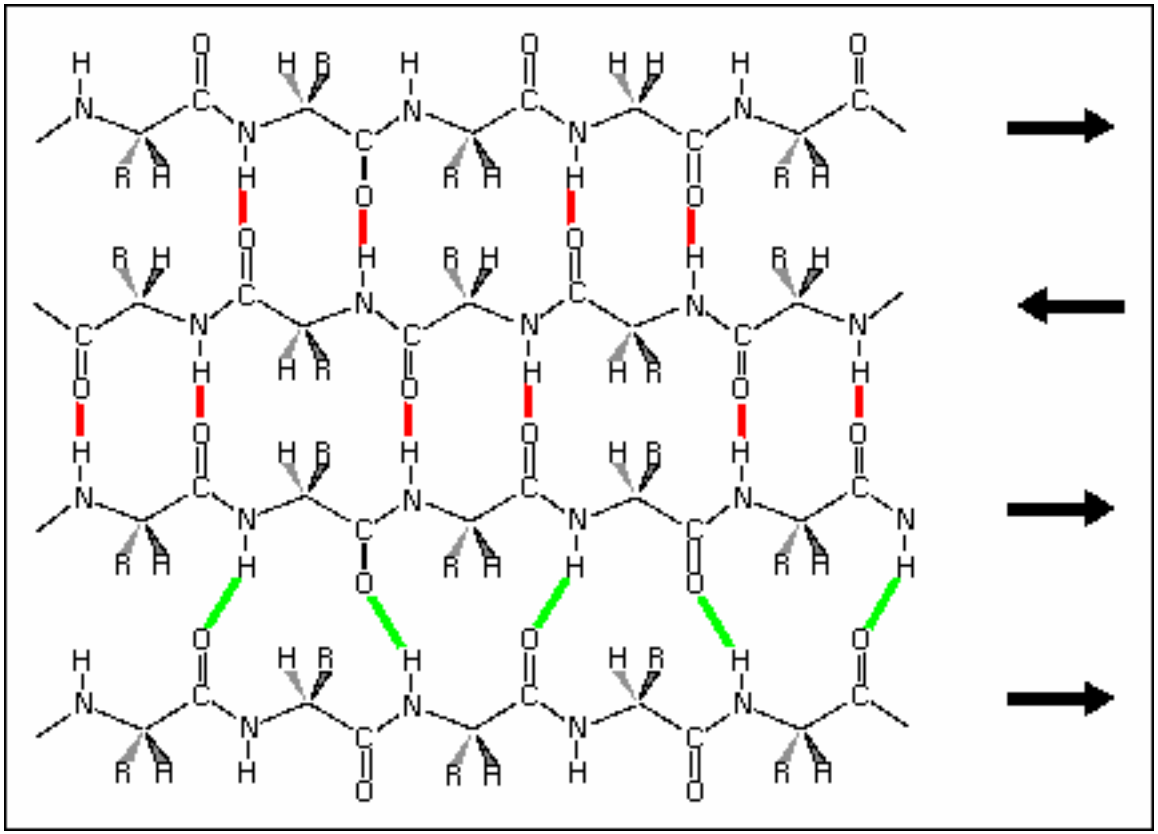
Watson and Crick's Original DNA Model



Peptide Bonds



Beta Sheets from Peptides

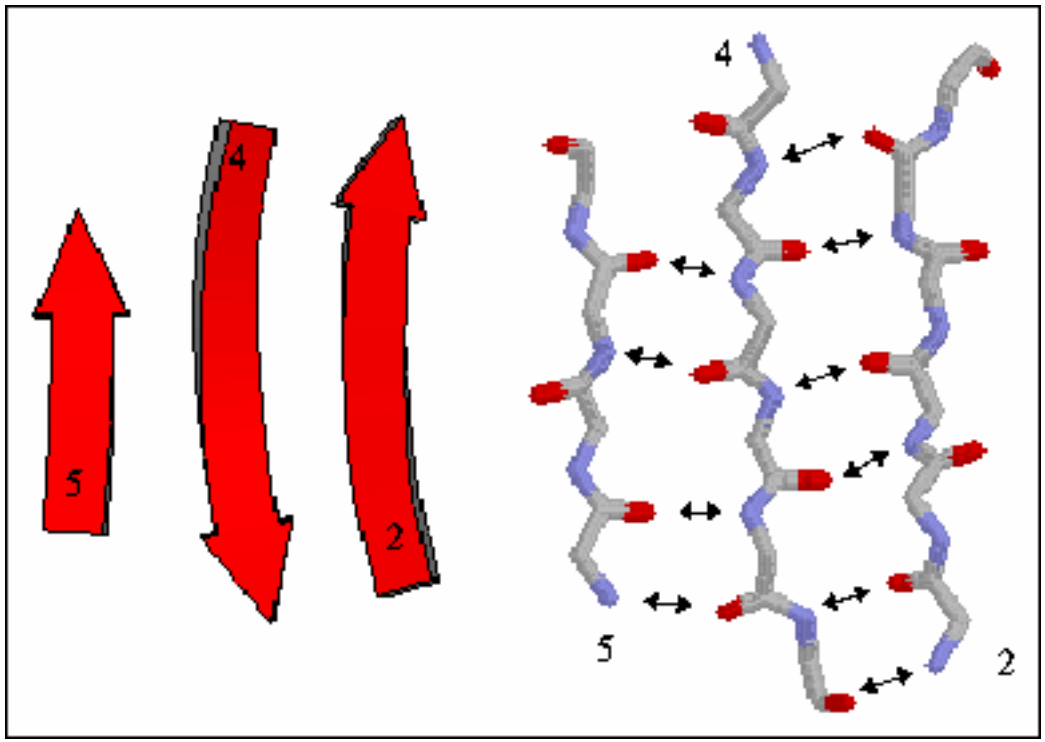


Average length is 6 residues
Most sheets contain <6 strands

Secondary structure

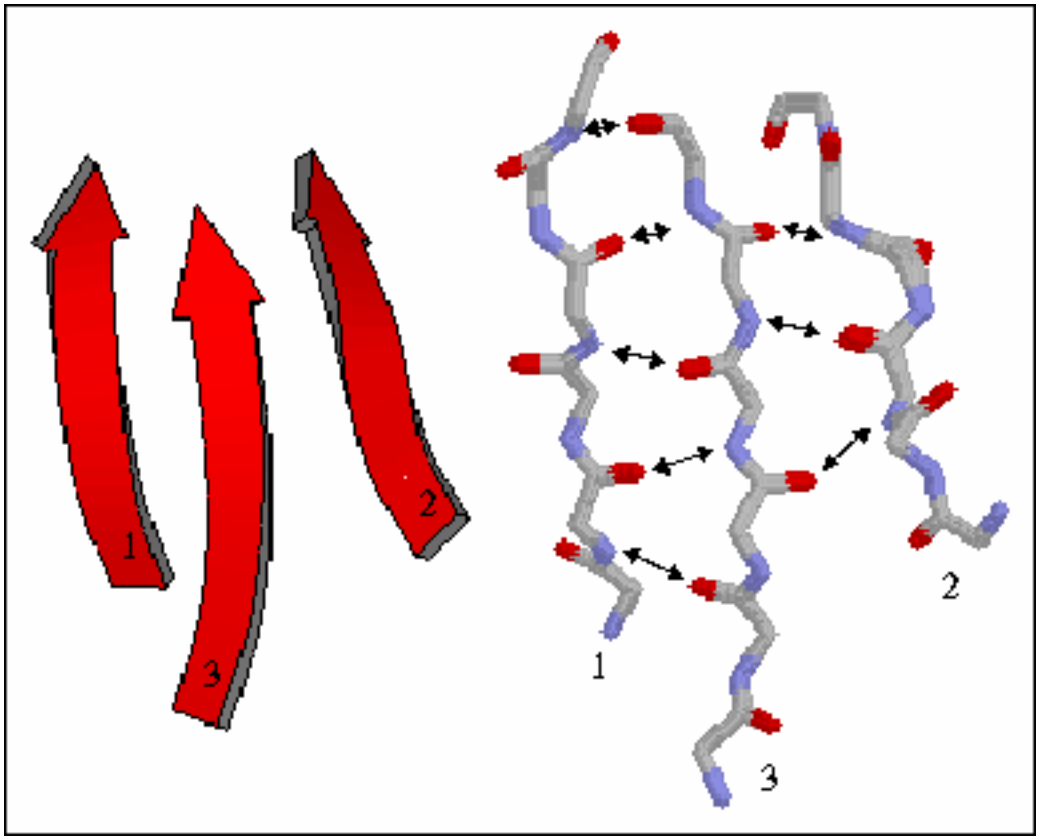
Antiparallel Beta Sheets

Thioredoxin



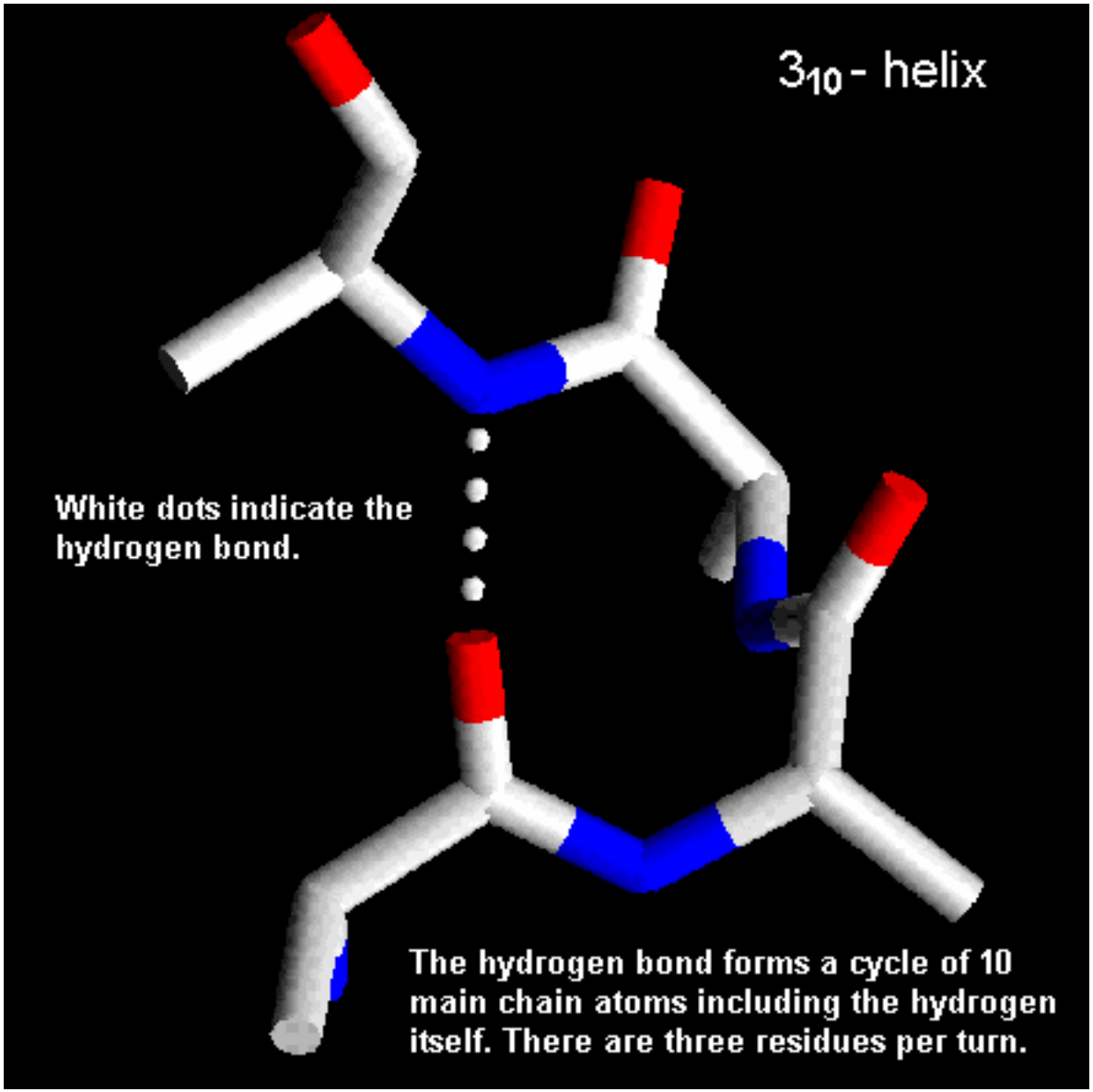
Antiparallel is intrinsically more stable due to optimal H-bond orientation

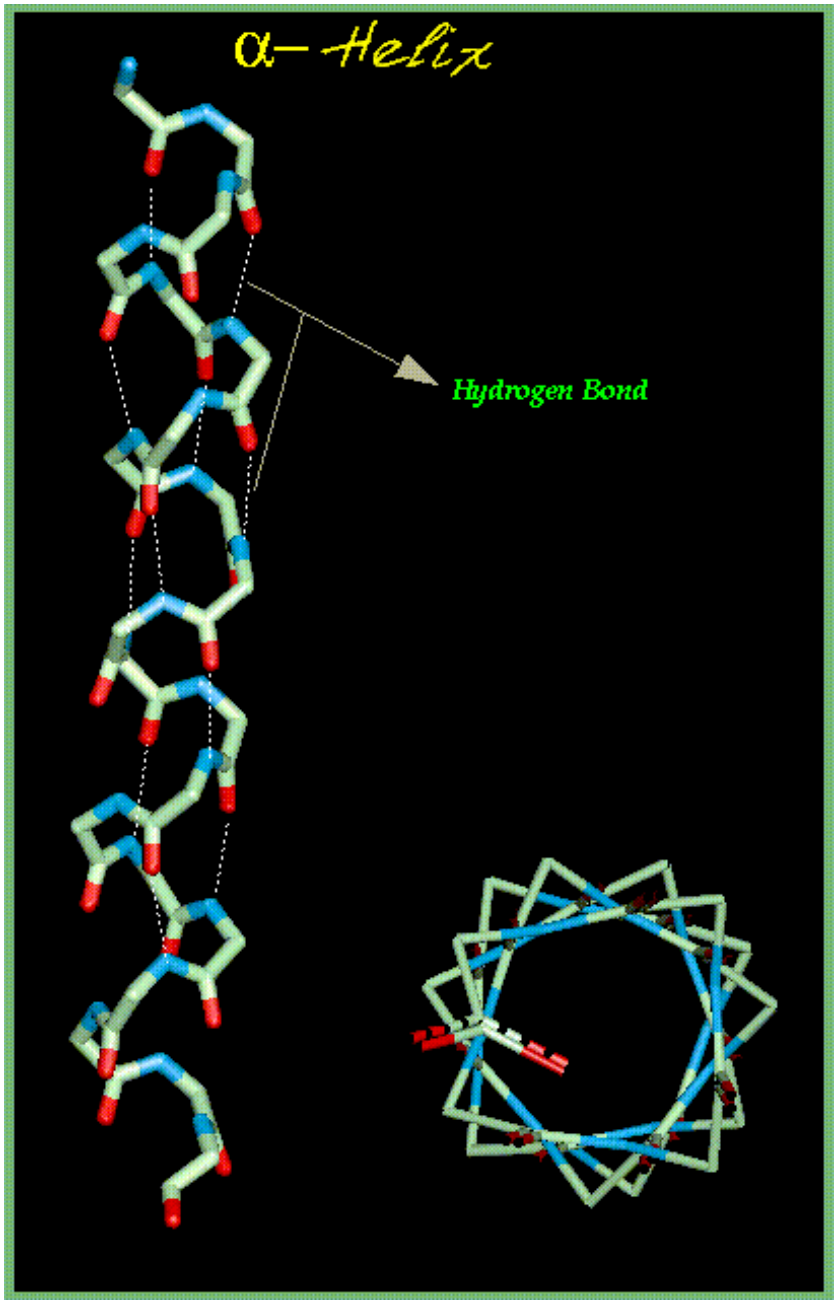
Parallel Beta Sheets

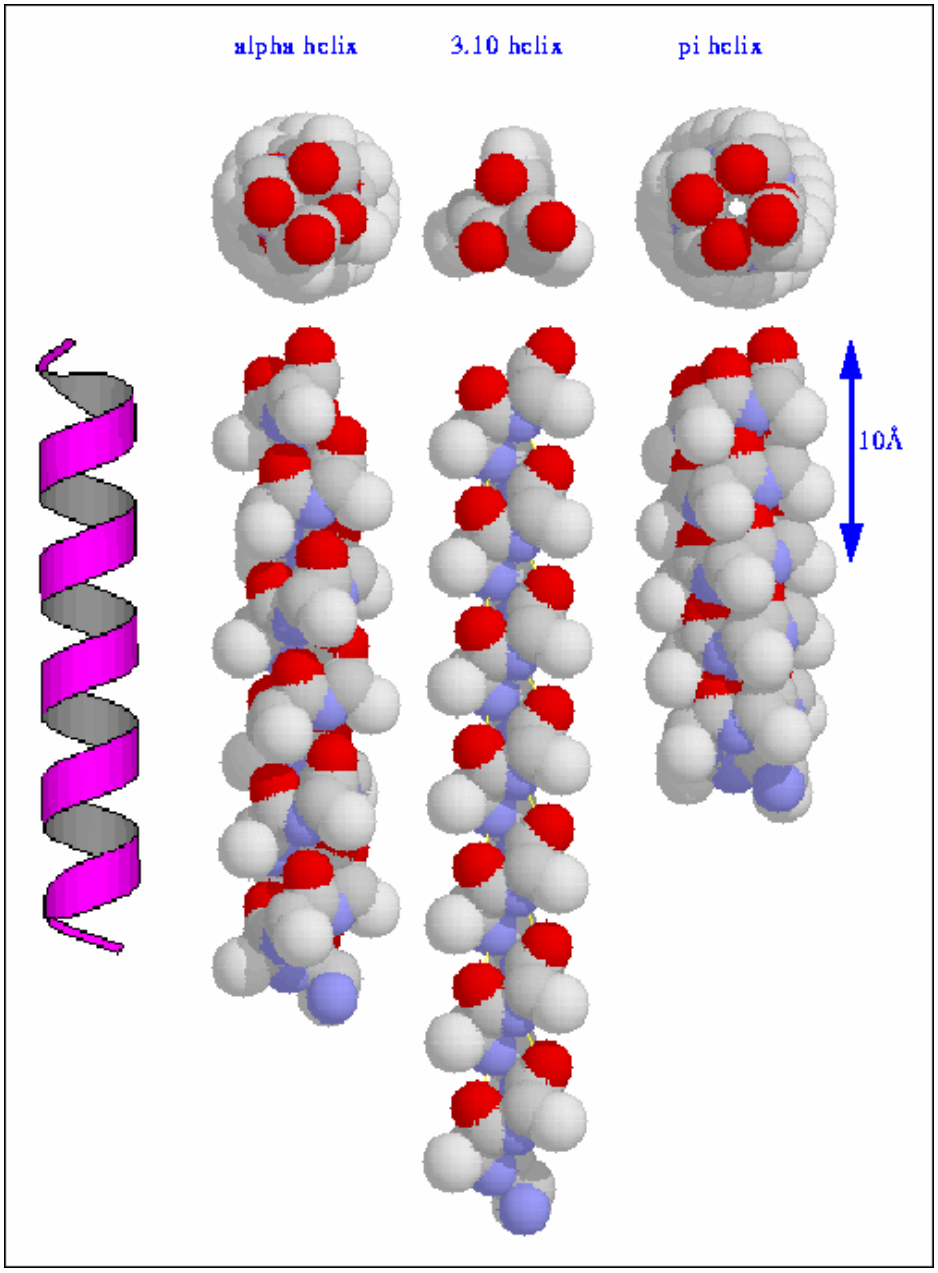


Overall **macrodipole** leaving an effective charge of ~ +1/15 unit elemental charge at the N-terminus and - 1/15 charge at the C-terminus of each strand of average length

Peptides form Alpha Helices




α- Helix
Hydrogen Bond


alpha helix
3.10 helix
pi helix
10Å

End

of

Hybridization

Part 2

Reading: Gray: (4-7)
OGN: (16.2)