Chapter 2. Alkanes and Cycloalkanes: Introduction to Hydrocarbons

2.1: Classes of Hydrocarbons

molecules that are made up of carbon and hydrogen

1. Aliphatic
   a. alkanes - contain C-C single bonds - $C_nH_{(2n+2)}$
      saturated hydrocarbons
   b. alkenes - contain C=C double bonds - $C_nH_{(2n)}$
   c. alkynes - contain C≡C triple bonds - $C_nH_{(2n-2)}$
2. Arenes (aromatics) - cyclic hydrocarbons with alternating C-C single and double bonds

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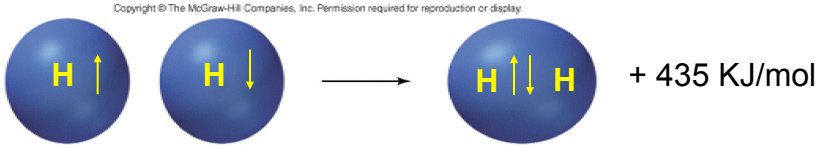
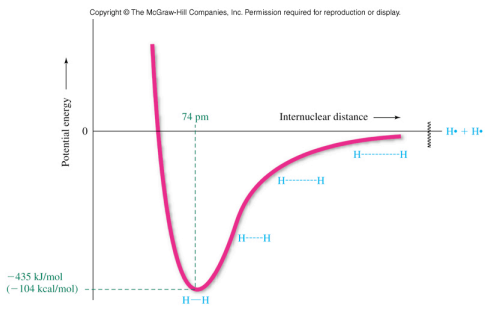
2.2: Electron Waves and Chemical Bonds (please read)

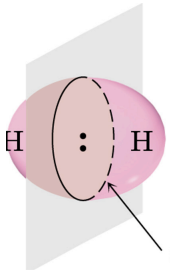
2.3: Bonding in H_2: The Valence Bond Model

electrons in atomic orbitals combine to form electron pairs in molecular orbitals



+ 435 KJ/mol





Sigma (σ) bond - orbital overlap is along internuclear axis

Circular cross-section

(Figure 2.1, p. 60)

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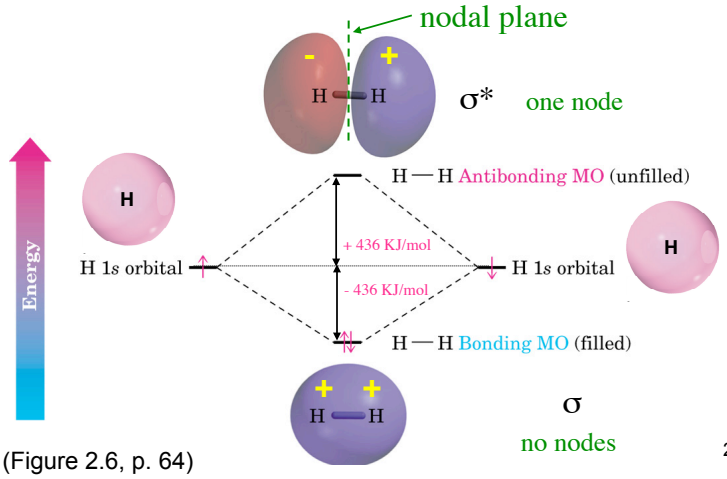
Principle of maximum overlap (L. Pauling) - the strength of a bond is directly proportional to the amount of orbital overlap

2.4: Bonding in H_2: The Molecular Orbital Model - Molecular orbitals (MOs) are linear combinations of atomic orbitals (AOs)

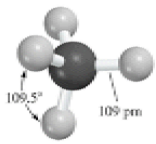
LCAO: # of MOs = # of AOs



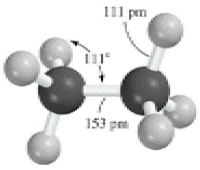
(Figure 2.6, p. 64)

2.5: Introduction to Alkanes: Methane, Ethane, and Propane

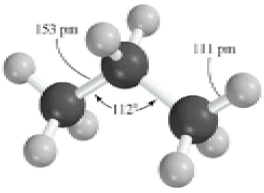
Alkanes have the general formula C_nH_{2n+2}



Methane
(CH_4)
CH_4
bp= -160° C



Ethane
(C_2H_6)
CH_3CH_3
bp= -89° C

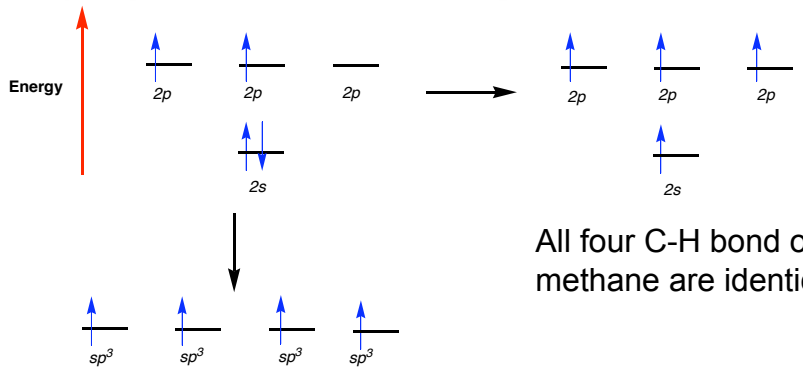


Propane
(C_3H_8)
$CH_3CH_2CH_3$
bp= -42° C

C-C bond length = 153 pm
C-H bond length = 111 pm
Bond angles between 109 - 112 ° (tetrahedral geometry)

(Figure 2.7, p. 64)

2.6: sp^3 Hybridization and Bonding in Methane



All four C-H bond of methane are identical

All four sp^3 hybrid orbital are equivalent

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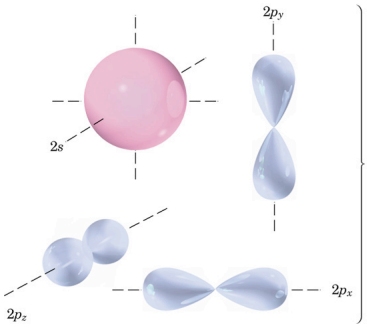
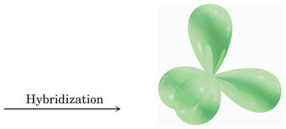
sp^3 Hybridized Orbitals = 1 part s-orbital + 3 parts p-orbitals

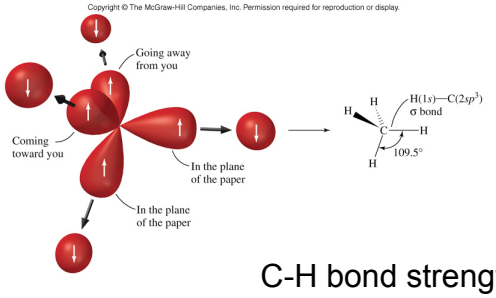
(Figure 2.9, p. 66)

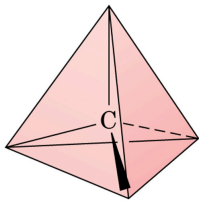




Four tetrahedral sp^3 orbitals

An sp^3 orbital





C-H bond strength = 435 KJ/mol

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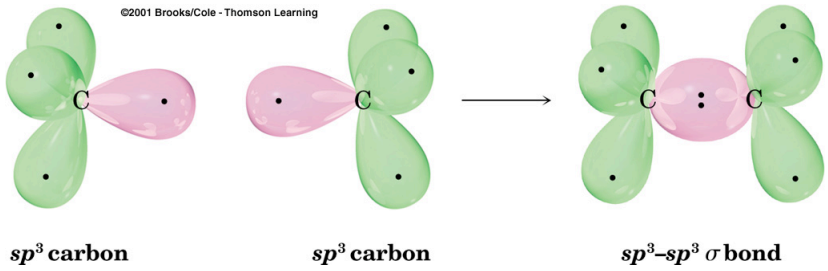
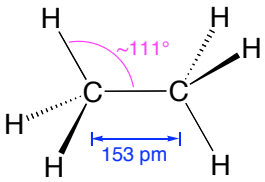
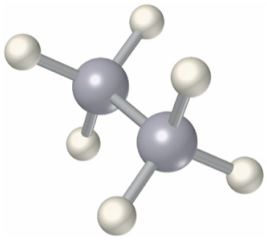
sp^3 hybridized orbital are more directional allowing for greater orbital overlap and strong bonds compared to unhybridized orbitals

2.7: Bonding in Ethane

(Figure 2.11, p. 68)







$\Delta H°_{C\text{-}C}$ = 376 KJ/mol

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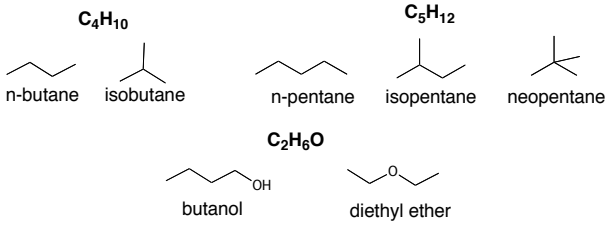
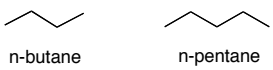
2.8: Isomeric Alkanes: The butanes
2.9: Higher *n*-Alkanes (please read)
2.10: The C_5H_{12} Isomers

Isomers: compounds with the same chemical formula, but different arrangement of atoms

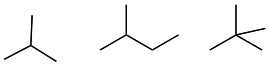
Constitutional isomer: have different connectivities (not limited to alkanes)



straight-chain or normal hydrocarbons



branched hydrocarbons



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2.11 - 2.15: Systematic Nomenclature (IUPAC System)

Prefix-Parent-Suffix

Parent- number of carbons
Prefix- substituents
Suffix- functional groups

Naming Alkanes General Formula: $C_nH_{(2n+2)}$
suffix: -ane

Parent Names: (Table 2.2, p. 71)

1	CH_4	**Meth**ane	CH_4
2	CH_3CH_3	**Eth**ane	C_2H_6
3	$CH_3CH_2CH_3$	**Prop**ane	C_3H_8
4	$CH_3(CH_2)_2CH_3$	**But**ane	C_4H_{10}
5	$CH_3(CH_2)_3CH_3$	**Pent**ane	C_5H_{12}
6	$CH_3(CH_2)_4CH_3$	**Hex**ane	C_6H_{14}
7	$CH_3(CH_2)_5CH_3$	**Hept**ane	C_7H_{16}
8	$CH_3(CH_2)_6CH_3$	**Oct**ane	C_8H_{18}
9	$CH_3(CH_2)_7CH_3$	**Non**ane	C_9H_{20}
10	$CH_3(CH_2)_8CH_3$	**Dec**ane	$C_{10}H_{22}$

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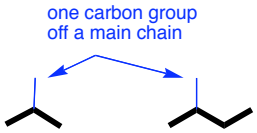
Alkyl substituents (group): carbon chains which are a substructure of a molecule



R= Rest of the molecule (mainchain)

1	CH_3-R	**Meth**yl
2	CH_3CH_2-R	**Eth**yl
3	$CH_3CH_2CH_2$-R	**Prop**yl
4	$CH_3(CH_2)_2CH_2$-R	**But**yl
5	$CH_3(CH_2)_3CH_2$-R	**Pent**yl
6	$CH_3(CH_2)_4CH_2$-R	**Hex**yl
7	$CH_3(CH_2)_5CH_2$-R	**Hept**yl
8	$CH_3(CH_2)_6CH_2$-R	**Oct**yl
9	$CH_3(CH_2)_7CH_2$-R	**Non**yl
10	$CH_3(CH_2)_8CH_2$-R	**Dec**yl

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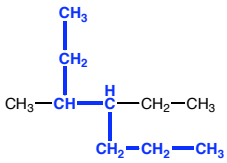
Rules for Systematic Nomenclature of Alkanes

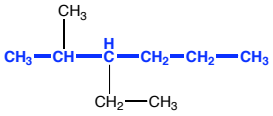
1. Find the parent chain

a. Identify the longest continuous carbon chain as the parent chain.

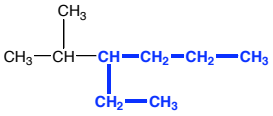


7 carbons = hept-

b. If more than one different chains are of equal length (number of carbons), choose the one with the greater number of branch points (substituents) as the parent.



2 branch pts.



1 branch pt.

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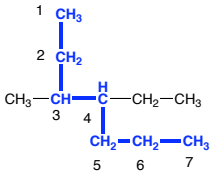
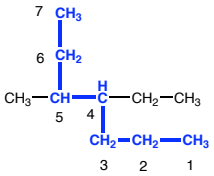
2. Numbering the carbons of the parent chain

a. Number the carbon atoms of the parent chain so that any branch points have the lowest possible number

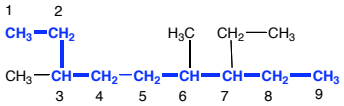


branch pts. at carbons 3 and 4

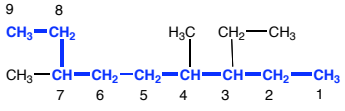


branch pts. at carbons 4 and 5

b. If there is branching equidistant from both ends of the parent chain, number so the second branch point has the lowest number.



branch pts. at carbons 3, 6, 7



branch pts. at carbons 3,4,7

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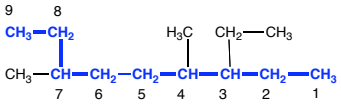
3. *Substituents*
   a. Identify and number the substituents and list them in alphabetical order.



Parent C-9 = nonane
3- ethyl
4-methyl
7-methyl } 4,7-dimethyl

   b. If there are two substituents on the same carbon, assign them the same number.

4. *Write out the name*
   a. Write out the name as a single word:
      hyphens (-) separate prefixes
      commas (,) separate numbers
   b. Substituents are listed in alphabetical order
   c. If two or more identical substituents are present use the prefixes: di- for two
      tri- for three
      tetra- for four

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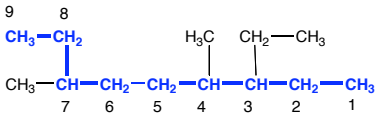
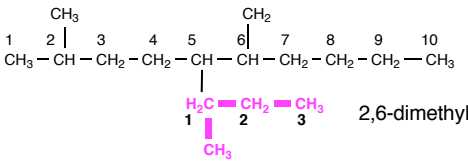
note: these prefixes (di-, tri-, tetra-, etc.) are not used for alphabetizing purposes



3- ethyl-4,7-dimethylnonane

5. *Complex Substituents (substituents with branching)*
   a. Named by applying the four previous rules with some modification
   b. Number the complex substituent separately from the parent. Begin numbering at the point of attachment to the parent chain
   c. Complex substituents are set off by parenthesis.



2,6-dimethyl-5-(1-methylpropyl)decane

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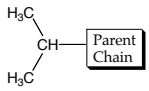
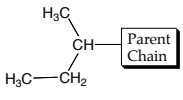
Nonsystematic (trivial) Names:

3-carbons:

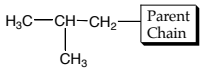


Isopropyl-
(1-methylethyl)

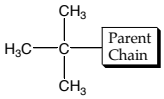
4-Carbons:



sec-butyl-
(1-methylpropyl)

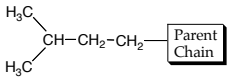


Isobutyl-
(2-methylpropyl)

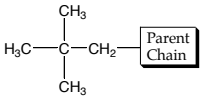


tert-butyl-
(1,1-dimethylethyl)

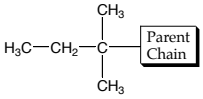
5- Carbons:



Isopentyl-, isoamyl
(3-methylbutyl)



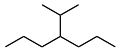
neopentyl-
(2,2-dimethylpropyl)



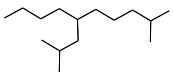
tert-pentyl-, tert-amyl
(1,1-dimethylpropyl)

Alphabetizing trivial names:

Iso- and neo are part of the alkyl group name and are used for alphabetizing.
sec- and tert- are not included in the alphabetical order.



4-(1-methylethyl)heptane
-or-
4-Isopropylheptane



2-methyl-6-(2-methylpropyl)decane
-or-
6-Isobutyl-2-methyldecane

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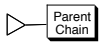
Cycloalkanes

Propane

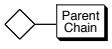
Cyclopropane



cyclopropyl

Butane

Cyclobutane



Cyclobutyl

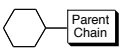
Pentane

Cyclopentane

Cyclopentyl

Hexane

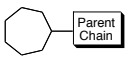
Cyclohexane



Cyclohexyl

Heptane

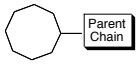
Cycloheptane



Cycloheptyl

Octane

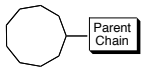
Cyclooctane



Cyclooctyl

Nonane

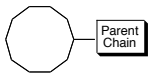
Cyclononane



Cyclononyl

Decane

Cyclodecane



Cyclodecyl

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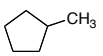
Naming Cycloalkanes General Formula: $C_nH_{(2n)}$

1. Parent Chain

a. Use the cycloalkane as the parent chain if it has a greater number of carbons than any alkyl substituent.

b. If an alkyl chain off the cycloalkane has a greater number of carbons, then use the alkyl chain as the parent and the cycloalkane as a **cycloalkyl-** substituent.

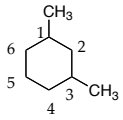


Methylcyclopentane

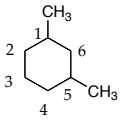
2-Cyclopropylbutane

2. Numbering the Cycloalkane

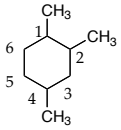
a. When numbering the carbons of a cycloalkane, start with a substituted carbon so that the substituted carbons have the lowest numbers (sum).



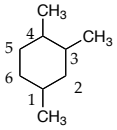
1,3-Dimethylcyclohexane



-not-
1,5-Dimethylcyclohexane



1,2,4-Trimethylcyclohexane
(1 + 2 + 4 = 7)



-not-
1,3,4-Trimethylcyclohexane
(1 +3 + 4 = 8)

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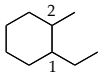
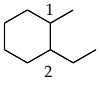
2. b. When two or more different substituents are present, number according to alphabetical order.



1-Ethyl-2-methylcyclohexane



-not-
2-Ethyl-1-methylcyclohexane

3. Halogen Substituents

Halogen substituents are treated exactly like alkyl groups:

-F	fluoro-
-Cl	chloro-
-Br	bromo-
-I	iodo-

1-Chloro-2-methylcyclobutane

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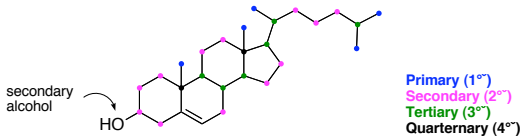
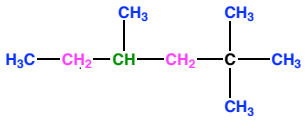
Degrees of Substitution

Primary (1°) Carbon: carbon that is bonded to only one other carbon
Secondary (2°) Carbon: carbon that is bonded to two other carbons
Tertiary (3°) Carbon: carbon that is bonded to three other carbons
Quarternary (4°) Carbon: carbon that is bonded to four other carbons



1° Hydrogens- hydrogens on a primary carbon. $-CH_3$ (methyl group)
2° Hydrogens- hydrogens on a secondary carbon. $-CH_2-$ (methylene group)
3° Hydrogens- hydrogens on a tertiary carbon. CH (methine group)



methyl group: 1° hydrogens
methylene group: 2° hydrogens
methine group: 3° hydrogens

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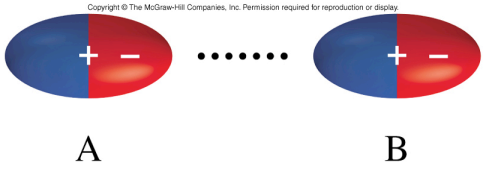
2.16: Sources of Alkanes and Cycloalkanes (please read)

2.17: Physical Properties of Alkanes and Cycloalkanes

Non-nonbonding intermolecular attractive forces
(van der Waals forces)

1. Dipole – Dipole
2. Dipole – Induced-dipole
3. Induced-dipole – Induced-dipole : small instantaneous dipoles that result from a distortion of the electron clouds. There is an attraction between molecules as result of these temporary dipoles



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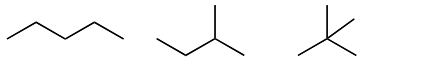
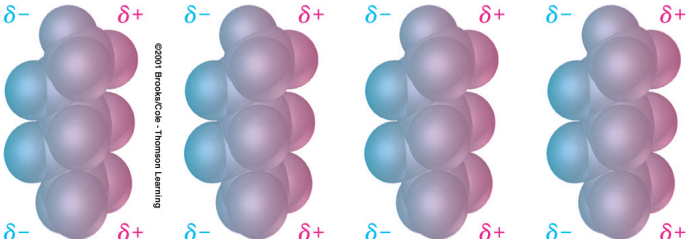
Alkanes show: regular increase in bp and mp as the molecular weight increase. Branching lowers the bp or alkanes

n-pentane bp= 36.1 °C
iso-pentane bp= 27.9 °C
neo-pentane bp= 9.5°C





Alkanes have low polarity and are hydrophobic (low water solubility). Solubility deceases are the number of carbons increase

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2.18: Chemical Properties: Combustion of Alkanes

Hydrocarbons (C-H bonds) are weak to extremely weak acids

Combustion of hydrocarbons (Oxidation)

$$C_nH_{2n+2} + O_2 \longrightarrow n\ CO_2 + (n+1)\ H_2O + \text{heat}$$

Heat ($\Delta H°$) of combustion = $H°_{(products)} - H°_{(reactants)}$

Measure of relative stability

2.19: Oxidation-Reduction in Organic Chemistry

Oxidation [O]: the loss of electrons.

Increase in the number of C-X bonds, where X is an atom more electronegative than carbon. Decrease in H content.

Reduction [H]: the gain of electrons.

Increase in number of C-Y bonds, where Y is an atom less electronegative than carbon. Increase on H content.

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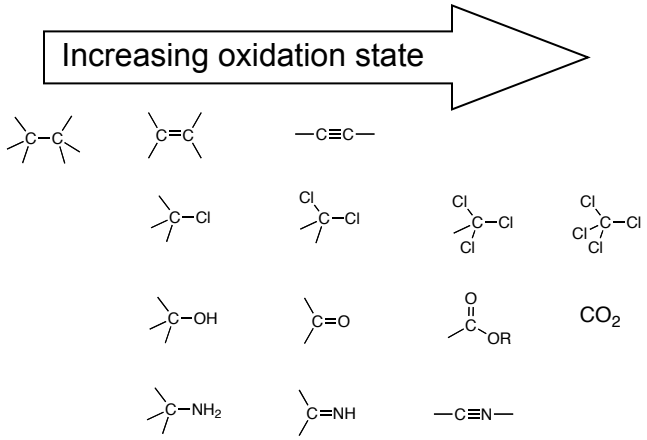

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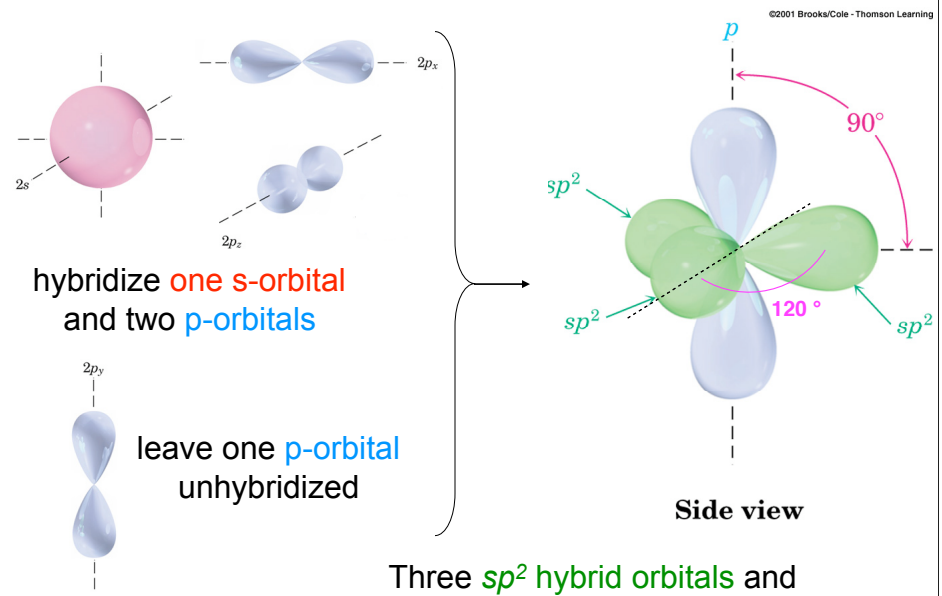
2.20: sp^2 Hybridization and Bonding in Ethylene



hybridize one s-orbital and two p-orbitals

leave one p-orbital unhybridized

Three sp^2 hybrid orbitals and one unhybridized p-orbital

(Figure 2.19, p. 89)

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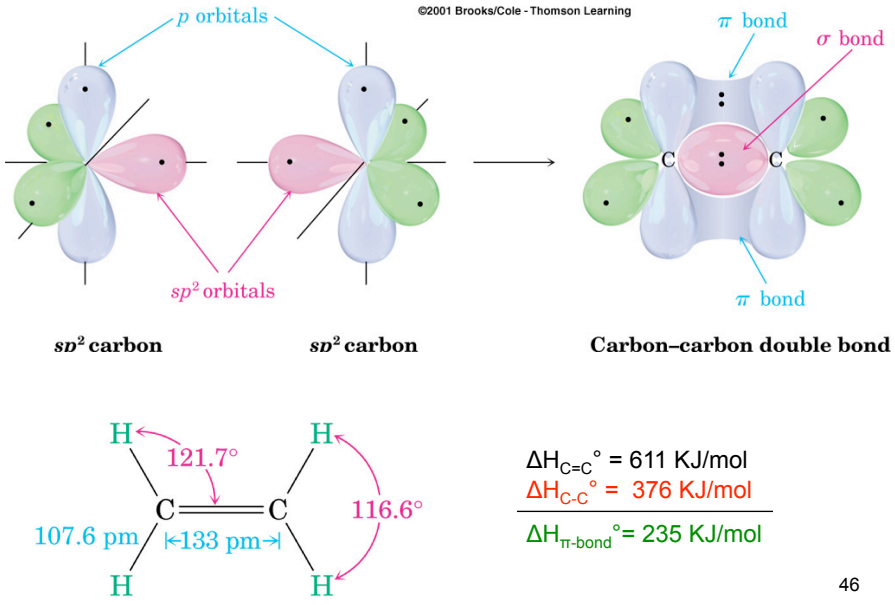
C=C double bonds- ethylene (C_2H_4)

(Figure 2.20, p. 90)



$\Delta H_{C=C}^{\circ}$ = 611 KJ/mol

ΔH_{C-C}° = 376 KJ/mol

$\Delta H_{\pi\text{-bond}}^{\circ}$ = 235 KJ/mol

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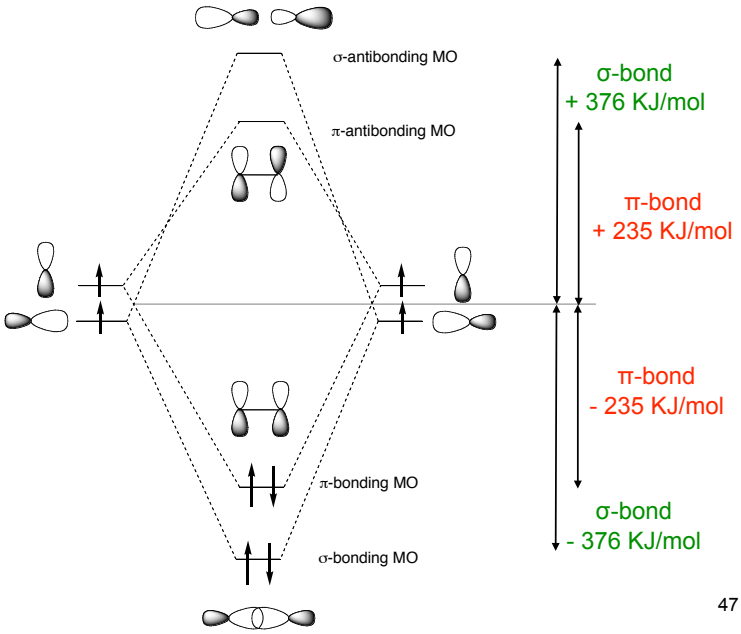
Molecular Orbitals of C=C



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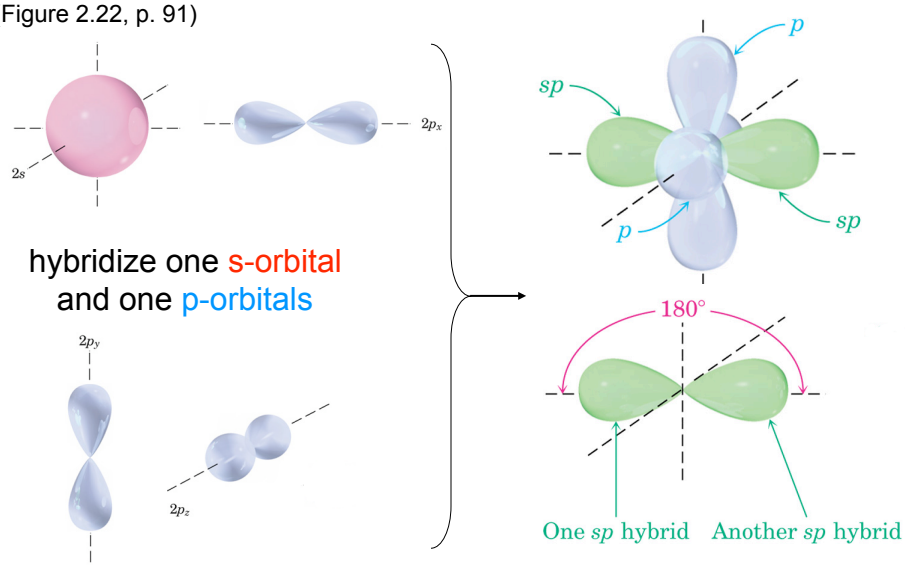
2.21: *sp* Hybridization and Bonding in Acetylene

(Figure 2.22, p. 91)



hybridize one s-orbital and one p-orbitals

leave two p-orbital unhybridized

two sp hybrid orbitals and two unhybridized p-orbital

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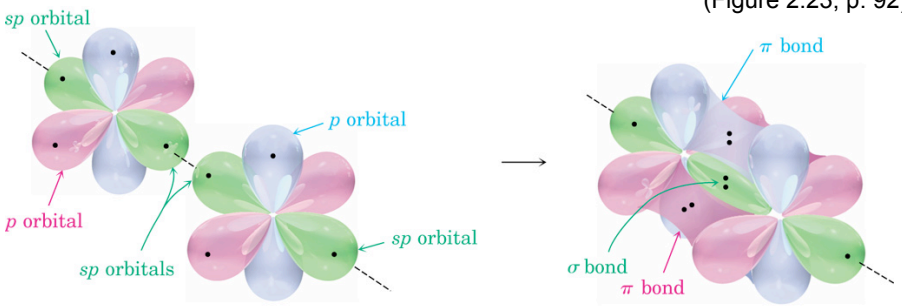
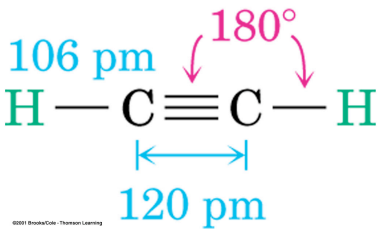
CΞC triple bonds- acetylene (C_2H_2)

one C-C σ-bond and two C-C π-bonds

(Figure 2.23, p. 92)



Carbon–carbon triple bond



$\Delta H_{C\equiv C}^{\circ}$ = 835 KJ/mol

ΔH_{C-C}° = 376 KJ/mol

$\Delta H_{1st\ \pi\text{-bond}}^{\circ}$ = 235 KJ/mol

$\Delta H_{2nd\ \pi\text{-bond}}^{\circ}$ = 224 KJ/mol

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