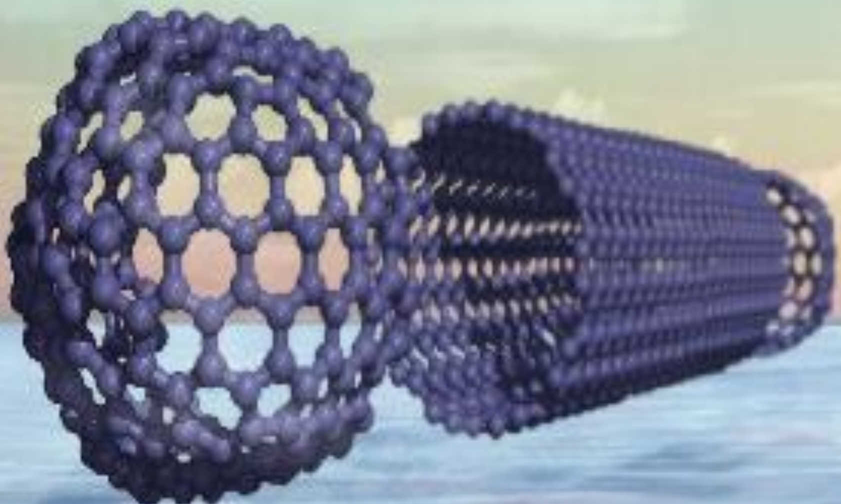
Organic Chemistry



By

Dr. Assem Barakat

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Syllabus: (CHEM 145 Health Science, 2 credits hour)

- **Hydrocarbon compounds** (chemical bonds, (Ionic, Covalent), atomic and molecular orbital, hybridization, polarity and inductive effect. (**2 Lectures**)
- **Alkanes, Cycloalkanes** (Alkyl group, IUPAC nomenclature, physical properties, sources, synthesis, reactions {Combustion, Halogenations, and Ring Opening}) (**3 Lectures**).
- **Reaction of Alkenes and Alkynes** (acidity of terminal alkynes, addition reactions (dehydrohalogenation from vicinal dihalides, dehydration). Isomerism (geometrical isomerism of alkenes and cycloalkanes). (**2 Lectures**)
- **Aromatic Compound** (aromatic character, Hϋkel rule, nomenclature, electrophilic aromatic substitution reactions (Alkylation, Acylation, Halogenation Sulphonation, Nitration) side chain halogenations and oxidation. Reactivity and orientation in monosubstituted benzene derivatives (**3 Lectures**).
- **1st Midterm Exam**

➧**Alkyl halides:** IUPAC nomenclature, classification, physical properties, synthesis (Alcohols with PX_3, PX_5, $SOCl_2$). Grignard reagents, nucleophilic substitution (CN, OH, NH_3, ……………………..)(**2 Lectures**)

➧**Alcohols:** IUPAC nomenclature, classification, physical properties, hydorgen bonding. Synthesis (from aldehyde and ketones, reaction of Grignard reagent with aldehyde and ketones). Reactions: acidity, formation of esters, ethers water elimination.

➧**Ethers and Epoxides:** Nomenclature, physical properties, Williamson Synthesis, epoxides from alkenes and halohydrins). Reactions: of ether with HI, reaction of epoxides with acids, bases and Grignard reagent (**4 Lectures**).

➧**Phenols:** Hydrogen bonding, acidity, synthesis (from sulphone salt and diazonium salts). Formation of esters (**1 Lecture**).

➧**Aldehydes and Ketones:** Nomenclature, physical properties, synthesis: Reactions: Nucleophilic addition reaction (Addition of Grignard reagent, HCN, H_2O), Acetals and Ketals, Hydrazones and oximes. (**2 Lecture**).

➧**2nd midterm exam**

- **Carboxylic acid:** Nomenclature, physical properties, Synthesis: (Alkyl and aryl nitrile hydrolysis, reaction with CO_2). Reactions (acidity, formation of salts, acid halides and esters, reduction) (**2 Lecture**).
- **Carboxylic acid derivatives:** Nomenclature, synthesis and hydrolysis, final revision.
- **Amines:** Nomenclature, physical properties, synthesis: (Reduction of amide and nitro compounds). Reactions: Basicity formation of diazonium salt (**1 Lecture**).
- **Final Exam.**

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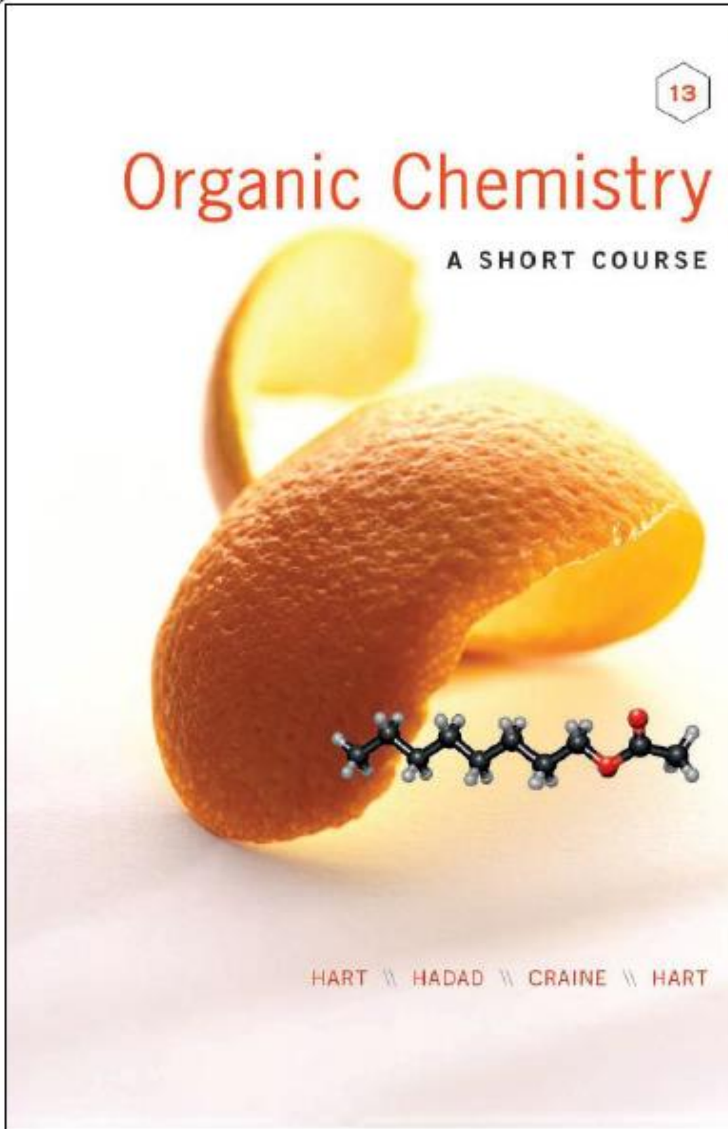

13th EDITION

Organic Chemistry

A SHORT COURSE

David J. Hart
The Ohio State University

Christopher M. Hadad
The Ohio State University

Leslie E. Craine
Central Connecticut State University

Harold Hart
Michigan State University

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Chapter 1
Carbon Compounds and Chemical Bonds

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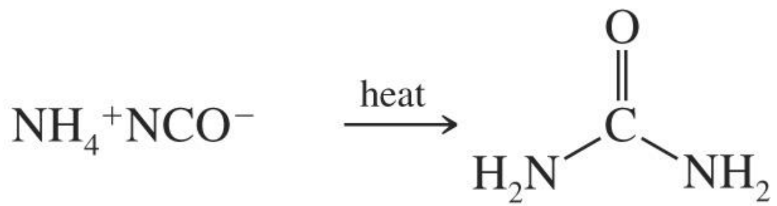
♦ Introduction

- **Organic Chemistry**
  - ➡ The chemistry of the compounds of carbon
  - ➡ The human body is largely composed of organic compounds
  - ➡ Organic chemistry plays a central role in medicine, Pharmacy, bioengineering etc.
- **Vitalism**
  - ➡ It was originally thought organic compounds could be made only by living things by intervention of a “vital force”
  - ➡ Fredrich Wöhler disproved vitalism in 1828 by making the organic compound urea from the inorganic salt ammonium cyanate by evaporation:

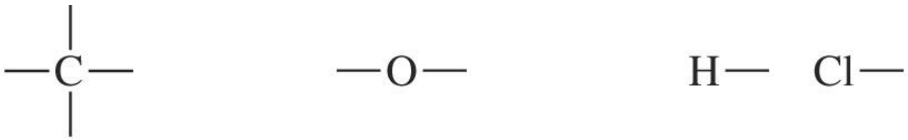


Ammonium cyanate **Urea**

♦ Structural Theory

● Central Premises

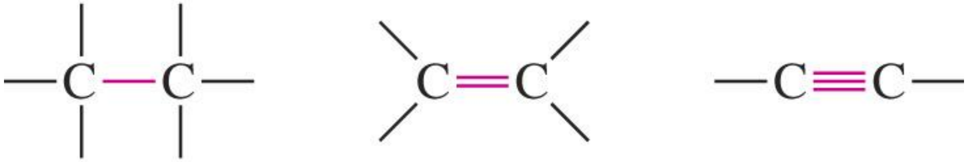
➡ **Valency: atoms in organic compounds form a fixed number of bonds**



Carbon atoms are tetravalent | **Oxygen atoms are divalent** | **Hydrogen and halogen atoms are monovalent**

➡ **Carbon can form one or more bonds to other carbons**

Carbon–carbon bonds



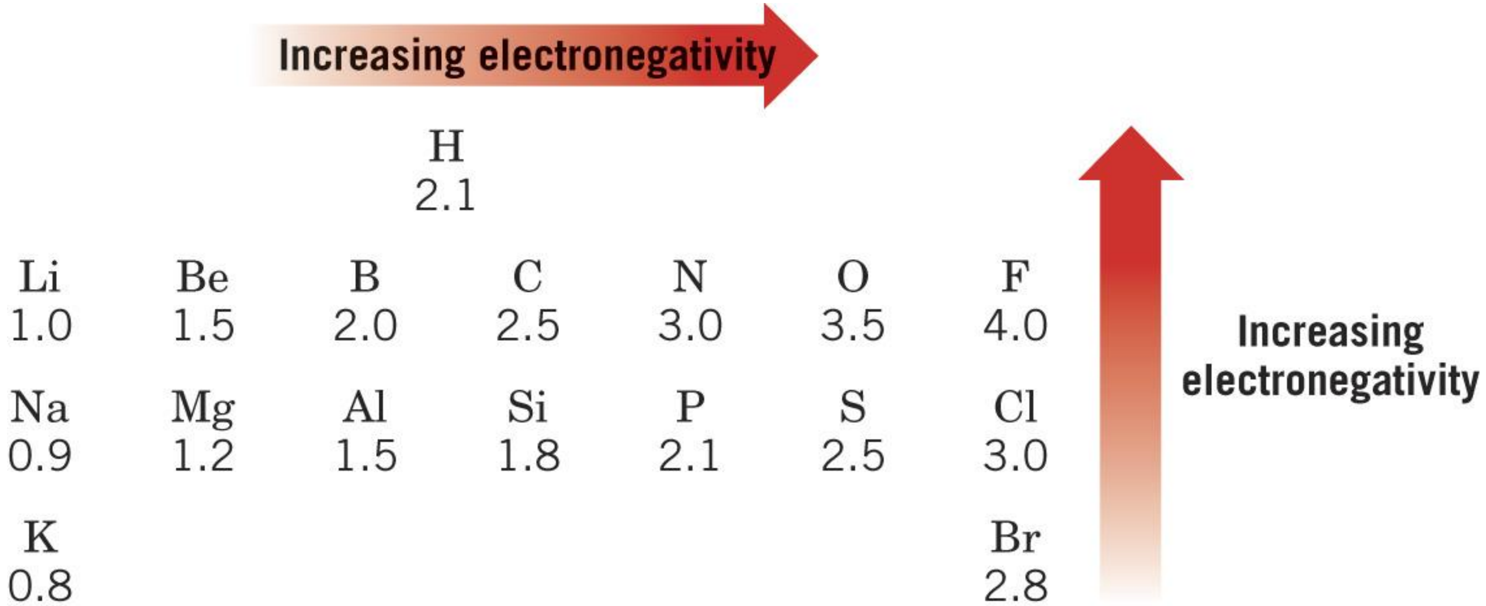
Single bond | **Double bond** | **Triple bond**

♦ Chemical Bonds: The Octet Rule

- **Octet Rule**
  - ➡ Atoms form bonds to produce the electron configuration of a noble gas (because the electronic configuration of noble gases is particularly stable)
  - ➡ For most atoms of interest this means achieving a valence shell configuration of 8 electrons corresponding to that of the nearest noble gas
  - ➡ Atoms close to helium achieve a valence shell configuration of 2 electrons
  - ➡ Atoms can form either ionic or covalent bonds to satisfy the octet rule

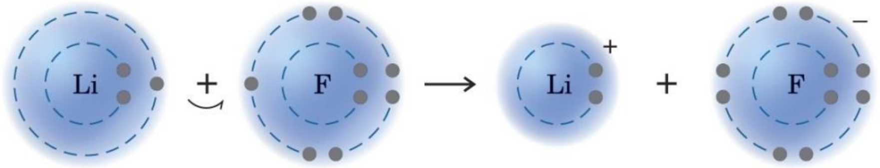
● Electronegativity

- ➡ **Electronegativity is the ability of an atom to attract electrons**
- ➡ **It increases from left to right and from bottom to top in the periodic table (noble gases excluded)**
  - ★ **Fluorine is the most electronegative atom and can stabilize excess electron density the best**

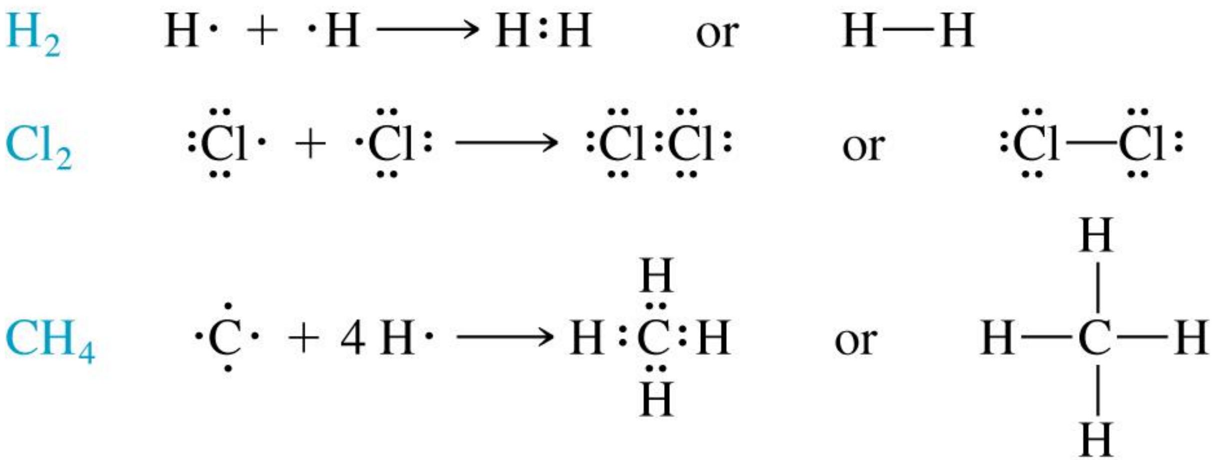


Ionic Bonds

- When ionic bonds are formed atoms gain or lose electrons to achieve the electronic configuration of the nearest noble gas
  - In the process the atoms become ionic
- The resulting oppositely charged ions attract and form ionic bonds
- This generally happens between atoms of widely different electronegativities
- Example
  - Lithium loses an electron (to have the configuration of helium) and becomes positively charged
  - Fluoride gains an electron (to have the configuration of neon) and becomes negatively charged
  - The positively charged lithium and the negatively charged fluoride form a strong ionic bond (actually in a crystalline lattice)



- **Covalent Bonds**
  - **Covalent bonds occur between atoms of similar electronegativity (close to each other in the periodic table)**
  - **Atoms achieve octets by *sharing* of valence electrons**
  - **Molecules result from this covalent bonding**
  - **Valence electrons can be indicated by dots (electron-dot formula or Lewis structures) but this is time-consuming**
  - **The usual way to indicate the two electrons in a bond is to use a line (one line = two electrons)**



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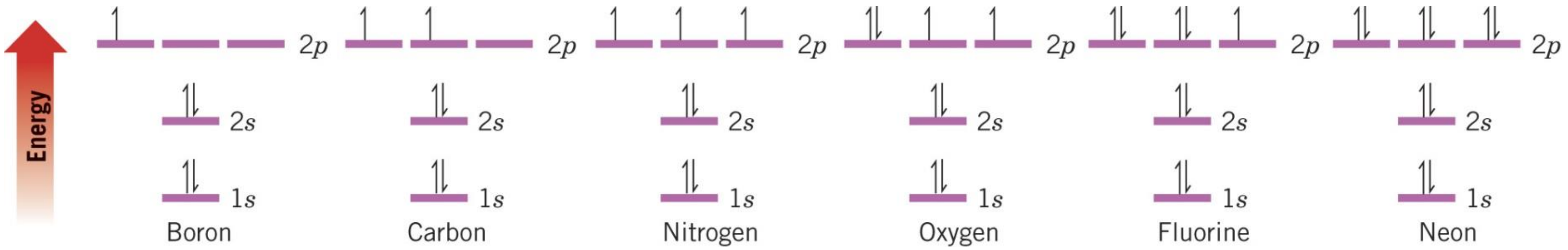
♦ Atomic Orbitals (AOs)

- The physical reality of Ψ is that when squared (Ψ^2) it gives the probability of finding an electron in a particular location in space
- Plots of Ψ^2 in three dimensions generate the shape of *s*, *p*, *d* and *f* orbitals
- Only *s* and *p* orbitals are very important in organic chemistry
- Orbital: a region in space where the probability of finding an electron is large
  - ★ The typical representation of orbitals are those volumes which contain the electron 90-95% of the time

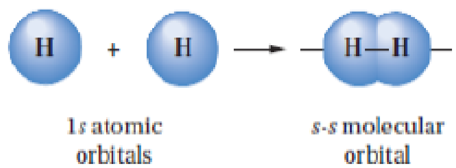
- **Atoms can be assigned electronic configuration using the following rules:**
  - ➡ **Aufbau Principle: The lowest energy orbitals are filled first**
  - ➡ **Pauli Exclusion Principle: A maximum of two spin paired electrons may be placed in each orbital**
  - ➡ **Hund's Rule: One electron is added to each degenerate (equal energy orbital) before a second electron is added**
- **Electronic Configurations of Some Second Row Elements**



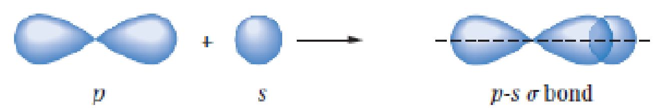
Sigma and pi Bonds

- **Sigma bonds (σ bonds)** can be formed from

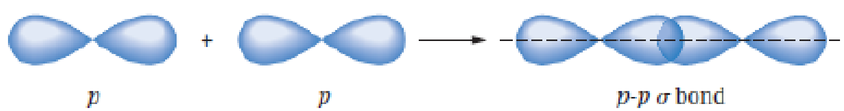
❖ The overlap of two *s* atomic orbitals.



❖ The overlap of two an *s* atomic orbital with a *p* atomic orbital.

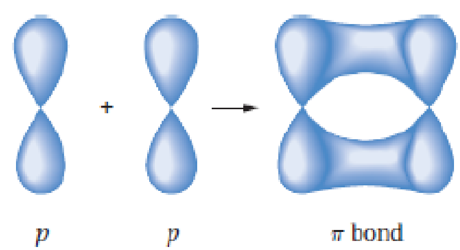


❖ The end-on overlap of two *p* atomic orbitals.



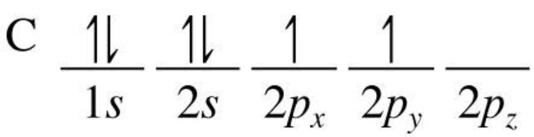
- **pi bonds (π bonds)** can be formed from

❖ The side-side overlap between two *p* atomic orbitals.



Hybridization

- **The Structure of Methane and Ethane: *sp*^{3} Hybridization**
  - **The structure of methane with its four identical tetrahedral bonds cannot be adequately explained using the electronic configuration of carbon**



Ground state of a carbon atom

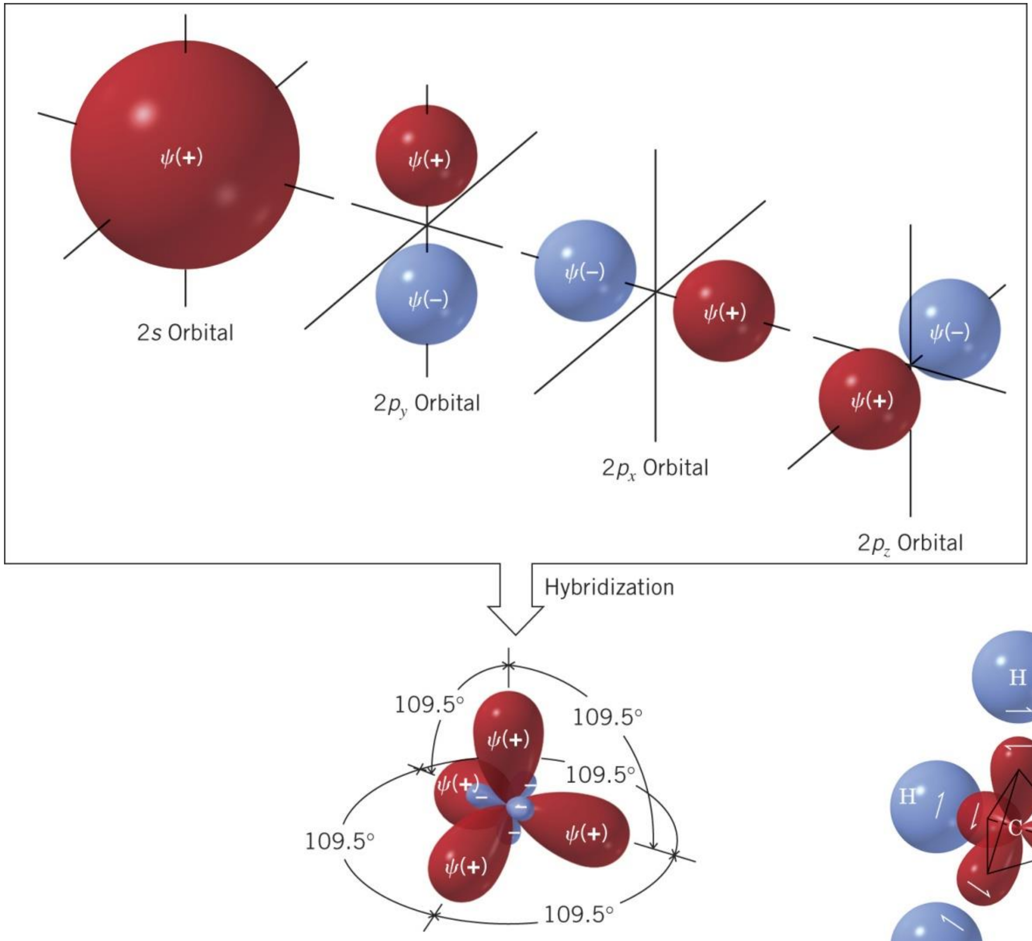
  - **Hybridization of the valence orbitals (2*s* and 2*p*) provides four new identical orbitals which can be used for the bonding in methane**
  - ***Orbital hybridization* is a mathematical combination of the 2*s* and 2*p* wave functions to obtain wave functions for the new orbitals**

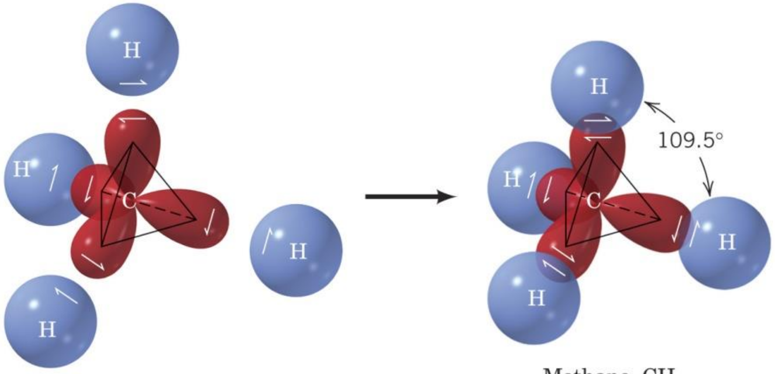
➡ **When one 2*s* orbital and three 2*p* orbitals are hybridized four new and identical sp^3 orbitals are obtained**

- ★ **When four orbitals are hybridized, four orbitals must result**
- ★ **Each new orbital has one part *s* character and 3 parts *p* character**
- ★ **The four identical orbitals are oriented in a tetrahedral arrangements**
- ★ **The antibonding orbitals are not derived in the following diagram**

➡ **The four sp^3 orbitals are then combined with the 1*s* orbitals of four hydrogens to give the molecular orbitals of methane**

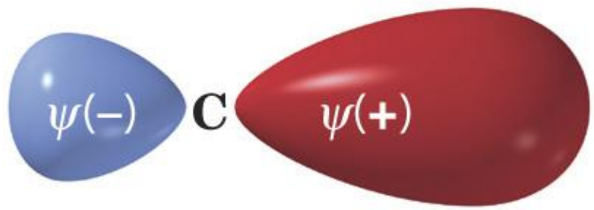
➡ **Each new molecular orbital can accommodate 2 electrons**


ψ(+)
2s Orbital
ψ(+)
ψ(−)
2p_y Orbital
ψ(−)
ψ(+)
2p_x Orbital
ψ(−)
ψ(+)
2p_z Orbital
Hybridization
109.5°
109.5°
109.5°
109.5°
109.5°
ψ(+)
ψ(+)
ψ(+)
ψ(+)

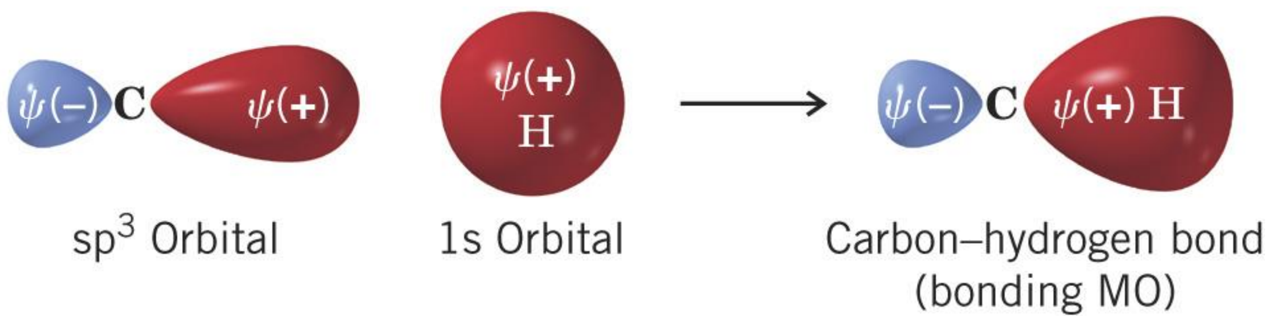

H
H
C
H
H
H
H
C
H
H
109.5°

Methane, CH_4

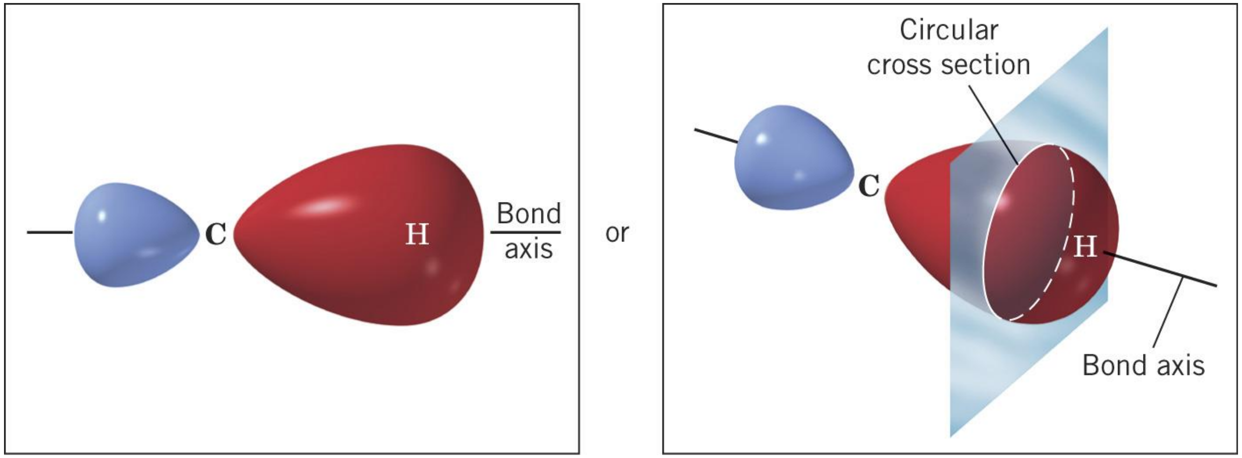
- An *sp*^{3} orbital looks like a *p* orbital with one lobe greatly extended
  - ★ Often the small lobe is not drawn



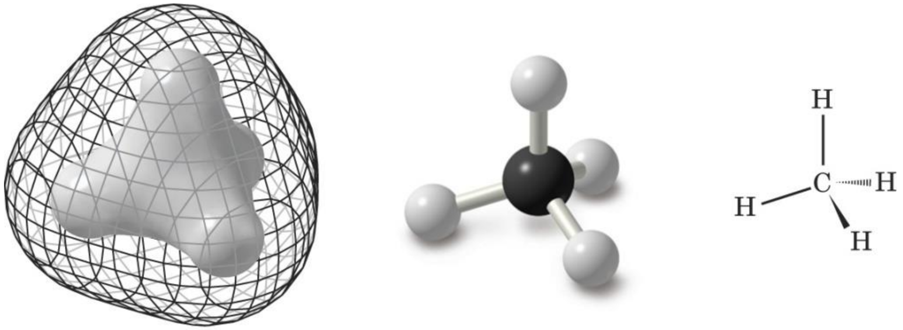
- The extended *sp*^{3} lobe can then overlap well with the hydrogen 1*s* to form a strong bond



- The bond formed is called a sigma (σ) bond because it is circularly symmetrical in cross section when view along the bond axis



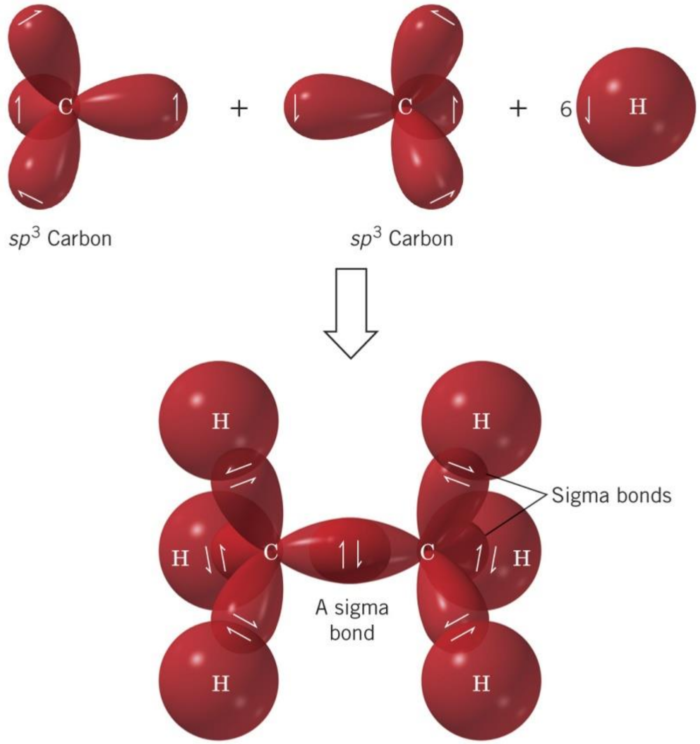
- **A variety of representations of methane show its tetrahedral nature and electron distribution**
  - ★ **a. calculated electron density surface b. ball-and-stick model c. a typical 3-dimensional drawing**



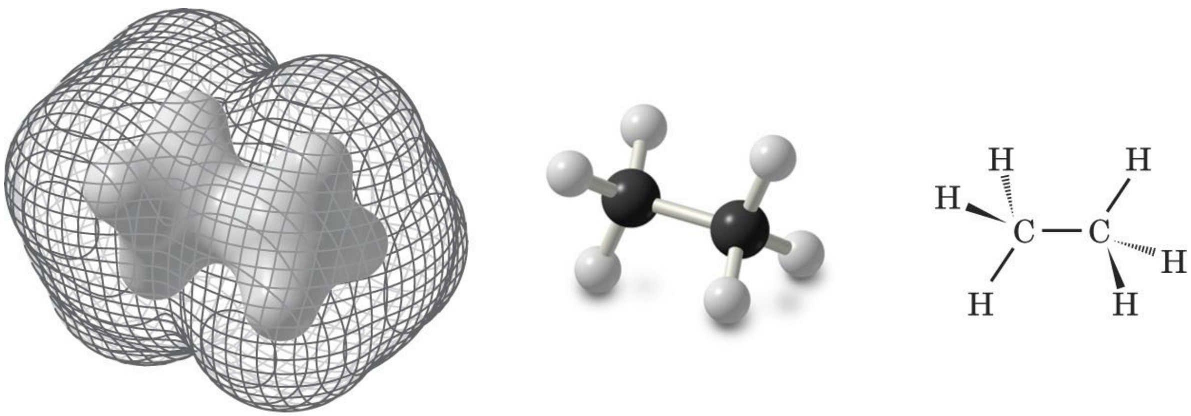
(a) (b) (c)

Ethane (C_2H_6)

- The carbon-carbon bond is made from overlap of two *sp*^{3} orbitals to form a σ bond
- The molecule is approximately tetrahedral around each carbon



- The representations of ethane show the tetrahedral arrangement around each carbon
  - a. calculated electron density surface b. ball-and-stick model c. typical 3-dimensional drawing

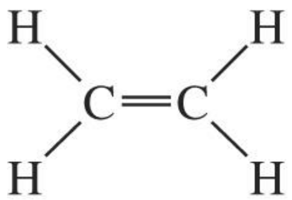


(a) (b) (c)

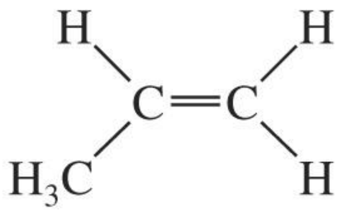
- Generally there is relatively free rotation about σ bonds
  - Very little energy (13-26 kcal/mol) is required to rotate around the carbon-carbon bond of ethane

♦ The Structure of Ethene (Ethylene) : *sp*^{2} Hybridization

- ➡ **Ethene (C_2H_2) contains a carbon-carbon double bond and is in the class of organic compounds called *alkenes***
  - ★ **Another example of the alkenes is propene**

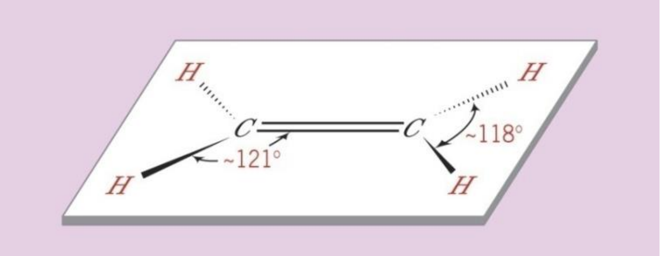


Ethene

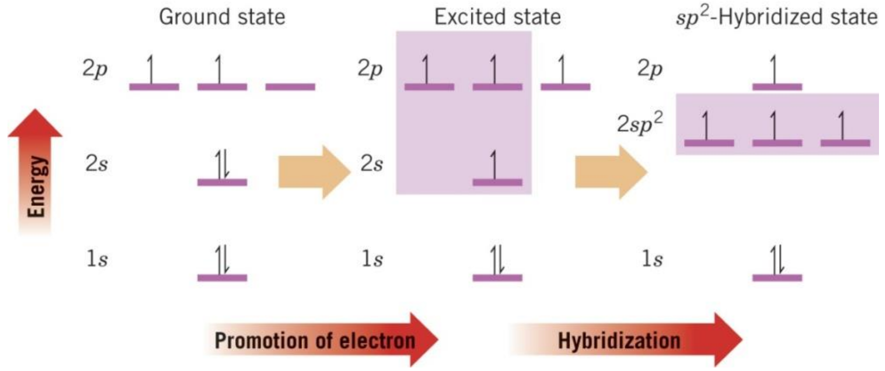


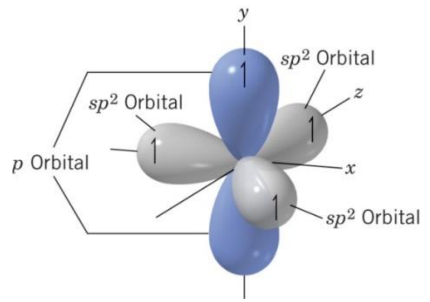
Propene

- ➡ **The geometry around each carbon is called *trigonal planar***
  - ★ **All atoms directly connected to each carbon are in a plane**
  - ★ **The bonds point towards the corners of a regular triangle**
  - ★ **The bond angle are approximately 120º**

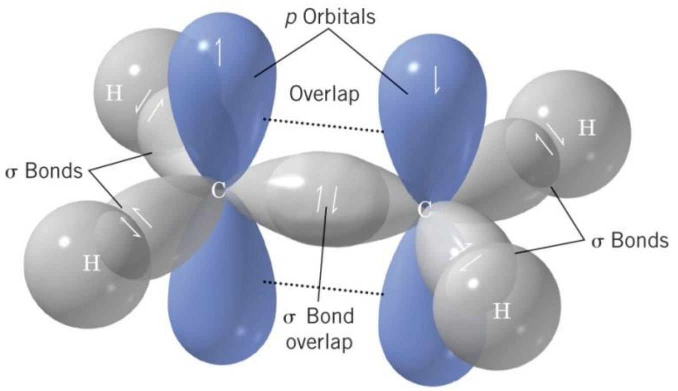


- There are three σ bonds around each carbon of ethene and these are formed by using *sp*^{2} hybridized orbitals
- The three *sp*^{2} hybridized orbitals come from mixing one *s* and two *p* orbitals
  - ★ One *p* orbital is left unhybridized
- The *sp*^{2} orbitals are arranged in a trigonal planar arrangement
  - ★ The *p* orbital is perpendicular (orthoganol) to the plane

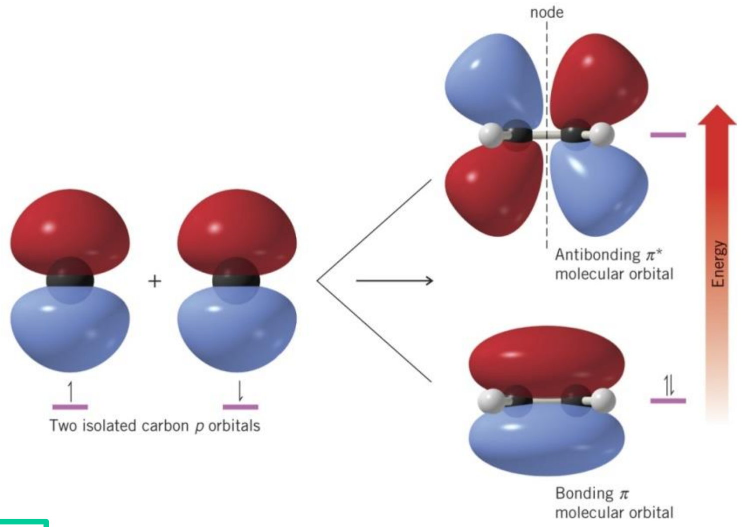




- Overlap of *sp*^{2} orbitals in ethylene results in formation of a σ framework
  - One *sp*^{2} orbital on each carbon overlaps to form a carbon-carbon σ bond; the remaining sp^2 orbitals form bonds to hydrogen
- The leftover *p* orbitals on each carbon overlap to form a bonding π bond between the two carbons
- A π bond results from overlap of *p* orbitals above and below the plane of the σ bond
  - It has a nodal plane passing through the two bonded nuclei and between the two lobes of the π molecular orbital

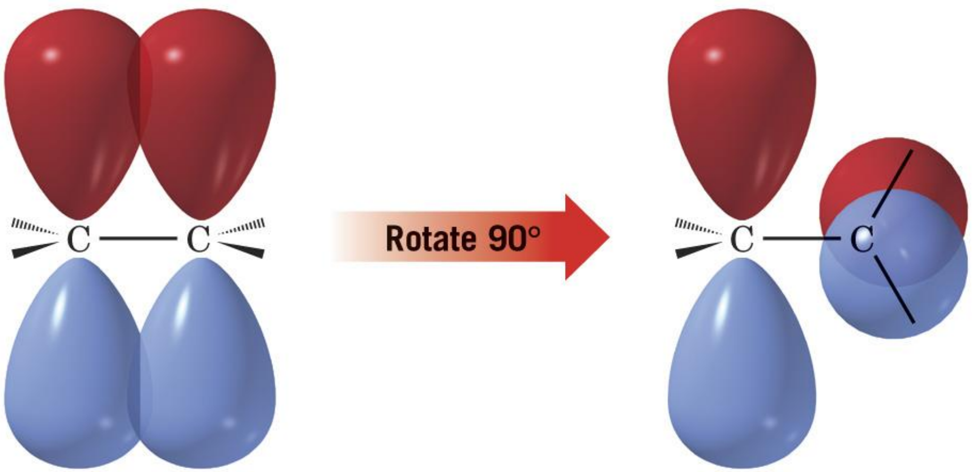


- The bonding π orbital results from overlap of *p* orbital lobes of the same sign
- The antibonding π* orbital results from overlap of *p* orbital lobes of opposite sign
  - The antibonding orbital has one node connecting the two nuclei and another node between the two carbons
- The bonding π orbital is lower in energy than the antibonding orbital
  - In the ground state two spin paired electrons are in the bonding orbital
  - The antibonding π*orbital can be occupied if an electron becomes promoted from a lower level (e.g. by absorption of light)



♦ Restricted Rotation and the Double Bond

- ➡ **There is a large energy barrier to rotation (about 264 kJ/mol) around the double bond**
  - ★ **This corresponds to the strength of a π bond**
  - ★ **The rotational barrier of a carbon-carbon single bond is 13-26 kJ/mol**
- ➡ **This rotational barrier results because the *p* orbitals must be well aligned for maximum overlap and formation of the π bond**
- ➡ **Rotation of the *p* orbitals 90º totally breaks the π bond**



♦ The Structure of Ethyne (Acetylene): *sp* Hybridization

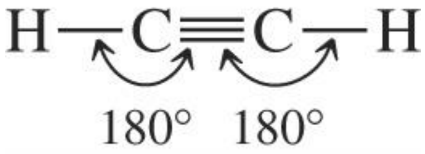
- ➡ **Ethyne (acetylene) is a member of a group of compounds called alkynes which all have carbon-carbon triple bonds**
  - ★ **Propyne is another typical alkyne**

$$H{-}C{\equiv}C{-}H \qquad\qquad CH_3{-}C{\equiv}C{-}H$$

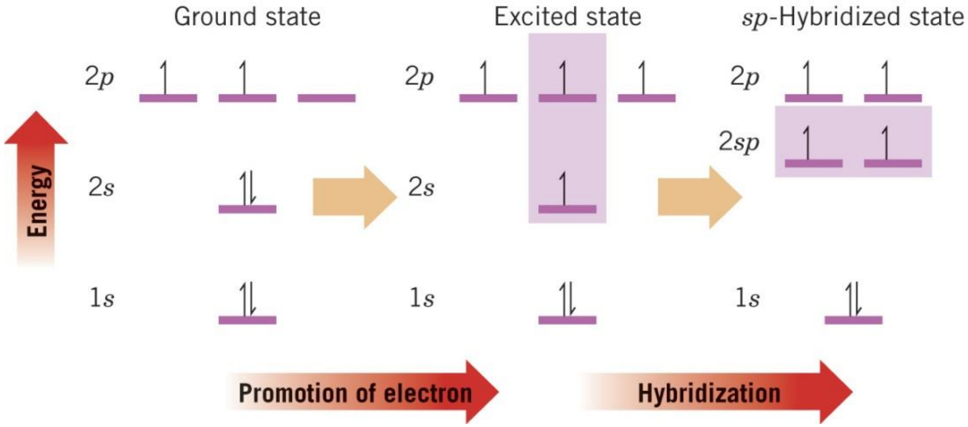
Ethyne (acetylene) (C_2H_2)

Propyne (C_3H_4)

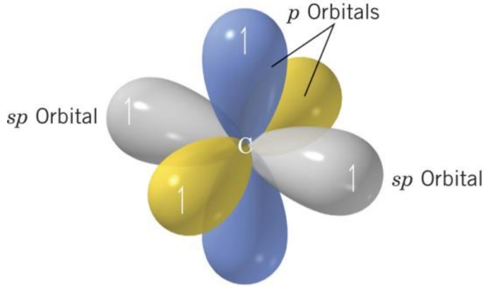
- ➡ **The arrangement of atoms around each carbon is linear with bond angles 180º**



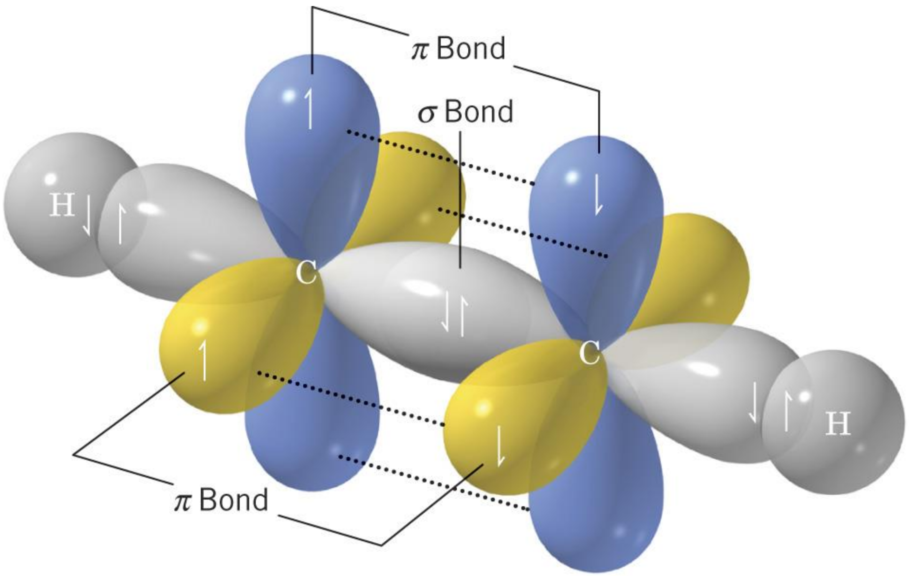
- **The carbon in ethyne is *sp* hybridized**
  - ★ **One *s* and one *p* orbital are mixed to form two *sp* orbitals**
  - ★ **Two *p* orbitals are left unhybridized**



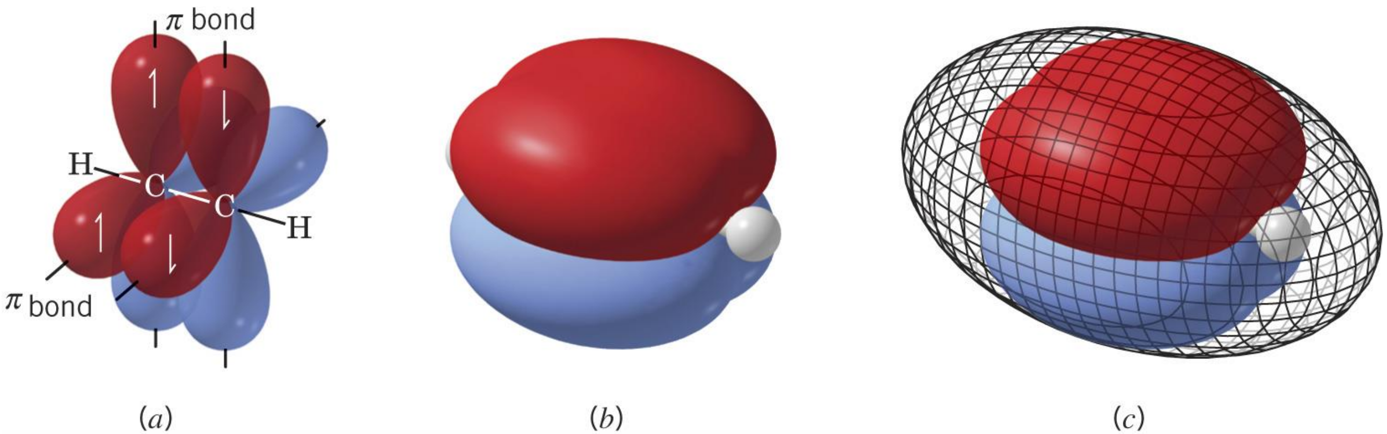
- **The two *sp* orbitals are oriented 180º relative to each other around the carbon nucleus**
  - ★ **The two *p* orbitals are perpendicular to the axis that passes through the center of the *sp* orbitals**



- In ethyne the *sp* orbitals on the two carbons overlap to form a σ bond
  - The remaining *sp* orbitals overlap with hydrogen 1s orbitals
- The *p* orbitals on each carbon overlap to form two π bonds
- The triple bond consists of one σ and two π bonds

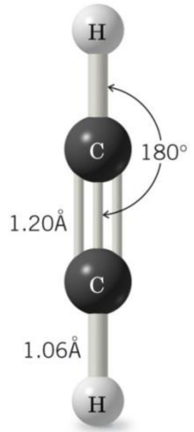


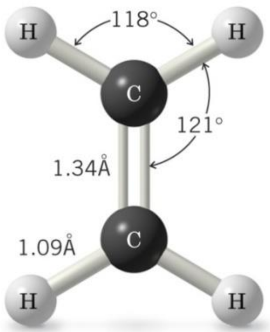
- **Depictions of ethyne show that the electron density around the carbon-carbon bond has circular symmetry**
  - **Even if rotation around the carbon-carbon bond occurred, a different compound would not result**

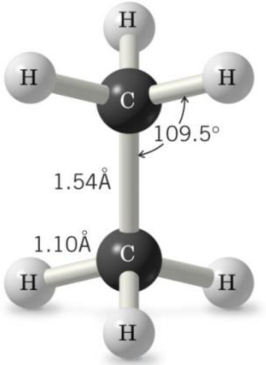


Bond Lengths of Ethyne, Ethene and Ethane

- **The carbon-carbon bond length is shorter as more bonds hold the carbons together**
  - **With more electron density between the carbons, there is more "glue" to hold the nuclei of the carbons together**
- **The carbon-hydrogen bond lengths also get shorter with more *s* character of the bond**
  - **2*s* orbitals are held more closely to the nucleus than 2*p* orbitals**
  - **A hybridized orbital with more percent *s* character is held more closely to the nucleus than an orbital with less *s* character**
  - **The *sp* orbital of ethyne has 50% *s* character and its C-H bond is shorter**
  - **The sp^3 orbital of ethane has only 25% s character and its C-H bond is longer**

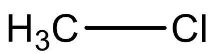


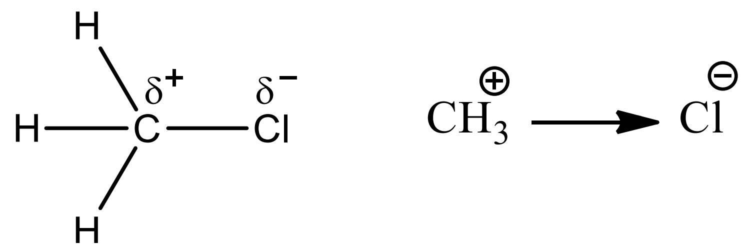




Inductive effect

Polarization of electron through **single bond**, and it depends on the difference in **electronegativity**

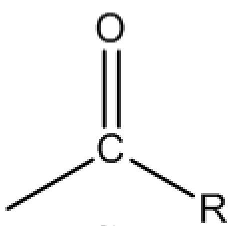




$-CH_3$, $-C_2H_5$
$-NH_2$, $-OH$
$-CH_3O$

Electron donating groups

$-NO_2$

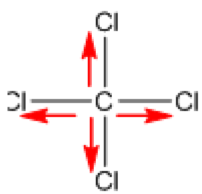


$-CN$

Electron withdrawing groups

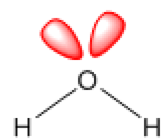
Dipole moment (depends on the inductive effect)

CCl_4



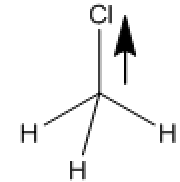
μ = zero

H_2O



$\mu \neq$ zero

CH_3Cl



$\mu \neq$ zero