Organic Chemistry, *Fourth Edition*

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Chapter 1

Structure and Bonding

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Chapter 1 Structure and Bonding

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1.1 The Periodic Table: Atomic Structure

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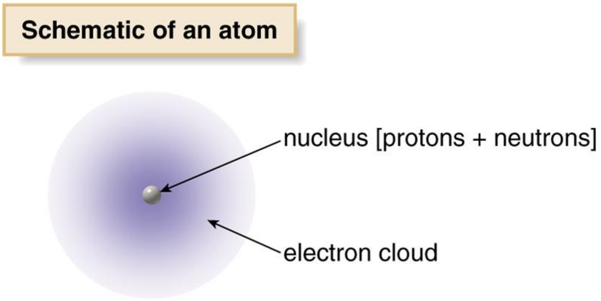

- The **nucleus** contains positively charged protons and uncharged neutrons.
- The **electron cloud** is composed of negatively charged electrons.

Atomic Structure

- The **atomic number** is the number of protons in the nucleus and also the number of electrons surrounding (i.e., protons = electrons).
- The **atomic mass** is the number of protons plus neutrons in the nucleus (e.g., ${}^{12}_{6}C$ has six protons and six neutrons).
- Carbon’s atomic number is 6; its atomic mass is 12.
- In a **neutral atom**, the number of protons equals the number of electrons.

Ions

Charged ions:

- **A cation is positively charged and has fewer electrons than its neutral form.**
- **An anion is negatively charged and has more electrons than its neutral form.**

Isotopes

Figure 1.1

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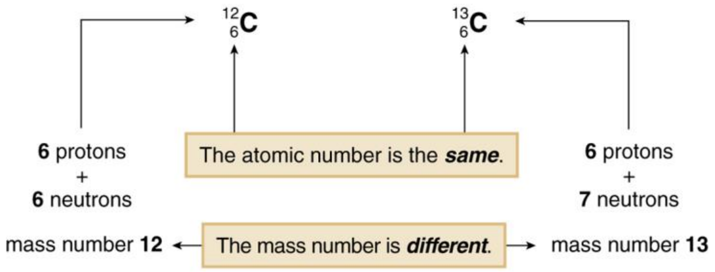

- **Isotopes are two atoms of the same element having a different number of neutrons.**
- **Most carbon atoms have 6 neutrons, but 1.1% have 7 neutrons**

The Periodic Table

- Elements in the same row are similar in size.
- Elements in the same column have similar electronic and chemical properties.

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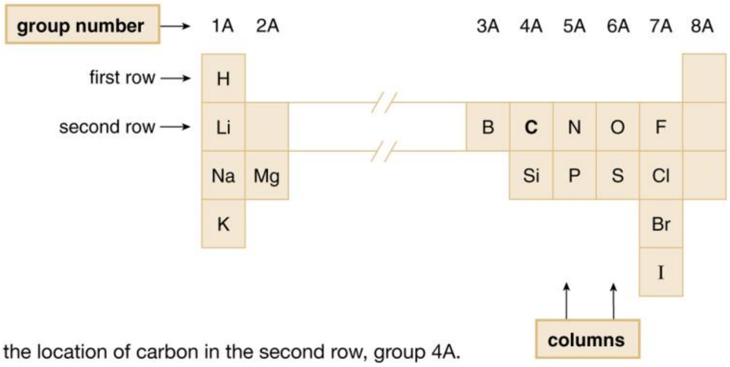

Figure 1.2

- Note the location of carbon in the second row, group 4A.

Atomic Orbitals

- An *s* orbital has a sphere of electron density and is lower in energy than the other orbitals of the same shell.
- A *p* orbital has a dumbbell shape and contains a node (no electron density) at the nucleus. It is higher in energy than an *s* orbital.

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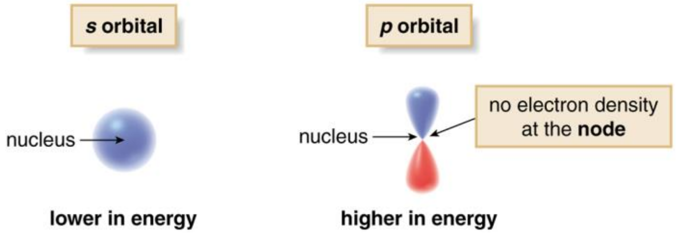

Periodic Table

The First Row

- **There is only one orbital in the first shell.**
- **Each shell can hold a maximum of two electrons.**
- **Therefore, there are two elements in the first row:**

H and He.

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Periodic Table

The Second Row

Each element in the second row of the periodic table has four orbitals available to accept additional electrons: *one 2s orbital*, and *three 2p orbitals*.

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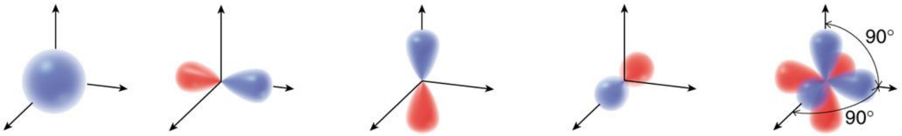

2*s* orbital

2p_x orbital

2p_y orbital

2p_z orbital

all three 2*p* orbitals drawn on the same set of axes

Periodic Table

The Second Row

- Each of the four orbitals in the second shell hold two electrons.
- There is a maximum capacity of eight valence electrons for elements in the second row.
- The second row of the periodic table consists of eight elements, obtained by adding electrons to the 2*s* and three 2*p* orbitals.

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group number	1A	2A	3A	4A	5A	6A	7A	8A
second row	Li	Be	B	C	N	O	F	Ne
number of valence electrons	1	2	3	4	5	6	7	8

1.2 Bonding

- Bonding is the joining of two atoms in a stable arrangement.
- Through bonding, atoms attain a complete outer shell of valence electrons (stable noble gas configuration).
- Atoms can form either ionic or covalent bonds to attain a complete outer shell (octet rule for second row elements).
    - Ionic bonds result from the transfer of electrons from one element to another.
    - Covalent bonds result from the sharing of electrons between two nuclei.

Ionic Bonding

- An **ionic bond** generally occurs when elements on the far **left side** of the periodic table combine with elements on the far **right side**, ignoring noble gases.
- A positively **charged cation** formed from the element on the left side attracts a negatively **charged anion** formed from the element on the right side (e.g., sodium chloride, NaCl).

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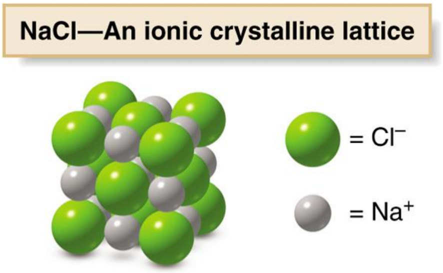

Ionic Bonding

- **Li** loses its one electron to make **Li^+** which has no electrons in second shell. However, it has a complete first shell.
- **F** gains one electron to make **F^-** which has a filled valence shell (an octet of electrons), like neon.

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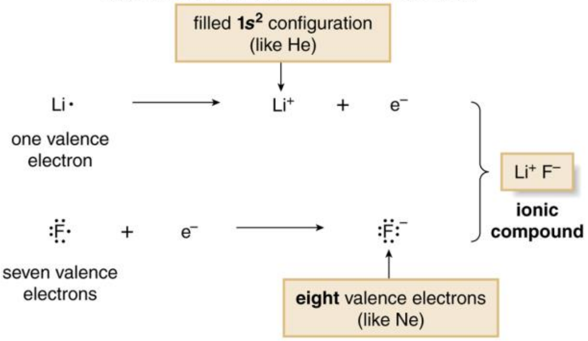

Covalent Bonding

- Covalent bonding occurs with elements like carbon in the middle of the table (e.g., CH_4) with elements that have similar electronegativity.
- Covalent bonds also occur between two of the same elements from the sides of the table (e.g., H_2, Cl_2).
- A covalent bond is a two-electron bond, and a compound with covalent bonds is called a molecule.

Covalent Bonding

Example: Bonding in Molecular Hydrogen (H_2)

- Hydrogen forms one covalent bond.
- When two hydrogen atoms are joined in a bond, each has a filled valence shell of two electrons.

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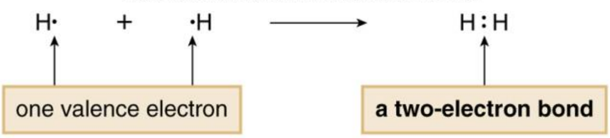

Valence Electrons

- **Second row elements can have no more than eight electrons around them. For neutral molecules, this has two consequences:**
  - **Atoms with 1-4 valence electrons form one, two, three, or four bonds, respectively, in neutral molecules (e.g., BF_3, CH_4).**
  - **Atoms with five or more valence electrons form enough bonds to give an octet (e.g., NH_3). This results in the following equation:**

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predicted number of bonds = 8 − number of valence electrons

Nonbonded Electrons

- **When second-row elements form fewer than four bonds, their octets consist of both bonding (shared) and nonbonding (unshared) electrons. Unshared electrons are also called *lone pairs*.**

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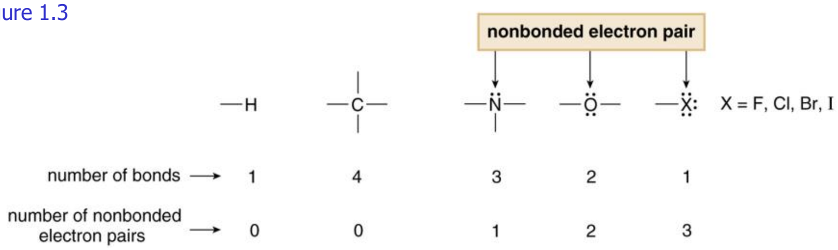
Figure 1.3



1.3 Lewis Structures

Lewis structures are electron dot representations for molecules.

General rules for drawing Lewis structures:

1. **Draw only the valence electrons.**
2. **Give every second-row element no more than eight electrons.**
3. **Give each hydrogen two electrons.**

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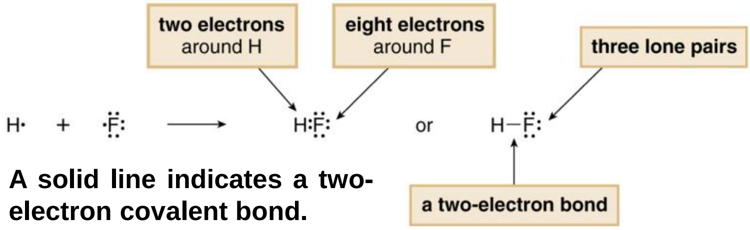

A solid line indicates a two-electron covalent bond.

How to Draw a Lewis Structure

Step [1] Arrange atoms next to each other that you think are bonded together.

- **Always place hydrogen and halogens on the edge because they form only one bond each.**

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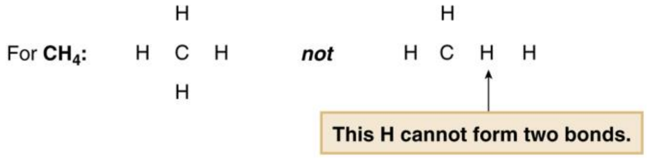

- **Place no more atoms around an atom than the number of bonds it usually forms.**

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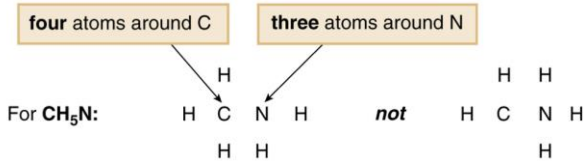

How to Draw a Lewis Structure

Step [2] **Count the electrons.**

- **Count the number of valence electrons from all atoms.**
- **Add one electron for each negative charge.**
- **Subtract one electron for each positive charge.**
- **This gives the total number of electrons that must be used in drawing the Lewis structure.**

Step [3] **Arrange the electrons around the atoms.**

- **Place a bond between every two atoms, giving two electrons to each H and no more than eight to any second-row atom.**
- **Use all remaining electrons to fill octets with lone pairs.**
- **If all valence electrons are used and an atoms does not have an octet, form multiple bonds.**

Step [4] **Assign formal charges to all atoms.**

Multiple Bonds

- **If all valence electrons are used and an atom does not have an octet, form multiple bonds.**

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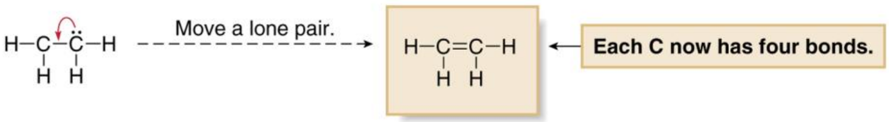

ethylene
a valid Lewis structure

- **To give both C's an octet, change one lone pair into one bonding pair between the two C's, forming a double bond.**

Formal Charge

- **Formal charge** is the charge assigned to individual atoms in a Lewis structure.
- **Formal charge is calculated as follows:**

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formal charge = **number of valence electrons** – **number of electrons an atom "owns"**

- **The number of electrons "owned" by an atom is determined by its number of bonds and lone pairs.**
- **An atom "owns" *all* of its unshared electrons and *half* of its shared electrons.**

Electron Ownership

The number of electrons "owned" by different atoms is indicated in the following examples:

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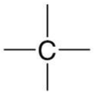

- C shares eight electrons.
- C "owns" **four** electrons.

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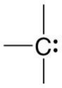

- C shares six electrons.
- C has two unshared electrons.
- C "owns" **five** electrons.

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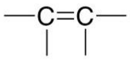

- Each C shares eight electrons.
- Each C "owns" **four** electrons.

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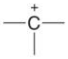
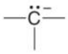
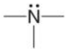
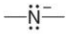
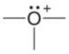
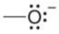
Table 1.1 Formal Charge Observed with Common Bonding Patterns for C, N, and O

Atom	Number of valence electrons	Formal charge +1	Formal charge 0	Formal charge –1
C	4			
N	5			
O	6			

1.4 Isomers

- **Sometimes more than one arrangement of atoms (Lewis structure) is possible for a given molecular formula.**

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ethanol

dimethyl ether

same molecular formula
C_2H_6O

- **These two compounds are called isomers.**
- **Isomers are different molecules having the same molecular formula. Ethanol and dimethyl ether are constitutional isomers.**

1.5 Exceptions to the Octet Rule

Elements in Groups 2A and 3A

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four electrons around Be

six electrons around B

Elements in the Third Row

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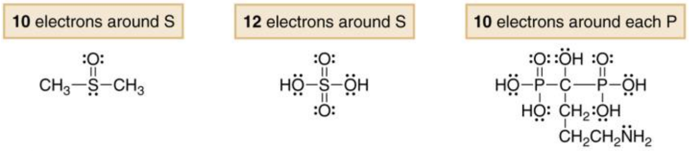

dimethyl sulfoxide
(abbreviated as DMSO)

sulfuric acid

alendronic acid

1.6 Resonance

- Some molecules cannot be adequately represented by a single Lewis structure. For example:

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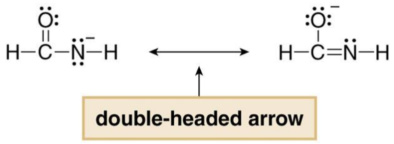

- These structures are called resonance structures or resonance forms. A double-headed arrow is used to separate the two resonance structures.
- Resonance structures are two Lewis structures having the same placement of atoms but a different arrangement of electrons.

Resonance Forms

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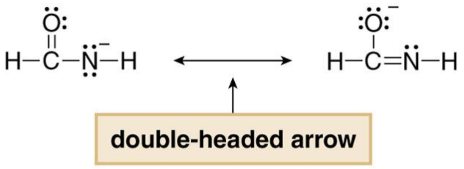


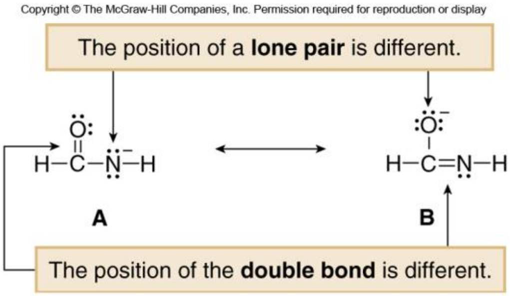
- Neither resonance structure is an accurate representation for $(HCONH)^-$. The true structure is a composite of both resonance forms and is called a resonance hybrid.
- The hybrid shows characteristics of both structures.
- Resonance allows certain electron pairs to be delocalized over two or more atoms, and this delocalization adds stability.
- A molecule with two or more resonance forms is said to be resonance stabilized.

Basic Principles of Resonance Theory

- Resonance structures are not real. An individual resonance structure does not accurately represent the structure of a molecule or ion. Only the hybrid does.
- Resonance structures are not in equilibrium with each other. There is no movement of electrons from one form to another.
- Resonance structures are not isomers. Two isomers differ in the arrangement of both atoms and electrons, whereas resonance structures differ only in the arrangement of electrons.

Drawing Resonance Structures

Rule [1]: Two resonance structures differ in the position of multiple bonds and nonbonded electrons. The placement of atoms and single bonds always stays the same.



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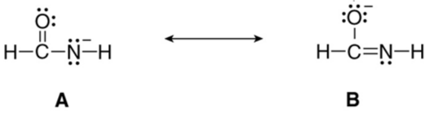
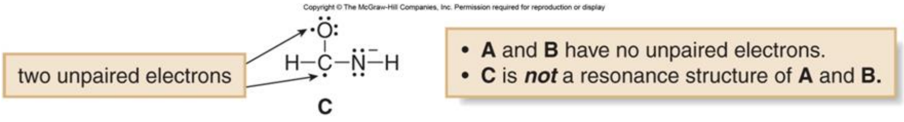
The position of a **lone pair** is different.

The position of the **double bond** is different.

Drawing Resonance Structures

Rule [2]: Two resonance structures must have the same number of unpaired electrons.





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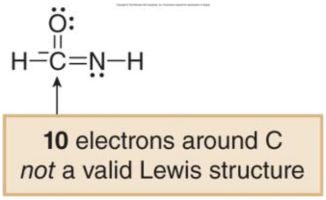
two unpaired electrons

- **A** and **B** have no unpaired electrons.
- **C** is ***not*** a resonance structure of **A** and **B.**

Rule [3]: Resonance structures must be valid Lewis structures. Hydrogen must have two electrons and no second-row element can have more than eight electrons.



10 electrons around C

not a valid Lewis structure

Curved Arrow Notation

- **Curved arrow notation is a convention that shows how electron position differs between two resonance forms.**
- **Curved arrow notation shows the movement of an electron pair. The tail of the arrow always begins at the electron pair, either in a bond or lone pair. The head points to where the electron pair "moves."**

Example 1:

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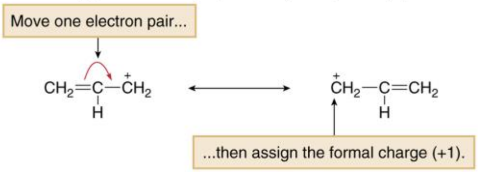

Move one electron pair...

...then assign the formal charge (+1).

Example 2:

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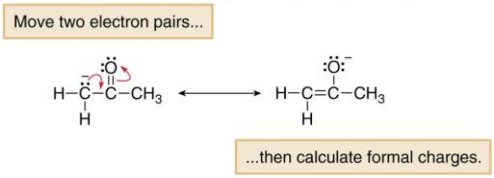

Move two electron pairs...

...then calculate formal charges.

Atoms Without Octets

Resonance structures can have an atom with fewer than 8 electrons.

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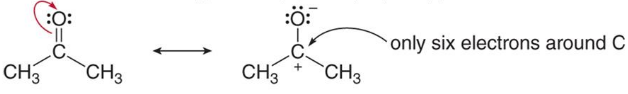

only six electrons around C

A **B**

a valid resonance structure

However, resonance structures can never have a second-row element with more than 8 electrons.

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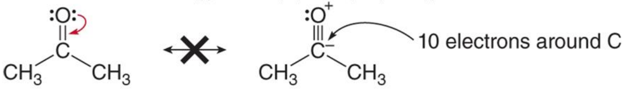

10 electrons around C

A **C**

not a valid resonance structure

Occurrence of Resonance

1. Two different resonance structures can be drawn when a lone pair is located on an atom directly bonded to a double bond.

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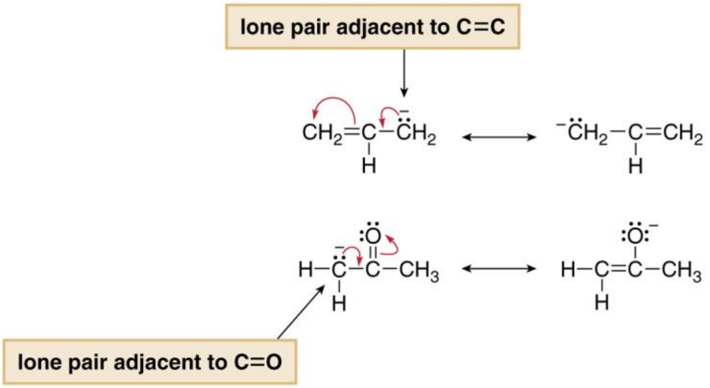

2. Multiple resonance structures can also be drawn when an atom bearing a (+) charge is bonded

to a double bond

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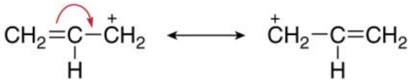
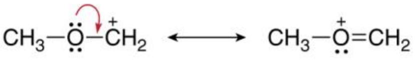
(+) charge adjacent to a double bond



or an atom with a lone pair.

(+) charge adjacent to an atom with a lone pair



The Resonance Hybrid

- A **resonance hybrid** is a composite of all possible resonance structures. In the resonance hybrid, the electron pairs drawn in different locations in individual resonance forms are **delocalized**.
- When two resonance structures are different, the hybrid looks more like the "**better**" resonance structure.
- The "**better**" resonance structure is called the **major contributor** to the hybrid, and all others are **minor contributors**.

Resonance Hybrids

A "**better**" resonance structure is one that **has more bonds** and fewer charges.

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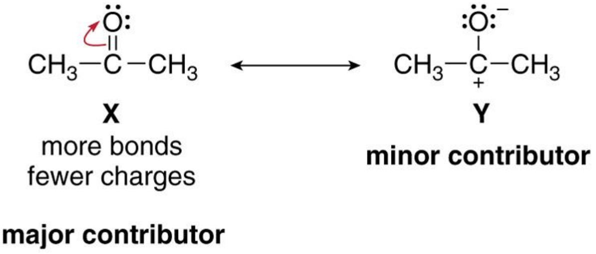

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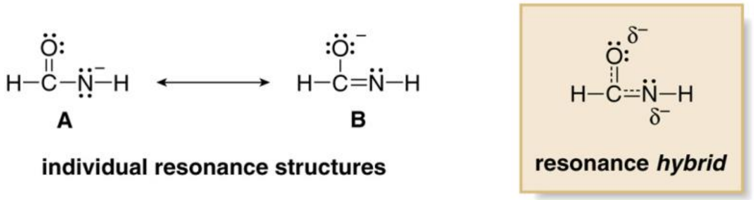

1.7 Determining Molecular Shape

Two variables define a molecule’s structure: ***bond length*** **and** ***bond angle*****.**

- **Bond length** ***decreases*** **across a row of the periodic table as the size of the atom** ***decreases*****.**

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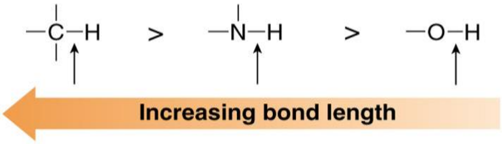

- **Bond length** ***increases*** **down a column of the periodic table as the size of an atom** ***increases*****.**

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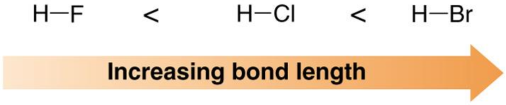

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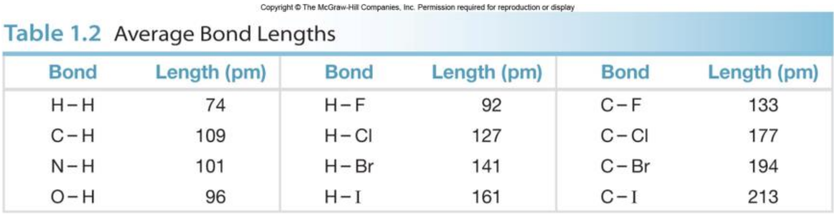

Table 1.2 Average Bond Lengths

Bond	Length (pm)	Bond	Length (pm)	Bond	Length (pm)
H–H	74	H–F	92	C–F	133
C–H	109	H–Cl	127	C–Cl	177
N–H	101	H–Br	141	C–Br	194
O–H	96	H–I	161	C–I	213

Molecular Geometry

- **The number of groups surrounding a particular atom determines its geometry. A group is either an atom or a lone pair of electrons.**
- **The most stable arrangement keeps these groups as far away from each other as possible. This is exemplified by Valence Shell Electron Pair Repulsion (VSEPR) theory.**

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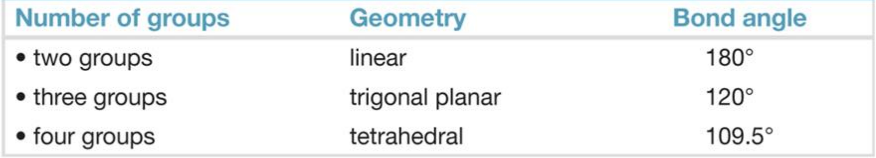

Number of groups	Geometry	Bond angle
• two groups	linear	180°
• three groups	trigonal planar	120°
• four groups	tetrahedral	109.5°

Two Groups Around an Atom

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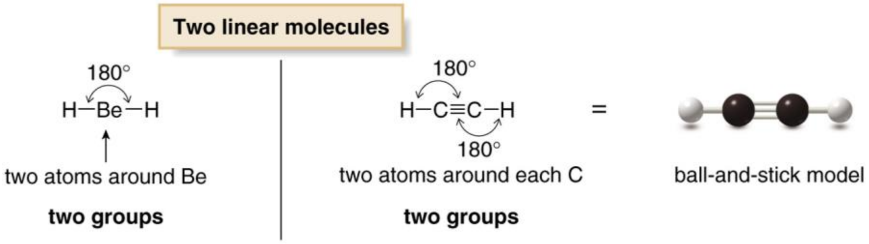
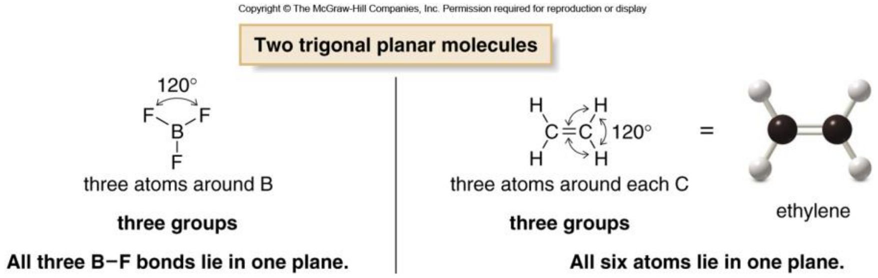


Three Groups Around an Atom



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Two trigonal planar molecules

three atoms around B

three groups

All three B−F bonds lie in one plane.

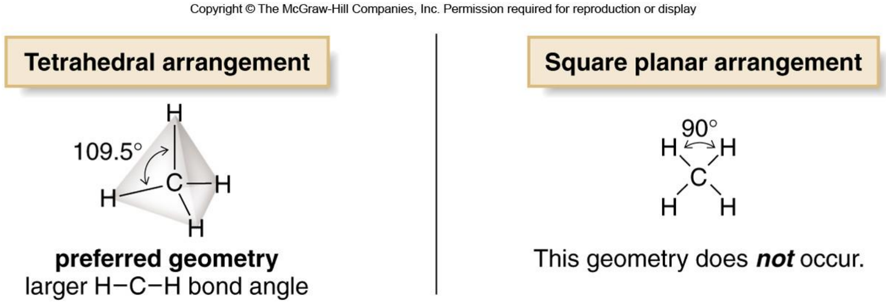
three atoms around each C

three groups

ethylene

All six atoms lie in one plane.

Four Groups Around an Atom



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Tetrahedral arrangement

preferred geometry
larger H−C−H bond angle

Square planar arrangement

This geometry does ***not*** occur.

Drawing Three-Dimensional Structures

- A solid line is used for a bond in the plane.
- A wedge is used for a bond in front of the plane.
- A dashed line is used for a bond behind the plane.

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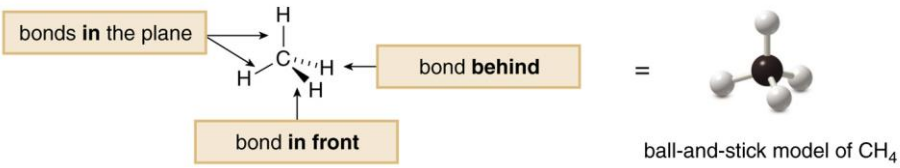

Equivalent Representations for Methane

- The molecule can be turned in many different ways, generating equivalent representations.
- All of the following are acceptable drawings for CH_4.

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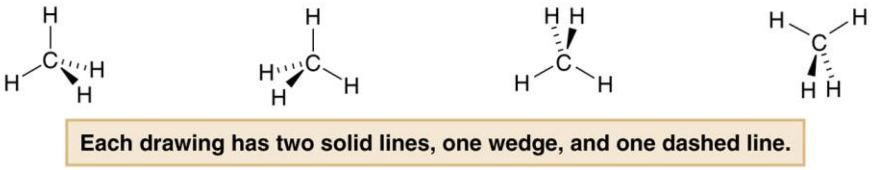

Each drawing has two solid lines, one wedge, and one dashed line.

Wedges and Dashes

- Note that wedges and dashes are used for groups that are really aligned one behind another.
- It does not matter in the following two drawings whether the wedge or dash is skewed to the left or right.

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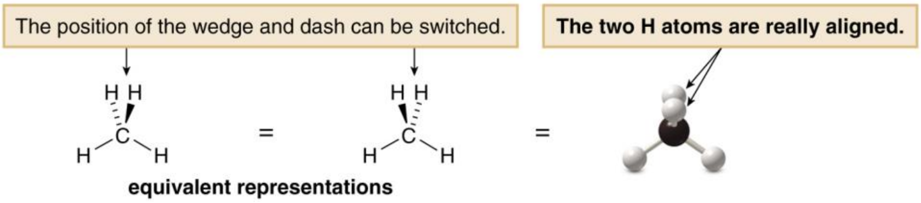

The position of the wedge and dash can be switched.

The two H atoms are really aligned.

equivalent representations

A Nonbonded Pair of Electrons is Counted as a “Group”

- In ammonia (NH_3), one of the four groups attached to the central N atom is a lone pair.
- The group geometry is a tetrahedron.
- The molecular shape is referred to as a trigonal pyramid.

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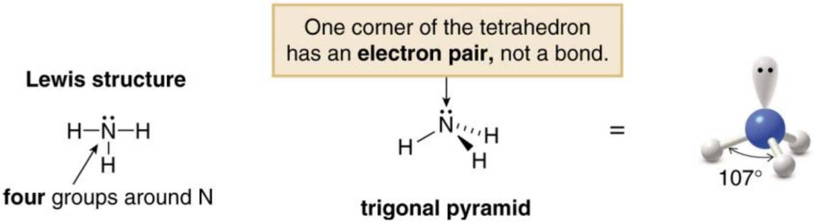

Lewis structure

One corner of the tetrahedron has an **electron pair,** not a bond.

four groups around N

trigonal pyramid

The 3-D Structure of Water

- In water (H_2O), two of the four groups attached to the central O atom are lone pairs.
- The group geometry is a tetrahedron.
- The molecular shape is referred to as bent.

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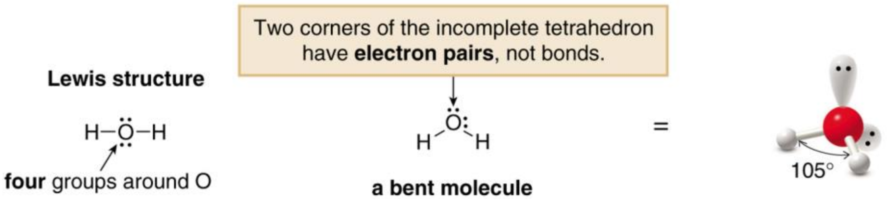
Two corners of the incomplete tetrahedron have **electron pairs**, not bonds.

Varying Bond Angles

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Methane (CH_4)

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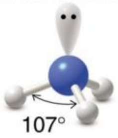

Ammonia (NH_3)

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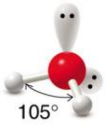

Water (H_2O)

- In both NH_3 and H_2O, the bond angle is smaller than the theoretical tetrahedral bond angle because of repulsion of the lone pairs of electrons.
- The bonded atoms are compressed into a smaller space with a smaller bond angle.

Summary: Predicting Geometry Based on Number of Groups

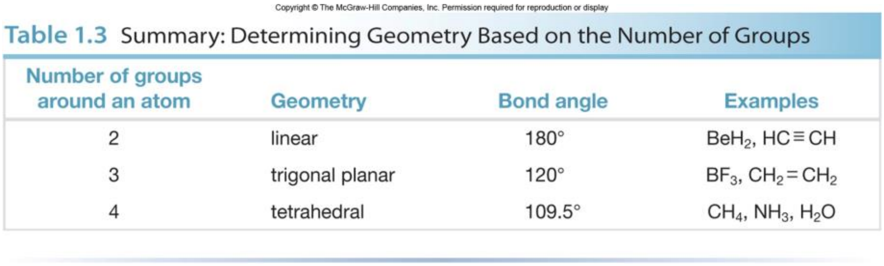

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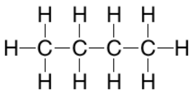
Table 1.3 Summary: Determining Geometry Based on the Number of Groups

Number of groups around an atom	Geometry	Bond angle	Examples
2	linear	180°	BeH_2, $HC{\equiv}CH$
3	trigonal planar	120°	BF_3, $CH_2{=}CH_2$
4	tetrahedral	109.5°	CH_4, NH_3, H_2O

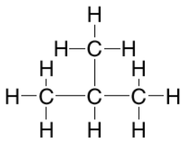
1.8 Drawing Organic Molecules—Condensed Structures

- All atoms are drawn in, but the two-electron bond lines are generally omitted.
- Atoms are usually drawn next to the atoms to which they are bonded.
- Parentheses are used around similar groups bonded to the same atom.
- Lone pairs are omitted.



= $CH_3CH_2CH_2CH_3$ or $CH_3(CH_2)_2CH_3$

2 CH_2 groups bonded together



= $(CH_3)_3CH$

Examples of Condensed Structures

Figure 1.4

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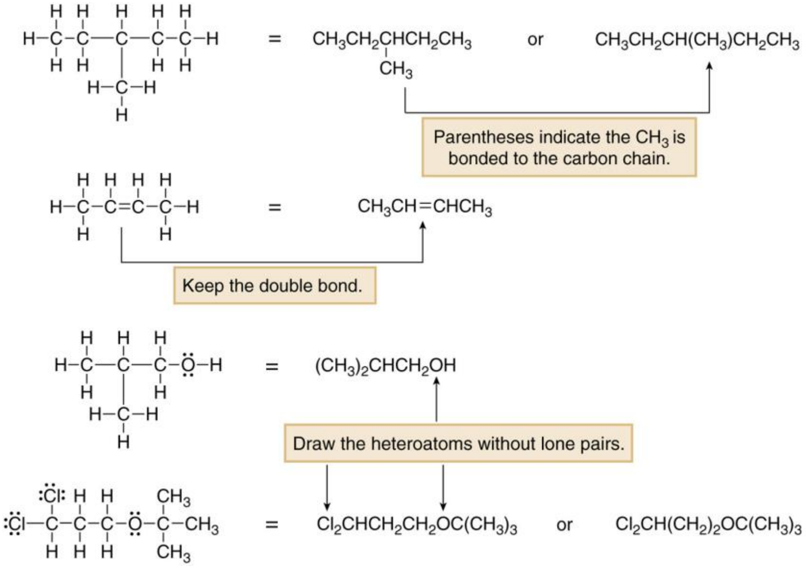

$CH_3CH_2CHCH_2CH_3$ (with CH_3 below) or $CH_3CH_2CH(CH_3)CH_2CH_3$

Parentheses indicate the CH_3 is bonded to the carbon chain.

$CH_3CH{=}CHCH_3$

Keep the double bond.

$(CH_3)_2CHCH_2OH$

Draw the heteroatoms without lone pairs.

$Cl_2CHCH_2CH_2OC(CH_3)_3$ or $Cl_2CH(CH_2)_2OC(CH_3)_3$

Condensed Structures with C=O

Figure 1.5

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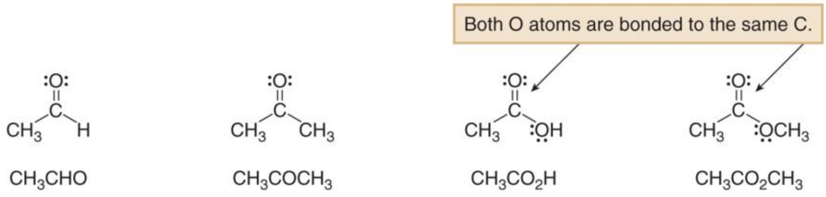

Both O atoms are bonded to the same C.

CH_3CHO CH_3COCH_3 CH_3CO_2H $CH_3CO_2CH_3$

In these examples, the only way for all atoms to have an octet is by having a carbon-oxygen double bond.

Skeletal Structures

- **Assume there is a carbon atom at the junction of any two lines or at the end of any line.**
- **Assume there are enough hydrogens around each carbon to make it tetravalent.**
- **Draw in all heteroatoms and the hydrogens directly bonded to them.**

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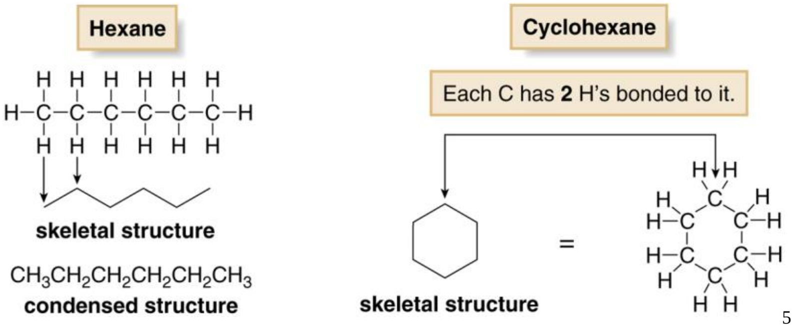

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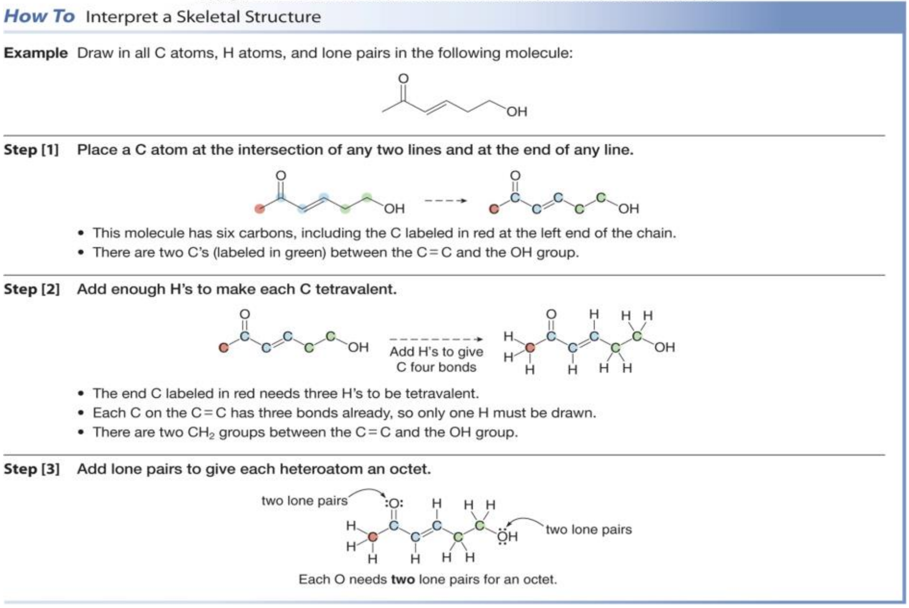

How To Interpret a Skeletal Structure

Example Draw in all C atoms, H atoms, and lone pairs in the following molecule:

Step [1] **Place a C atom at the intersection of any two lines and at the end of any line.**

- This molecule has six carbons, including the C labeled in red at the left end of the chain.
- There are two C's (labeled in green) between the C = C and the OH group.

Step [2] **Add enough H's to make each C tetravalent.**

- The end C labeled in red needs three H's to be tetravalent.
- Each C on the C = C has three bonds already, so only one H must be drawn.
- There are two CH_2 groups between the C = C and the OH group.

Step [3] **Add lone pairs to give each heteroatom an octet.**

Each O needs **two** lone pairs for an octet.

Interpreting Skeletal Structures

Figure 1.6

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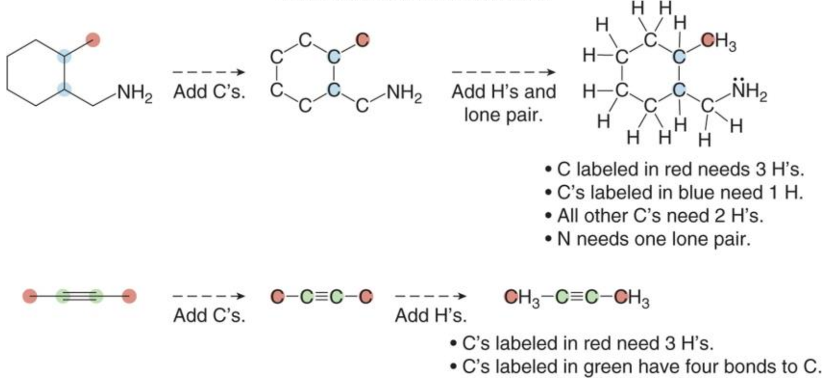

- C labeled in red needs 3 H's.
- C's labeled in blue need 1 H.
- All other C's need 2 H's.
- N needs one lone pair.

- C's labeled in red need 3 H's.
- C's labeled in green have four bonds to C.

Skeletal Structures with Charged Carbon Atoms

- **A charge on a carbon atom takes the place of one hydrogen atom.**
- **The charge determines the number of lone pairs. Negatively charged carbon atoms have one lone pair and positively charged carbon atoms have none.**

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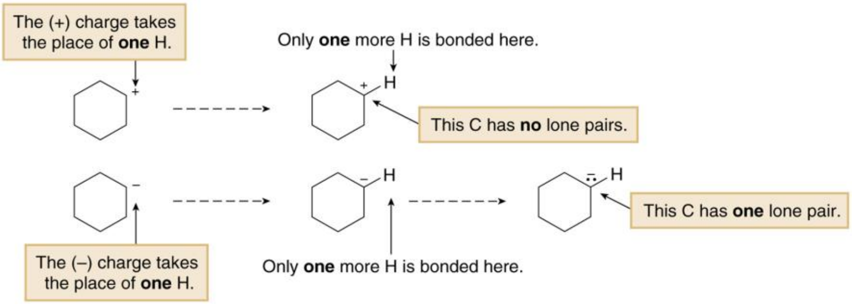

The (+) charge takes the place of **one** H.

Only **one** more H is bonded here.

This C has **no** lone pairs.

This C has **one** lone pair.

The (–) charge takes the place of **one** H.

Only **one** more H is bonded here.

Lone Pairs on Heteroatoms

- Skeletal structures often leave out lone pairs on heteroatoms, ***but don’t forget about them*.**
- **Use the formal charge to determine the number of lone pairs.**

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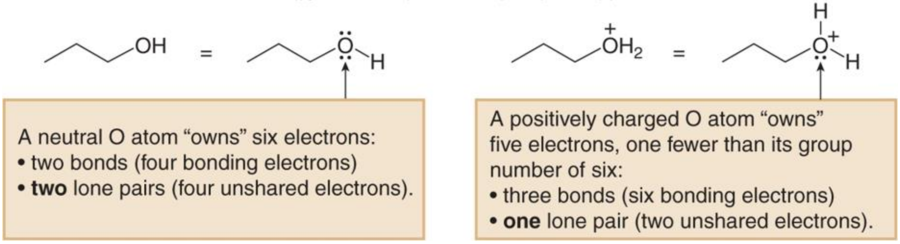

A neutral O atom “owns” six electrons:
- two bonds (four bonding electrons)
- **two** lone pairs (four unshared electrons).

A positively charged O atom “owns” five electrons, one fewer than its group number of six:
- three bonds (six bonding electrons)
- **one** lone pair (two unshared electrons).

1.9 Orbitals and Bonding: Hydrogen

- **When the 1*s* orbital of one H atom overlaps with the 1*s* orbital of another H atom, a sigma (σ) bond that concentrates electron density between the two nuclei is formed.**
- **This bond is cylindrically symmetrical because the electrons forming the bond are distributed symmetrically about an imaginary line connecting the two nuclei.**

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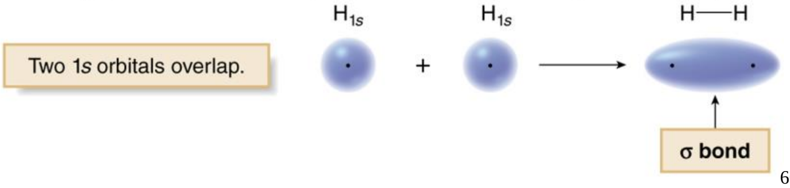
Two 1*s* orbitals overlap.

Orbitals and Bonding: Methane

- To account for the bonding patterns observed in more complex molecules, we must take a closer look at how the 2*s* and 2*p* orbitals of atoms in the second row are utilized.
- In addition to its two core electrons, carbon has four valence electrons.
- In its ground state, carbon places two electrons in the 2*s* orbital and one each in 2*p* orbitals.

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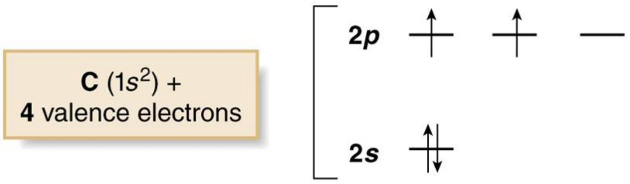

Note: The lowest energy arrangement of electrons for an atom is called its **ground state**.

Divalent Carbon

- In this description, carbon should form only two bonds because it has only two unpaired valence electrons.
- However, the resulting species, CH_2, is very unstable and cannot be isolated under typical laboratory conditions.
- Note that in CH_2, carbon would not have an octet of electrons.

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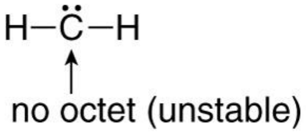

Tetravalent Carbon

- Promotion of an electron from a 2*s* to a vacant 2*p* orbital would form four unpaired electrons for bonding.
- This higher energy electron configuration is called an electronically excited state.

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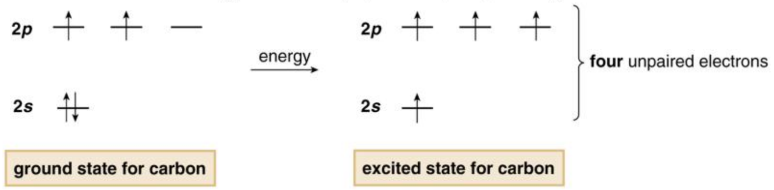

- Carbon would form two different types of bonds: three with 2*p* orbitals and one with a 2*s* orbital.
- Experimental evidence points to carbon forming four identical bonds in methane.

Hybrid Orbitals

- To solve this dilemma, chemists have proposed that atoms like carbon do not use pure *s* and pure *p* orbitals in forming bonds.
- Instead, atoms use a set of new orbitals called hybrid orbitals.
- *Hybridization* is the combination of two or more atomic orbitals to form the same number of hybrid orbitals, each having the same shape and energy.

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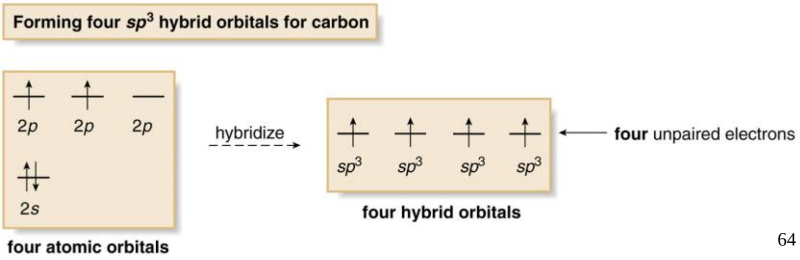

Shape and Orientation of sp^3 Hybrid Orbitals

- The mixing of a spherical 2*s* orbital and three dumbbell shaped 2*p* orbitals together produces four hybrid orbitals, each having one large lobe and one small lobe.

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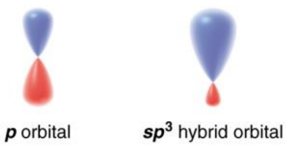

- The four hybrid orbitals are oriented towards the corners of a tetrahedron, and form four equivalent bonds.

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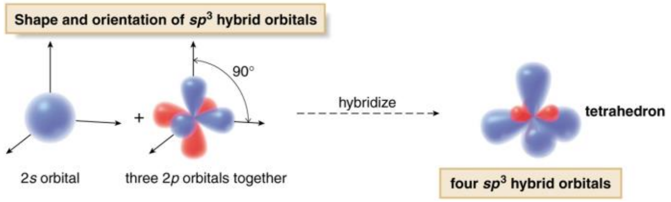

Bonding Using sp^3 Hybrid Orbitals

- Each bond in CH_4 is formed by overlap of an sp^3 hybrid orbital of carbon with a 1*s* orbital of hydrogen.
- These four bonds point to the corners of a tetrahedron.

Figure 1.7

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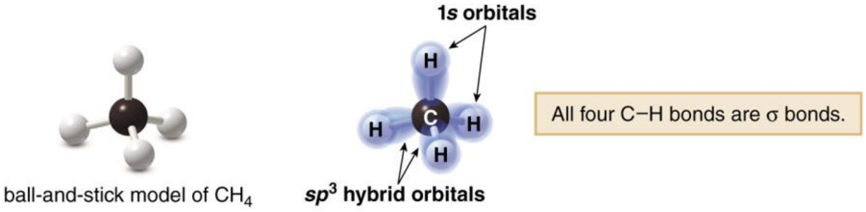

Other Hybridization Patterns

Figure 1.8

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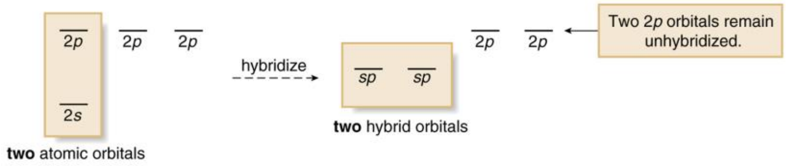

- Forming **two *sp* hybrid orbitals** uses **one 2s** and **one 2*p* orbital,** leaving **two 2*p* orbitals** ***unhybridized.***

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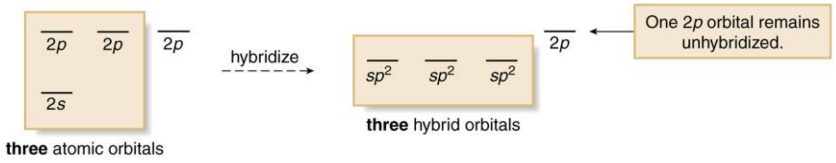

- Forming **three *sp*^{2} hybrid orbitals** uses **one 2*s*** and **two 2*p* orbitals,** leaving **one 2*p* orbital** ***unhybridized.***

Figure 1.9

sp and sp^2 Hybridization Examples

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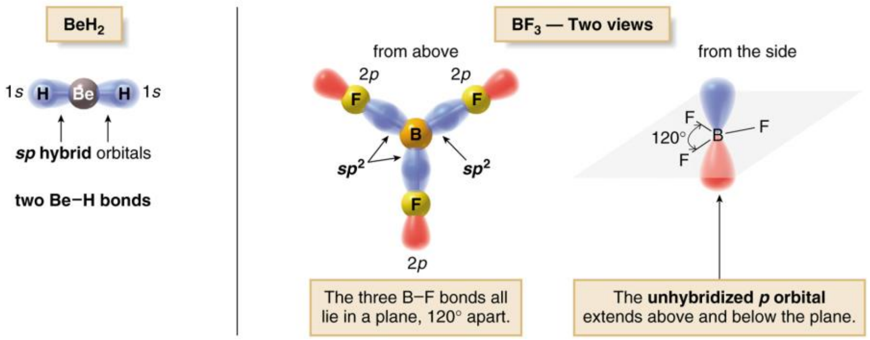

Determining Hybridization

- **Count the number of groups (atoms and nonbonded electron pairs) around the atom.**
- **The number of groups corresponds to the number of atomic orbitals that must be hybridized to form the hybrid orbitals.**

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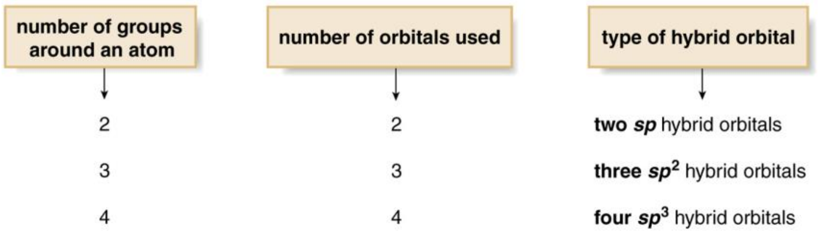

number of groups around an atom	number of orbitals used	type of hybrid orbital
2	2	**two** ***sp*** hybrid orbitals
3	3	**three** sp^2 hybrid orbitals
4	4	**four** sp^3 hybrid orbitals

Remember lone pairs counted as a group

Hybrid orbitals of NH_3 and H_2O

Figure 1.10

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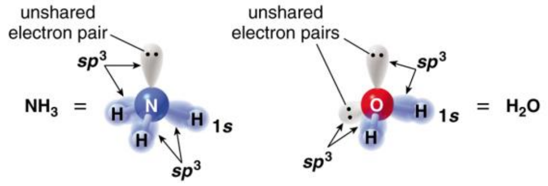

1.10 Hybridization and Bonding in Ethane

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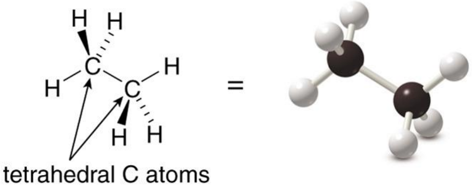

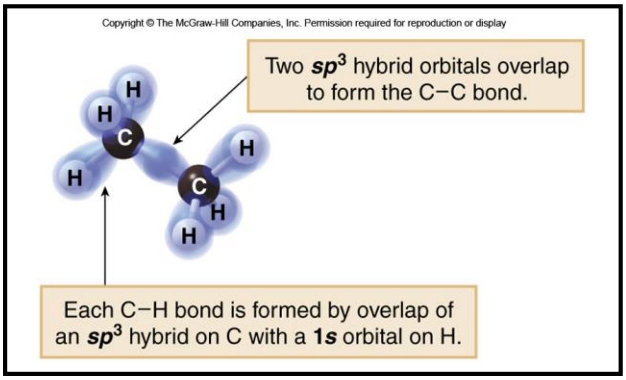
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Two sp^3 hybrid orbitals overlap to form the C–C bond.

Each C–H bond is formed by overlap of an sp^3 hybrid on C with a $1s$ orbital on H.

Ethane, CH_3-CH_3

- **Making a model of ethane illustrates one additional feature about its structure.**
- **Rotation occurs around the central C—C σ bond.**

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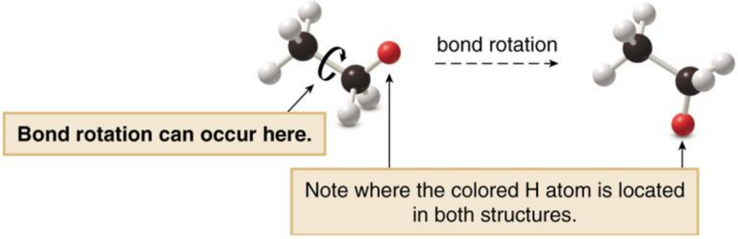
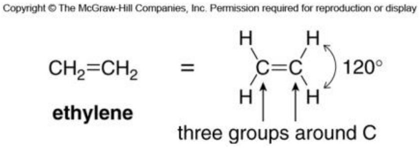


Bond rotation can occur here.

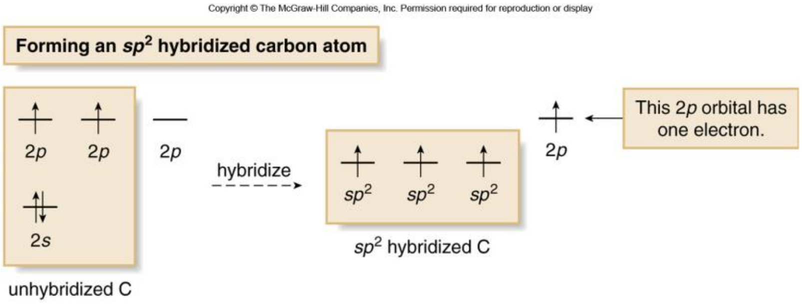
Note where the colored H atom is located in both structures.

Hybrid Orbitals in Ethylene



Each carbon is trigonal planar.

Each carbon is *sp*^{2} hybridized.



σ and π Bonds in Ethylene

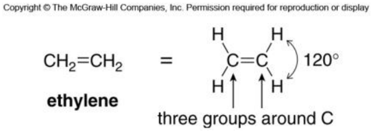
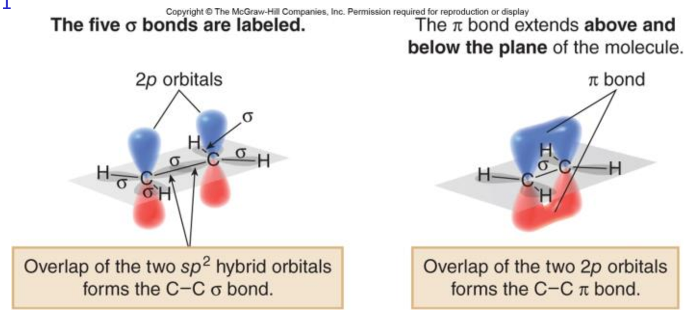


Figure 1.11



No Free Rotation in Ethylene

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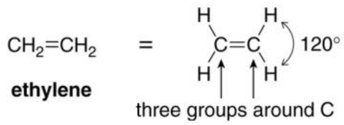
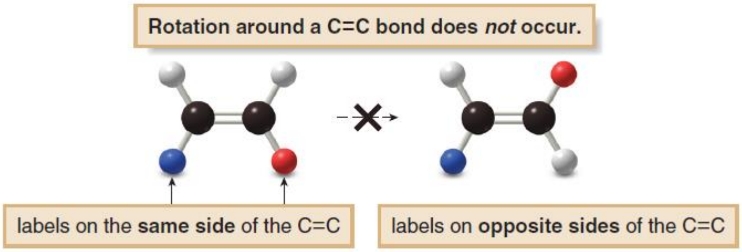


- Unlike the C—C bond in ethane, rotation about the C—C double bond in ethylene is restricted.
- It can only occur if the π bond first breaks and then reforms, a process that requires considerable energy.



sp Hybrid Orbitals

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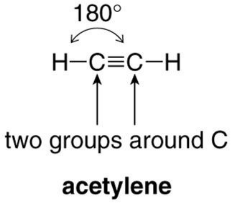

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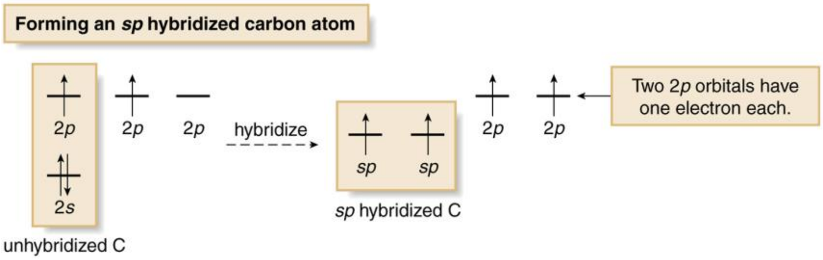

Acetylene (Ethyne)

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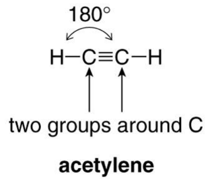

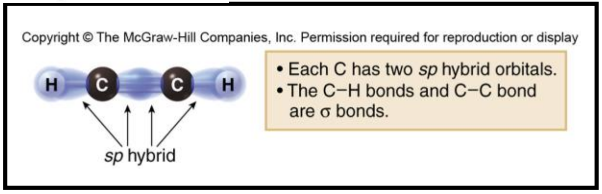
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- Each C has two *sp* hybrid orbitals.
- The C−H bonds and C−C bond are σ bonds.

Each carbon atom has two unhybridized 2*p* orbitals that are perpendicular to each other and to the *sp* hybrid orbitals.

Triple Bonds

- **The side-by-side overlap of two 2*p* orbitals on one carbon with two 2*p* orbitals on the other carbon creates the second and third bonds of the triple bond.**
- **All triple bonds are composed of one sigma and two pi bonds.**

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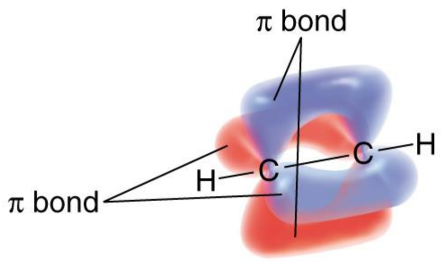

Summary of Bonding in Acetylene

Figure 1.12

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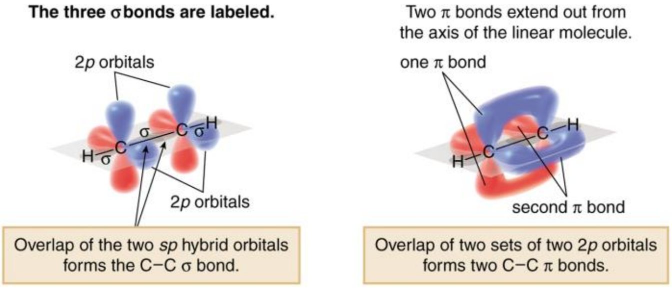

Overlap of the two *sp* hybrid orbitals forms the C–C σ bond.

Overlap of two sets of two 2*p* orbitals forms two C–C π bonds.

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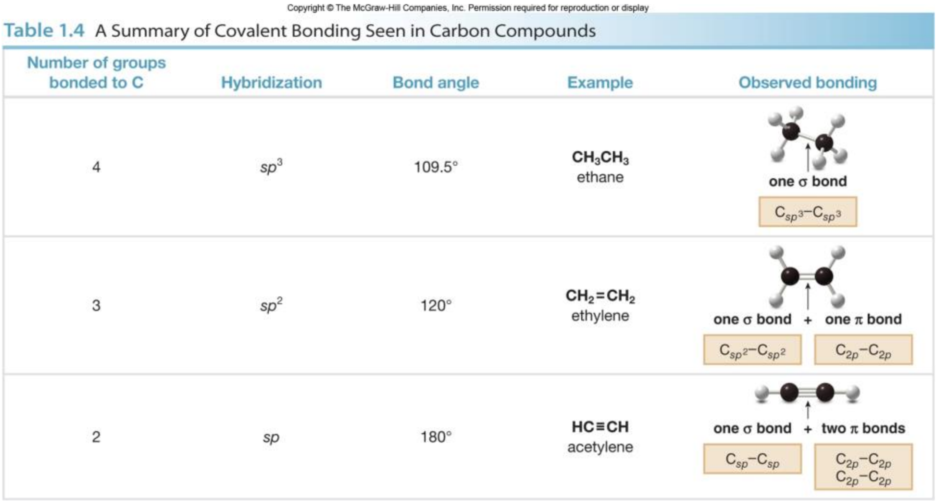

Table 1.4 A Summary of Covalent Bonding Seen in Carbon Compounds

Number of groups bonded to C	Hybridization	Bond angle	Example	Observed bonding
4	sp^3	109.5°	CH_3CH_3 ethane	one σ bond $C_{sp^3}–C_{sp^3}$
3	sp^2	120°	$CH_2{=}CH_2$ ethylene	one σ bond + one π bond $C_{sp^2}–C_{sp^2}$ $C_{2p}–C_{2p}$
2	sp	180°	$HC{\equiv}CH$ acetylene	one σ bond + two π bonds $C_{sp}–C_{sp}$ $C_{2p}–C_{2p}$ $C_{2p}–C_{2p}$

1.11 Bond Length and Bond Strength

- **As the number of electrons between two nuclei increases, bonds become shorter and stronger.**
- **Triple bonds are shorter and stronger than double bonds, which are shorter and stronger than single bonds.**

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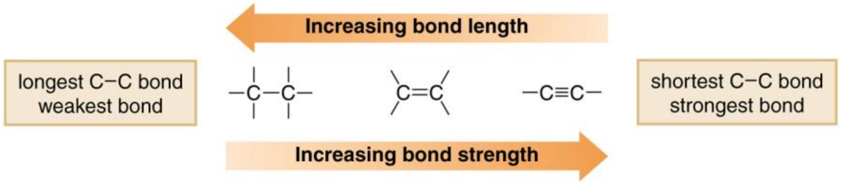

Carbon-Hydrogen Bonds

- **The length and strength of C—H bonds vary depending on the hybridization of the carbon atom.**

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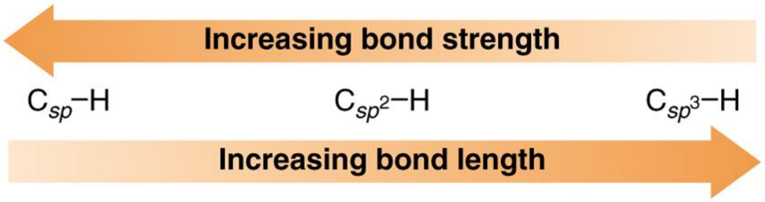

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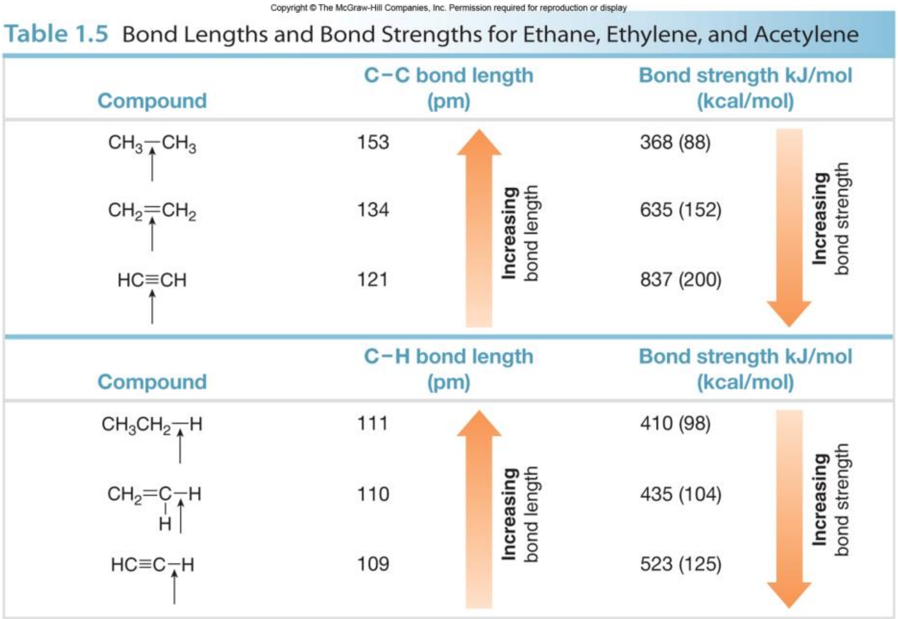

Table 1.5 Bond Lengths and Bond Strengths for Ethane, Ethylene, and Acetylene

Compound	C–C bond length (pm)	Bond strength kJ/mol (kcal/mol)
CH_3-CH_3	153	368 (88)
$CH_2=CH_2$	134	635 (152)
$HC\equiv CH$	121	837 (200)

Compound	C–H bond length (pm)	Bond strength kJ/mol (kcal/mol)
CH_3CH_2-H	111	410 (98)
$CH_2=\underset{H}{C}-H$	110	435 (104)
$HC\equiv C-H$	109	523 (125)

Percent *s*-Character

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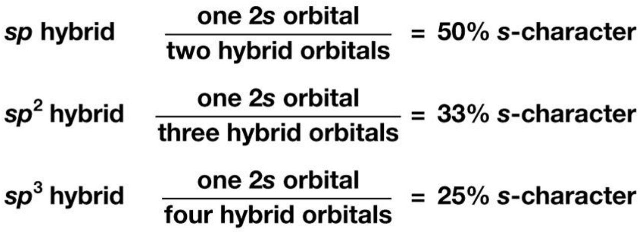

sp hybrid $\frac{\text{one 2}s\text{ orbital}}{\text{two hybrid orbitals}}$ = 50% *s*-character

sp² hybrid $\frac{\text{one 2}s\text{ orbital}}{\text{three hybrid orbitals}}$ = 33% *s*-character

sp³ hybrid $\frac{\text{one 2}s\text{ orbital}}{\text{four hybrid orbitals}}$ = 25% *s*-character

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Increased percent *s*-character ⇢ Increased bond strength ⇢ Decreased bond length

1.12 Electronegativity

Electronegativity is a measure of an atom’s attraction for electrons in a bond.

Electronegativity values for some common elements:

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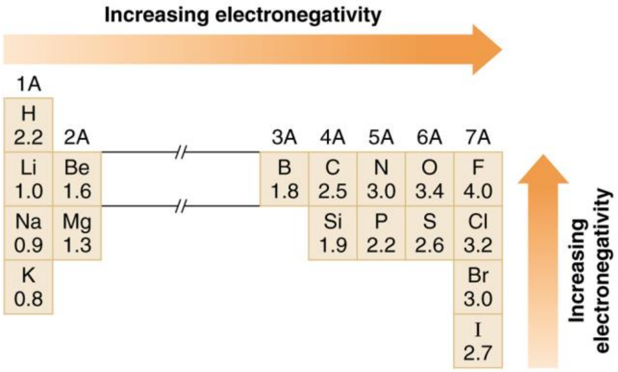
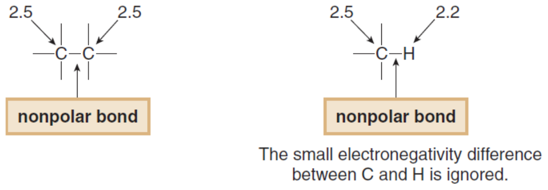
Figure 1.13



Bond Polarity

- **Electronegativity values are used to indicate whether the electrons in a bond are equally shared or unequally shared between two atoms.**
- **When electrons are equally shared, the bond is nonpolar.**



Nonpolar Bonds

- **A carbon—carbon bond is nonpolar.**
- **C—H bonds are considered to be nonpolar because the electronegativity difference between C and H is small.**
- **Whenever two different atoms having similar electronegativities are bonded together, the bond is nonpolar.**

Polar Bonds

- **Bonding between atoms of different electronegativity values results in unequal sharing of electrons.**
- **Example: In the C—O bond, the electrons are pulled away from C (2.5) toward O (3.4), the element of higher electronegativity. The bond is polar, or *polar covalent*. The bond is said to have dipole; that is, separation of charge.**

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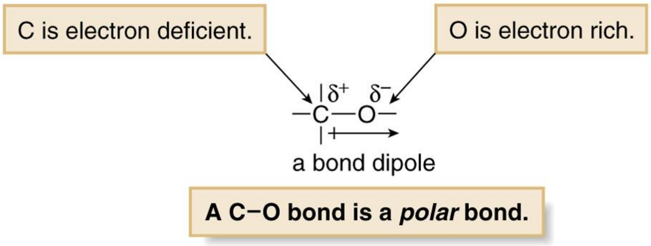

Depicting Polarity

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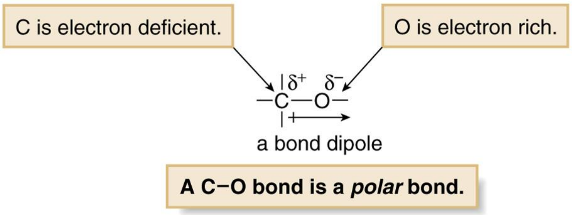

- The δ^+ means the indicated atom is electron deficient.
- The δ^- means the indicated atom is electron rich.
- The direction of polarity in a bond is indicated by an arrow with the head of the arrow pointing towards the more electronegative element.
- The tail of the arrow is drawn at the less electronegative element.

1.13 Polarity of Molecules

Use the following procedure to determine if a molecule has a net dipole:

- Use electronegativity differences to identify all of the polar bonds and the directions of the bond dipoles.
- Determine the geometry around individual atoms by counting groups, and decide if individual dipoles cancel or reinforce each other in space.

Figure 1.14 **Electrostatic potential plot of CH_3Cl**

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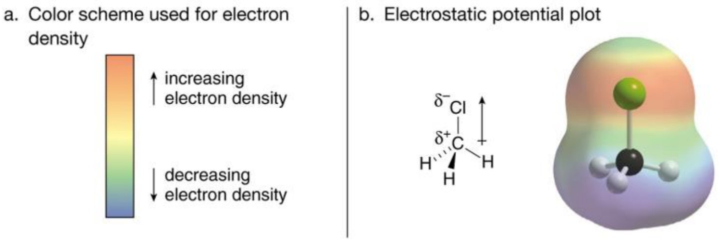

Polar Molecules

A polar molecule has either one polar bond, or two or more bond dipoles that reinforce each other. An example is water:

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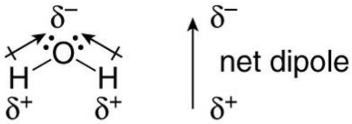

The net dipole bisects the H—O—H bond angle.
The two individual dipoles reinforce.

H_2O is a polar molecule.

Nonpolar Molecules

A nonpolar molecule has either no polar bonds, or two or more bond dipoles that cancel. An example is carbon dioxide:

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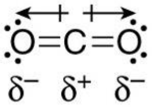

no net dipole
The two dipoles cancel.

CO_2 is a nonpolar molecule.

Electrostatic Potential for Polar and Nonpolar Molecules

The dipoles of H_2O and CO_2 can also be visualized using electrostatic potential plots.

Figure 1.15

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