# ORBITAL PICTURE OF BONDING: ORBITAL COMBINATIONS, HYBRIDIZATION THEORY, & MOLECULAR ORBITALS

## LEARNING OBJECTIVES

To introduce the basic principles of molecular orbital theory and electronic geometry of molecules.

## ORBITAL COMBINATIONS

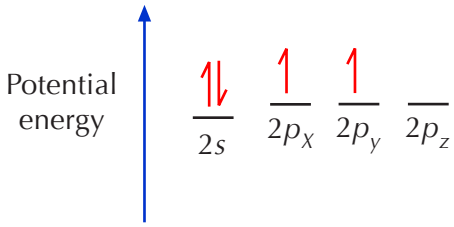
Atomic orbitals can be combined and reshaped –much like dough– to make other orbitals of different shapes and properties. There are two basic types of orbitals that can result from such processes. They are:

**1. HYBRID ORBITALS**. They result from combinations of orbitals **within** a given atom, either prior to or as bonding with another atom takes place.

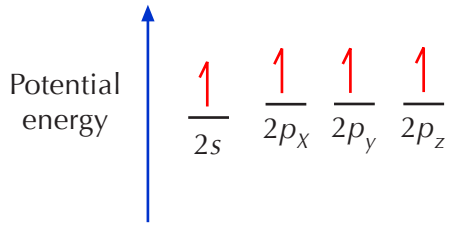
**2. MOLECULAR ORBITALS**. They result from combinations of orbitals **between** atoms as bonding takes place to form molecules.

## ORBITAL HYBRIDIZATION THEORY

If we look at the valence shell configuration of carbon, we find two paired electrons in the 2*s* orbital, and two unpaired electrons in the $2p_X$ and $2p_Y$ orbitals, one in each:



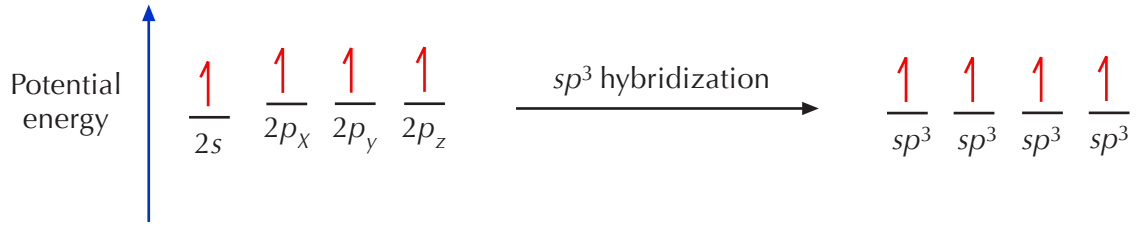

In order to fulfill the octet rule, carbon must use its 4 valence electrons when bonding to other atoms. However, only unpaired electrons can bond. That means that **the two paired electrons occupying the 2s orbital must become unpaired before they can bond**. Since the energy gap between the 2*s* and 2*p* orbitals is very small, one of the 2*s* electrons can be promoted to the empty 2*p* orbital, leading to the following situation:



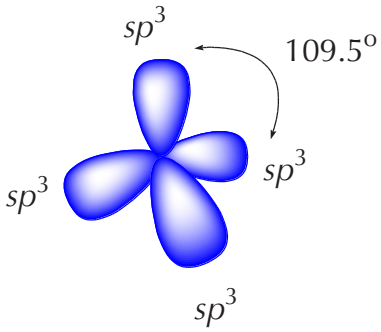

Now the four electrons appear to be ready for bonding, but there is a problem. The 2*p* orbitals are known to be at right angles to each other. If bonding occurs in this state, the 3 equivalent *p* electrons would form 3 equivalent bonds oriented at 90° to each other, and the *s* electron would form a bond of a different type and orientation from the other three. No such compound exists. The simplest hydrocarbon –methane ($CH_4$)– is known to have tetrahedral geometry, where the four C–H bonds are all equivalent and positioned at 109.5° angles to each other. In addition, there are some carbon compounds where the bond angles are 120° or even 180°. **The shapes and relative positions of the valence orbitals in atomic carbon do not explain the shapes and relative positions of the bonds in carbon compounds**.

HYBRIDIZATION THEORY ATTEMPTS TO EXPLAIN THE ACTUAL SHAPES OF MOLECULES BY INVOKING THE FORMATION OF HYBRID ORBITALS DURING, OR PRIOR TO, THE BONDING PROCESS.

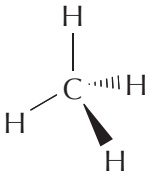
Going back to the carbon model with four unpaired electrons in the valence shell, we can take it as a point of departure for formation of hybrid orbitals. The first step is to take either 2, 3, or all four of those orbitals and equalize their energies. Let's say that we take all four of them and form 4 equivalent new orbitals. These orbitals are now of the same energy, which is intermediate between those of the original 2*s* and 2*p* orbitals. At the same time, we cannot name the new orbitals *s* or *p*, for they're neither. We have to find a new name that reflects the fact that they were created from **one *s* orbital and three *p* orbitals**. We will call them ***sp*³ orbitals**. The process that leads to their formation is called ***sp*³ hybridization**.




All four $sp^3$ orbitals that result from this process are **equivalent**. That means that they have **the same size, shape, and energy**. According to VSEPR (valence shell electron pair repulsion) theory, such orbitals will orient themselves in 3-D space **to be as far apart from each other as possible**. The resulting shape is then a tetrahedron, where the carbon nucleus is at the center and the orbitals point to the corners of the tetrahedron. The ideal angle between orbitals is then 109.5 degrees.




When an $sp^3$ hybridized carbon bonds to hydrogen, it forms methane, whose geometry is known to be tetrahedral.




A 3-D representation of methane. The single lines represent bonds that are positioned on the plane of the paper. The solid wedge represents a bond coming out of the plane of the paper towards the front. The broken wedge represents a bond going behind the plane of the paper towards the back.

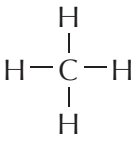
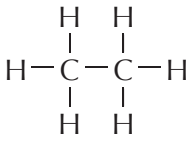
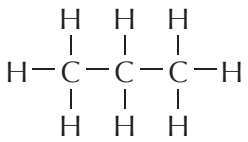
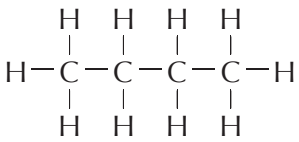
## HYDROCARBONS

Hydrocarbons are substances containing only carbon and hydrogen. Hydrocarbons are classified into the following major categories: **alkanes**, **alkenes**, **alkynes**, and **aromatic hydrocarbons**. In the following pages we will do an overview of the basic characteristics of the first three, but will postpone the study of aromatics until later.

## ALKANES AND $sp^3$ HYBRIDIZATION OF CARBON

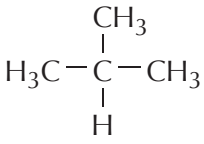
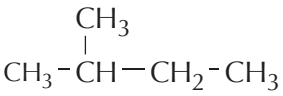
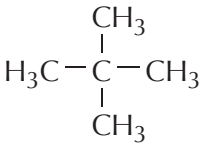
**Alkanes are hydrocarbons where all the carbon atoms are $sp^3$-hybridized, all bonds are single bonds, and all carbons are tetrahedral**. *Methane* is the simplest alkane, followed by *ethane*, *propane*, *butane*, etc. The carbon chain constitutes the basic skeleton of alkanes. Carbon chains with four or more atoms can be **linear** or **branched**. Some examples are shown below including Lewis, molecular, and condensed formulas. Refer to chapter 2 of the Wade textbook for additional examples.

**Linear alkanes**

|  |  |  |  |
|---|---|---|---|
| methane | ethane | propane | butane |
| $CH_4$ | $C_2H_6$ | $C_3H_8$ | $C_4H_{10}$ |
| $CH_4$ | $CH_3CH_3$ | $CH_3CH_2CH_3$ | $CH_3CH_2CH_2CH_3$ |
| $CH_4$ | $CH_3-CH_3$ | $CH_3-CH_2-CH_3$ | $CH_3-CH_2-CH_2-CH_3$ |

Some examples of branched alkanes are shown below. Notice that sometimes Lewis formulas become cumbersome and difficult to write without cluttering. Condensed formulas are more convenient to use in such situations.

**Branched alkanes**

|  |  |  |
|---|---|---|
| isobutane | isopentane | neopentane |
| $C_4H_{10}$ | $C_5H_{12}$ | $C_5H_{12}$ |
| $(CH_3)_3CH$ | $(CH_3)_2CHCH_2CH_3$ | $(CH_3)_4C$ |

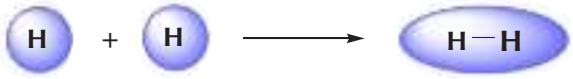
As can be seen from the above examples, **all alkanes have the general formula $C_nH_{2n+2}$** where $n$ is the total number of carbon atoms. This holds regardless of whether the alkane is linear or branched.

## SIGMA BONDING

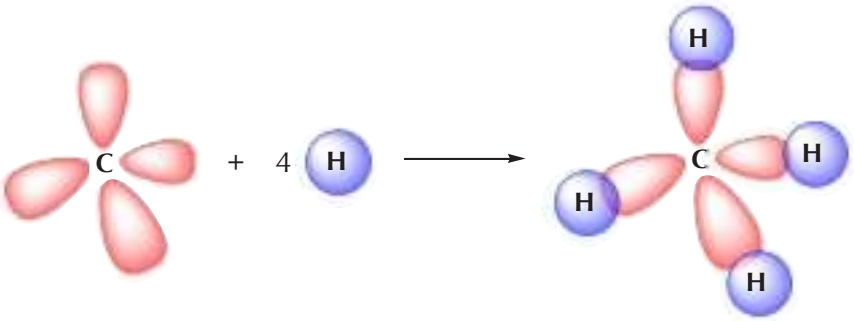
When atomic orbitals (pure or hybrid) of different atoms overlap to form covalent bonds, they may approach each other in two major ways: **head to head**, or **sideways**. Only head to head overlap is possible with *s*-orbitals because they are spherical. Hybrid orbitals also undergo mostly head to head overlap when forming covalent bonds. *p*-orbitals, on the other hand, can approach each other either sideways or head to head. For now, however, we are concerned only with head to head overlap because that's the only type that occurs in alkanes. We'll discuss sideways overlap later in connection with alkenes and alkynes, that is, hydrocarbons that have double and triple bonds respectively.

***When orbitals approach each other in a head to head fashion, the resulting covalent bonds are called sigma bonds***.

As illustrations, consider the bonds that have already been studied. The bond between two hydrogen atoms is an example of sigma bonding. The bonds between the $sp^3$ orbitals of hybridized carbon and the *s* orbitals of hydrogen in methane are also example of sigma bonds.

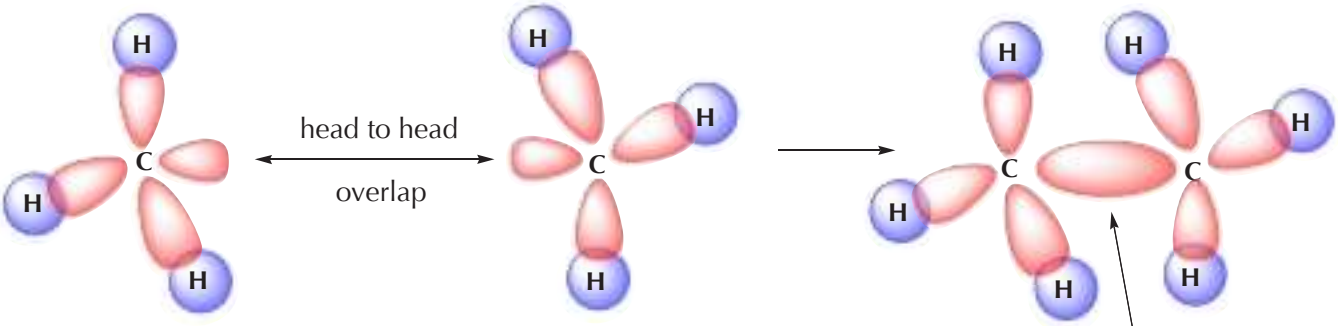



sigma bond
between *s* orbitals




sigma bonds
between *s* and $sp^3$ orbitals

Two $sp^3$ carbons can also overlap to form a C–C sigma bond where two $sp^3$ orbitals overlap head to head, such as in the formation of the ethane molecule:

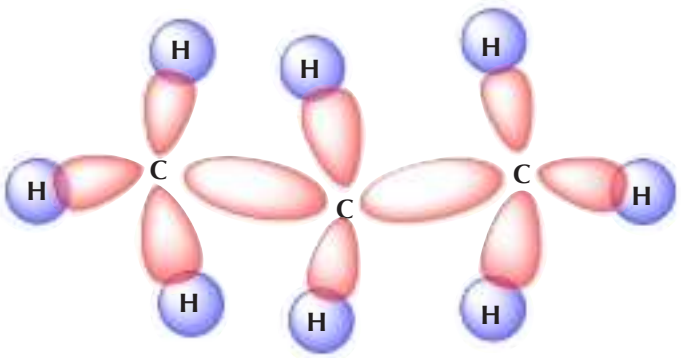


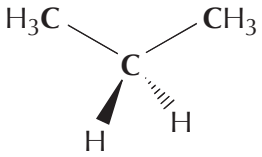

sigma bond
between two $sp^3$ orbitals

It can be easily seen that **the only type of covalent bonds present in alkanes are sigma bonds**, also loosely known as single bonds.

LINE-ANGLE FORMULAS

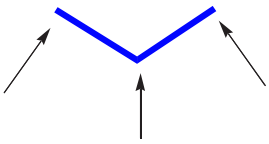
In alkanes of 3 carbon atoms or more, the main carbon chain acquires a zig-zag structure due to the 109.5° angle between C–C bonds, such as in propane:

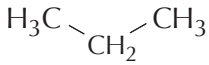



Two representations of propane, where the zig-zag structure of the carbon chain becomes apparent

Writing Lewis formulas, or even condensed formulas, for alkanes of many carbon atoms can quickly become cumbersome. A short hand notation that uses zig-zag lines has been developed. The resulting representations are known as **line-angle formulas**. The beginning and the end of the zig-zag line, as well as any breaks in direction represent carbon atoms.

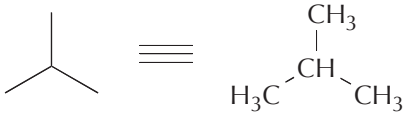


Line angle representation for propane equivalent to  or $CH_3CH_2CH_3$

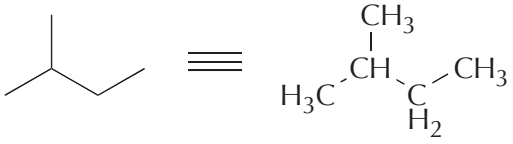
The arrows point to the positions of the carbon atoms.

Every carbon atom has to form 4 bonds. **The bonds that are not shown are assumed to be bonds to hydrogen.** Other examples are:

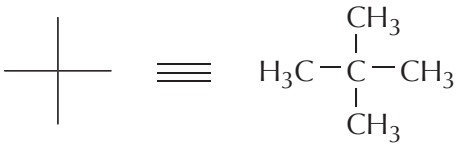
butane




isobutane



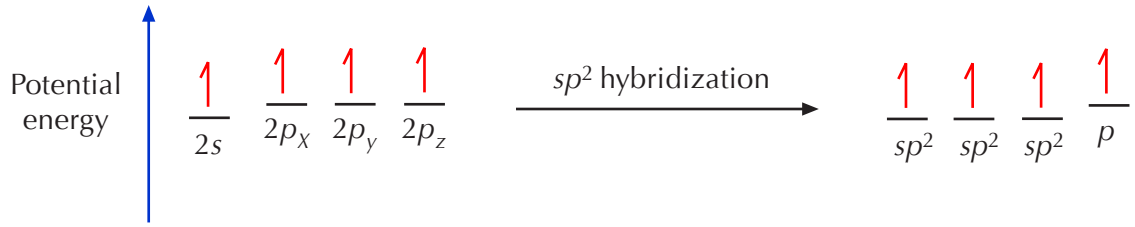

isopentane



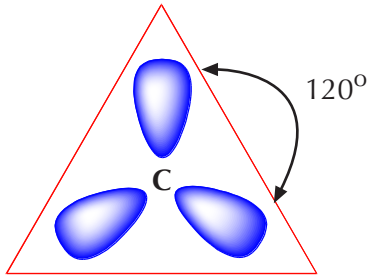

neopentane

## ALKENES AND $sp^2$ HYBRIDIZATION OF CARBON

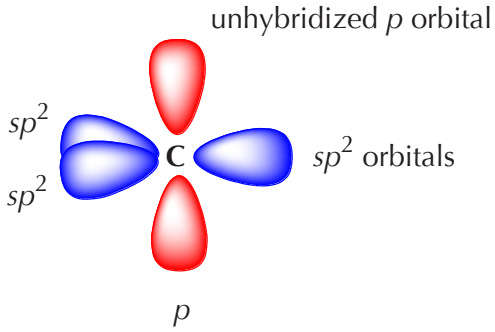
We will now reproduce the $sp^3$ hybridization process for carbon, but instead of taking one *s* and three *p* orbitals to make four equivalent $sp^3$ orbitals, this time we'll take only **one *s* and two *p* orbitals to make three equivalent $sp^2$ orbitals, leaving one *p* orbital untouched**. The process is shown below.



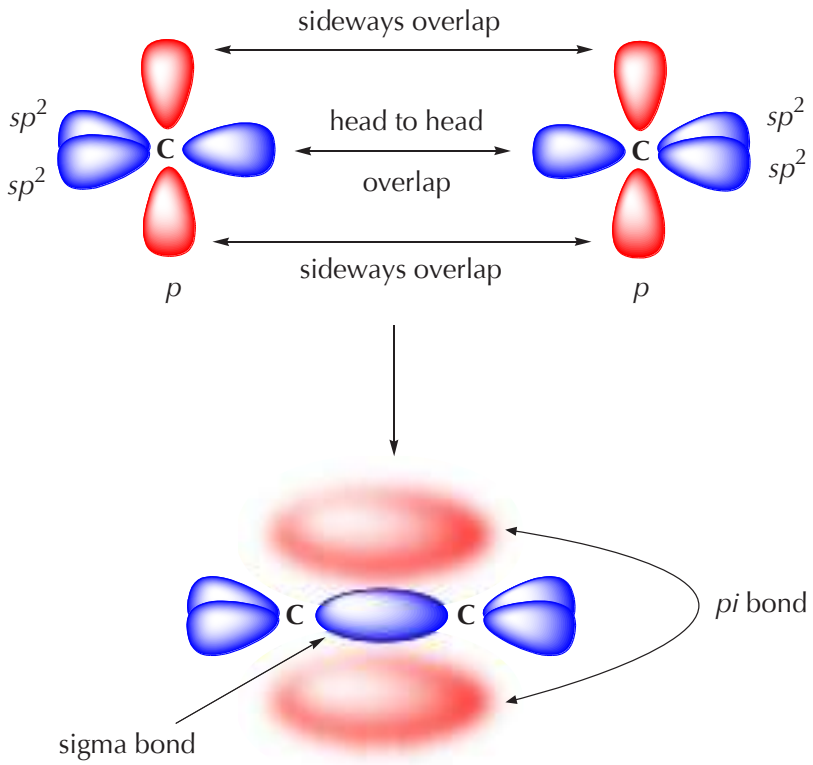

As shown, the three resulting $sp^2$ orbitals are equivalent in energy, but the remaining *p* orbital has not been affected. It still retains its original energy and shape. Again, according to VSEPR theory, equivalent orbitals will arrange themselves in 3-D space to be as far apart from each other as possible. Therefore, the three equivalent $sp^2$ orbitals will arrange themselves in a **trigonal planar** configuration. That is to say, the carbon nucleus will be at the center of an equilateral triangle, and the three $sp^2$ orbitals will point to the corners of that triangle. **The ideal angle between $sp^2$ orbitals is therefore $120^o$**. A **top view** of this arrangement is shown below.




In this top view, the **unhybridized *p* orbital** cannot be seen because it also arranges itself to be as far apart from the $sp^2$ orbitals as possible. That is to say, **it is positioned at right angles to those orbitals**, with one lobe coming out of the plane of the page and the other going behind the page. To see this arrangement clearly, we must switch to a **side view** of the orbital system.




When two $sp^2$ hybridized carbon atoms approach each other to bond, two $sp^2$ orbitals approach each other head to head, and **two *p* orbitals approach each other sideways**. The bond formed by the $sp^2$ orbitals is a sigma bond, and **the bond formed by the *p* orbitals is called a *pi* bond**. The process is shown below.

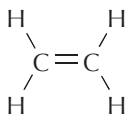



The illustration above tries to convey a basic feature of the *pi* bond as compared to the sigma bond. The sigma bond is short and strong. As a rule, **head to head overlap is the most efficient way to bond and results in relatively strong and stable bonds**. The *pi* bond, on the other hand, is relatively long and diffuse. **Sideways overlap is less efficient than head to head overlap and results in formation of weaker bonds**.

This has some implications in the properties and chemical reactivity of sigma and *pi* bonds. The electrons in the sigma bond (or sigma electrons) are more tightly bound to the nucleus and don't move too much. In other words, they are more **LOCALIZED**. The electrons in the *pi* bond (or *pi* electrons) are less tightly bound by the nucleus, and therefore **they are relatively mobile**. Under certain conditions, they have the capability to become **DELOCALIZED**, that is to say, they can move in the molecular skeleton from one atom to another, or even become spread over several atoms, according to principles we'll study later.

At the same time, in chemical reactions where electrons are to be traded, **the *pi* electrons are more readily available because they are more exposed and less tightly bound by the nucleus**. It is relatively easy to break a *pi* bond compared to the sigma bond. The principles of all this chemistry will be discussed later in the course.

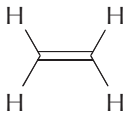
**ALKENES ARE HYDROCARBONS THAT CONTAIN AT LEAST ONE *PI* BOND AS PART OF THEIR MOLECULAR STRUCTURE**. By this definition, the simplest possible alkene must contain two carbon atoms. It is called **ethene**. Below is a Lewis and a line-angle representation of ethene, which is sometimes informally called **ethylene**. Notice that although C–H bonds are not usually shown in line-angle formulas, sometimes they are included for enhanced clarity. In this case a pure line-angle formula for ethene would look awkward because it would resemble an equal sign (=).




Lewis formula

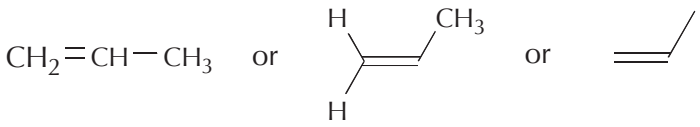
$CH_2{=}CH_2$

condensed formula



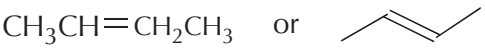

line-angle formula

Notice that **a Lewis representation does not differentiate between the sigma and the *pi* bonds** in the so-called "double bond." It simply shows the two together as two equal dashes. The orbital picture better represents the actual nature of the two types of bonds. Additional examples are shown below. For a full discussion of the structure of alkenes refer to chapter 7 of the Wade textbook.



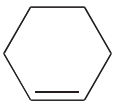

propene

1-butene

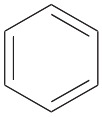



2-butene

cyclopentene



cyclohexene

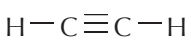


benzene

Observe that **the general formula for open chain monoalkenes –that is, alkenes that do not form cyclic structures and which contain only one pi bond– is $C_nH_{2n}$** where *n* is the total number of carbon atoms.

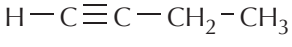
## ALKYNES AND *sp* HYBRIDIZATION OF CARBON

The process for understanding the *sp* hybridization process for carbon is basically an extension of the other two types ($sp^3$ and $sp^2$). You should try to work out this scheme on your own and see if your predictions agree with those presented in the textbook. *sp* hybridization gives rise to the formation of hydrocarbons known as alkynes. **Alkynes contain at least one triple bond**, and have **linear geometry** around the carbons comprising the triple bond. Therefore, the ideal angle between the *sp* hybrid orbitals is **180º**. Some examples of alkynes are shown below. For additional information refer to chapter 9 of the Wade textbook.

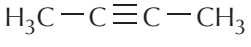



Ethyne, or acetylene

propyne




1-butyne

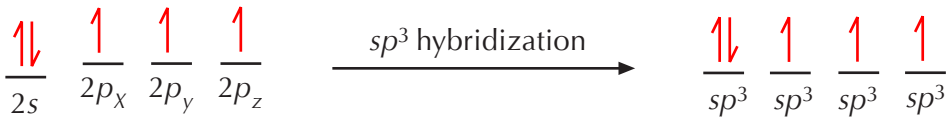



2-butyne

Observe that **the general formula for open chain monoalkynes is $C_nH_{2n-2}$** where *n* is the total number of carbon atoms.

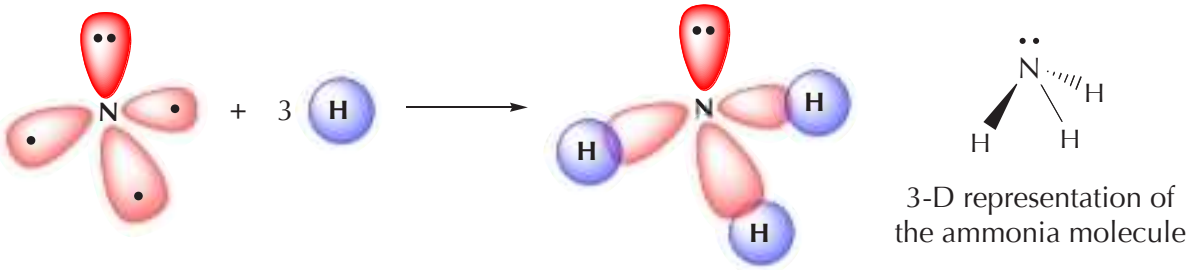
## ORBITAL HYBRIDIZATION IN NITROGEN AND OXYGEN

The hybridization schemes for nitrogen and oxygen follow the same guidelines as for carbon. For example, $sp^3$ hybridization for nitrogen results in formation of four equivalent $sp^3$ orbitals, except that this time only three of them contain unpaired electrons, and one of them contains paired electrons. A similar situation holds true for oxygen, which ends up with two of the $sp^3$ orbitals occupied with unpaired electrons, and the other two with paired electrons.



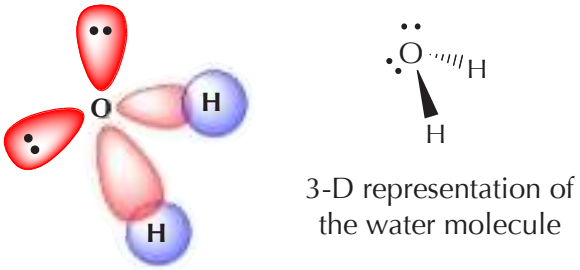

Nitrogen: 5 valence electrons

The four $sp^3$ orbitals again orient themselves in 3-D space to be as far apart from each other as possible, but the ideal 109.5° angle becomes distorted because the orbital with two electrons repels the others more strongly than they repel themselves. However the geometry of this arrangement is still fundamentally tetrahedral. When this $sp^3$ hybridized nitrogen bonds to hydrogen, the three unpaired electrons are used for bonding, and the remaining pair remains as nonbonding electrons.



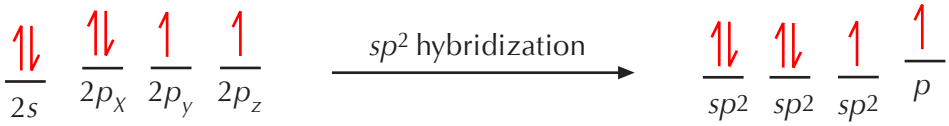

3-D representation of the ammonia molecule

A similar analysis for oxygen should lead to formation of two $sp^3$ orbitals with unpaired electrons, and two with paired electrons. Thus, when $sp^3$ oxygen bonds with hydrogen it forms water, which has a distorted tetrahedral angle, and two pairs of nonbonding electrons in the structure.



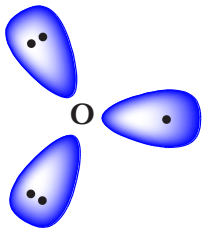

3-D representation of the water molecule

Now, what happens when nitrogen or oxygen become $sp^2$ hybridized? The exact same thing that happened with carbon, with some minor changes. Let's go through the process with oxygen to illustrate how it bonds to carbon to make a class of substances known as carbonyl compounds.

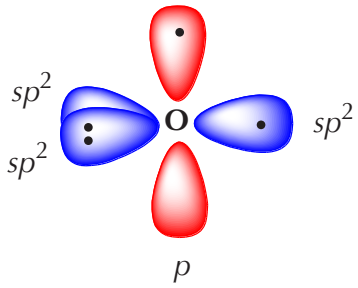



Oxygen: 6 valence electrons

Three equivalent *sp*2 orbitals have formed, two of them containing paired electrons, and one containing a single unpaired electron. The unhybridized *p* orbital remains, with an unpaired electron in it. Again, VSEPR theory dictates that the three equivalent *sp*2 orbitals will acquire a trigonal planar arrangement, while the unhybridized *p* orbital will remain at right angles to the *sp*2 orbitals.

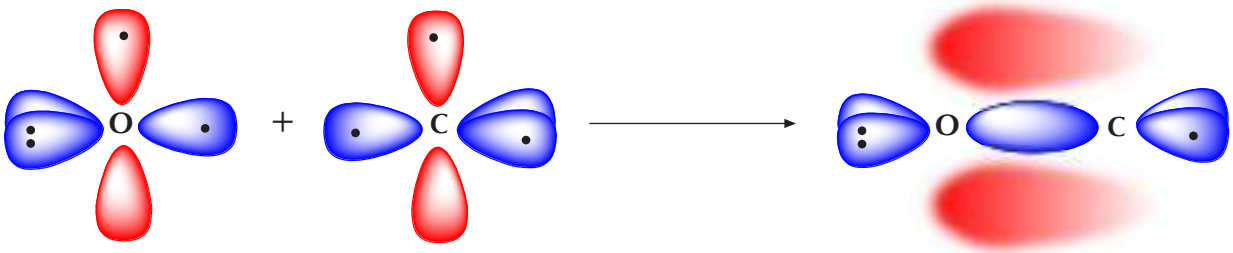


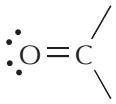

***sp*2 oxygen, top view**



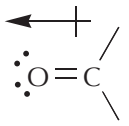

***sp*2 oxygen, side view**

When an *sp*2 oxygen approaches an *sp*2 carbon for bonding, the process is analogous to that followed by two *sp*2 carbons that bond to form a "double bond." Only those orbitals containing unpaired electrons can bond. In this case, the *sp*2 orbitals from oxygen and carbon that contain unpaired electrons will overlap head to head to form a sigma bond. At the same time, the *p* orbitals will overlap sideways to form a pi bond. Thus, we have the effective formation of a C=O "double bond."



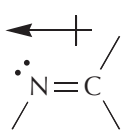

$sp^2$ oxygen + $sp^2$ carbon ⟶  C=O double bond

Notice that the *pi* bond in the C=O "double bond" appears distorted, indicating higher electron density around the oxygen than around the carbon. This is because **the C=O bond is polar**. The more electronegative oxygen atom attracts bonding electrons towards itself more strongly than carbon.

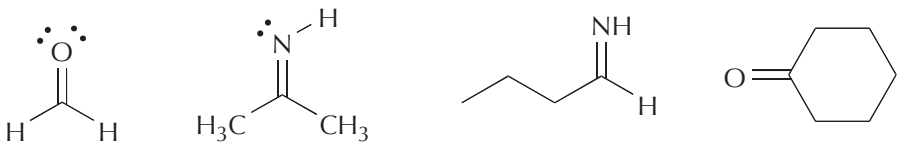


The C=O double bond is polar

A similar analysis for nitrogen leads to the picture and geometry of a C=N double bond:



Some examples of compounds containing $sp^2$ carbon, nitrogen, and oxygen are shown below. Notice that Lewis and line-angle formulas frequently neglect showing the lone pairs of electrons. Unless there is a specific purpose for showing nonbonding electrons, they are usually omitted and assumed to be present.




By going through an analogous process for ***sp* hybridization** of nitrogen and oxygen we can arrive at the molecular structure of species containing carbon-nitrogen and carbon-oxygen triple bonds. Notice that an oxygen containing a triple bond must also carry a positive charge in observance of the rules of covalent bonding.

Also notice that when two *sp* or $sp^2$ atoms are bonded together to form a double or triple bond, they both must be of the same hybridization. There are some exceptions, but this is true in most common situations.

## SUMMARY

The preceding discussion covers the most common cases of atom hybridization encountered in this course. The following summarizes the concepts associated with each type of hybridization.

| | | | | |
|---|---|---|---|---|
| ***sp*³ hybridization** | 4 orbitals | tetrahedral geometry | ideal angle: 109.5° | single bonds |
| ***sp*² hybridization** | 3 orbitals | trigonal planar geometry | ideal angle: 120° | double bonds |
| ***sp* hybridization** | 2 orbitals | linear geometry | ideal angle: 180° | triple bonds |