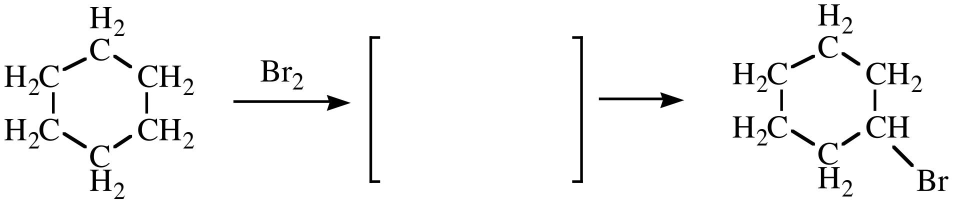
1. Lewis Structures.

1.1 What is Organic Chemistry? Why Study It?

Organic chemistry is the study of the chemical behavior of compounds containing the element C. C is unique among all the elements for its ability to form strong bonds to itself. Some of you may have read SF novels in which Si-based life is presented as a possible alternative to C-based life. This is more fiction than science, because Si—Si bonds are quite weak and prone to cleavage. C can join to itself in long chains that point in all directions of space, and it is this property that makes it possible for millions of carbon-containing compounds to exist.

In this course we'll be studying the *structure, reactivity, and synthesis* of organic compounds. For example, we'll look at the following reaction.



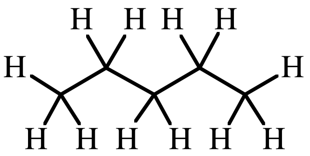
We'll ask, what are the three-dimensional shapes of the starting material and the product? What parts of the starting material are likely to be transformed under given conditions? What are the unstable intermediates in this reaction, if any? How many different products can be obtained? And, what is the nature of the bonds that are broken and the bonds that are formed?

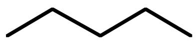
1.2 Ways of drawing structures.

Even before we begin taking about Lewis structures, I would like to discuss one of the ways in which organic chemistry is a new language that you must learn. You are used to drawing chemical structures in which every element is represented by its elemental symbol.

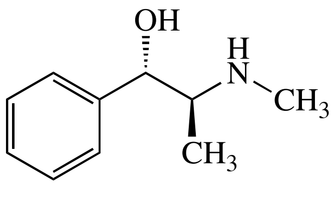
Organic chemists, however, are lazy. Once we get up to five or more C atoms, drawing in all the C and H atoms becomes very tedious. So we have a shorthand: we omit the C atoms. A C atom is indicated by the presence of a junction between two bonds. But drawing out all the H atoms is still tedious. So we also omit all of the H atoms and the C–H bonds. Now the structure is very easy to draw. *The skeletal structure shown below on the right is understood to have enough H atoms at each C atom to satisfy the valency of that C atom.*

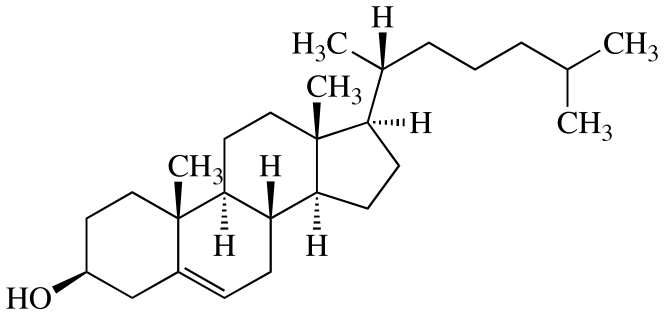
$CH_3CH_2CH_2CH_2CH_3$





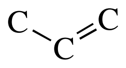
Note that only H atoms attached to C may be omitted. H atoms attached to heteroatoms (anything other than C or H) must be drawn out, although they may be done in the condensed form.



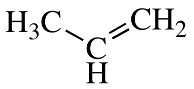


Some rules:

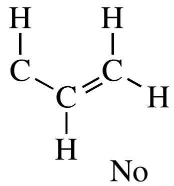
1. If you write a C, you must write the H atoms attached to that C (in condensed form or by drawing out the bonds).
2. If you write one H attached to a C, you must write all the H atoms attached to that C.
3. Never omit H atoms attached to heteroatoms (O, N, etc.).



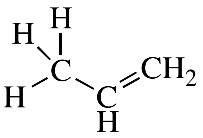
No



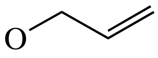
Yes



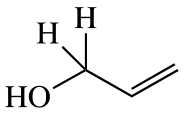
No



Yes



No

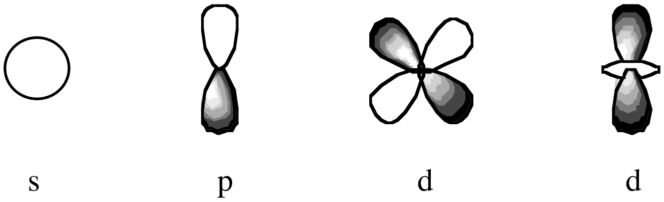


Yes

1.3 Electronic Structure of Atoms and Molecules. Valence Structures.

Remember that every atom has a characteristic number of electrons, given by its number in the periodic table. H has 1, C has 6, N has 7, O has 8, Cl has 17. Every electron in an atom resides in a region of space called an *orbital,* which has its own characteristic energy. Orbitals are divided into groups called *shells*. It takes two electrons to fill shell 1, which has only one s orbital. It takes eight electrons to fill shell 2, which has one s and three p orbitals. The order of energy of orbitals is as follows: 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s .... (The 3d orbital needs not to be filled for shell 3 to be considered filled.)

Some atomic orbitals



Following the *aufbau principle,* the electrons in an atom go into these orbitals in order of increasing energy. So the following atoms have the electronic structures shown.

H	$1s^1$
C	$1s^2\ 2s^2\ 2p^2$
O	$1s^2\ 2s^2\ 2p^4$
F	$1s^2\ 2s^2\ 2p^5$
F^-	$1s^2\ 2s^2\ 2p^6$
Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$

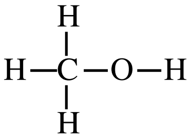
The electrons with which we are concerned are the outer-shell, or *valence,* electrons. The valence electrons are the electrons in the outermost shell. For neutral atoms the number can be obtained by looking at the element's column in the periodic table. H has 1, C has 4, N has 5, O and S have 6, F and the other halogens have 7. F^- has no or eight valence electrons, depending on how you count it, because its outer shell is filled.

Atoms link together to form molecules because they "like" to achieve a filled shell configuration. They achieve this by giving up or taking electrons (ionic bonds) or by sharing electrons (covalent bonds). In organic chemistry, we can have molecules that consist of as few as two atoms (CO) or those that consist of millions of atoms (DNA). The tremendous diversity of structures is what makes life possible. In organic compounds, most bonds are covalent.

If you are given a molecular structure, even a rather complex one, you can use a series of rules to construct the electronic structure of that molecule. Consider amide ion NH_2^-, ammonium ion NH_4^+, methanol CH_3OH, hydrogen cyanide HCN, and methyl acetate, $CH_3CO_2CH_3$.

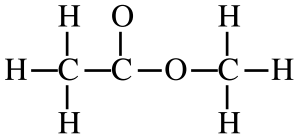
(1) Count the total number of valence electrons. Add one for every negative charge and subtract one for every positive charge. So, e.g., NH_2^- has 8 valence electrons ($5 + 2\times1 + 1$) and NH_4^+ has 8 also ($5 + 4\times1 - 1$). Methanol has 14, HCN has 10, and methyl acetate has 30 valence electrons ($3\times4 + 6\times1 + 2\times6$).

(2) Attach the atoms in the correct order using single bonds, being careful to give no atom more than four bonds (duet for H). Each bond uses two valence electrons. There are often many ways of combining the same atoms (this is called isomerism), and so you must have more information than just the empirical formula to do this. This may be supplied by an extended formula or by other information that we will learn to interpret later in the course. For NH_2^- and NH_4^+, there is only one way to attach the atoms to each other. These use up 4 electrons and 8 electrons, respectively, leaving 4 and 0 unused electrons, respectively. For methanol, the way the formula is written suggests that there are three H's attached to C and one attached to O. For HCN, there are two ways to arrange the atoms (H–C–N or C–N–H), but we can tell by the way the formula is written that the atoms should be attached H–C–N. We use up four electrons, leaving six. For methyl acetate, there are several ways to arrange the atoms, but we can tell by the way the formula is written that the atoms should be attached as shown. (The designation CH_3, the methyl group, indicates C bound to three H atoms and one other atom.) This uses up 20 valence electrons, leaving 10 more.



$$\begin{array}{ccccccc} & & \mathrm{H} & & & & \\ & & | & & & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{H} \\ & & | & & & & \\ & & \mathrm{H} & & & & \end{array}$$

H—C—N

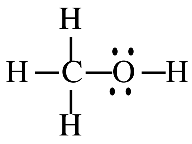


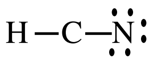
$$\begin{array}{ccccccccccc} & & \mathrm{H} & & \mathrm{O} & & & & \mathrm{H} & & \\ & & | & & | & & & & | & & \\ \mathrm{H} & - & \mathrm{C} & - & \mathrm{C} & - & \mathrm{O} & - & \mathrm{C} & - & \mathrm{H} \\ & & | & & & & & & | & & \\ & & \mathrm{H} & & & & & & \mathrm{H} & & \end{array}$$

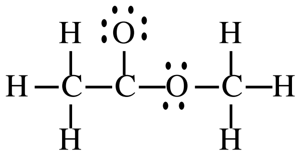
When you are constructing the single bond framework of an organic compound, it is useful to remember that H and the halogen atoms are normally found on the periphery of an organic structure, and not in the middle, because they have only one free valence. The CH_3 group has only one valence, too.

(3) Place the extra valence electrons on the *heteroatoms* (atoms that are different from C and H) or *between pairs of neighboring electron-deficient atoms,* being careful to give no more than a total of 8 electrons to each atom. (Each bond to an atom counts as two electrons.) *Usually C makes a total of four bonds, N three, O two, and H and the halogens one*. For NH_4^+, no extra electrons need to be placed. For NH_2^-, four electrons go on N. For methanol, the four electrons go on O. For HCN, the six electrons go on N. For methyl acetate, the five pairs of

electrons can be distributed among the two O atoms to give the structure shown. (Alternatively, two pairs of electrons may be placed on each O and one pair between the electron-deficient C and upper O.)

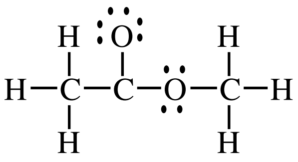






(4) Are any atoms electron-deficient by two or more electrons? If so, take a lone pair of electrons on a next-door neighbor and turn it into a bond between the electron-poor atom and its neighbor. If you have a choice of neighbors from which to borrow a pair of electrons, choose it from the neighbor that lacks its "normal" number of bonds. Neither NH_2^-, NH_4^+, nor CH_3OH have any electron-deficient atoms. In HCN, the C atom only has four electrons around it, so it needs to borrow two pairs of electrons from N. A triple bond between C and N results. In methyl acetate, the second carbon atom has only 3 bonds, giving it 6 electrons in its outer shell, so it is electron-deficient. We can amend this by borrowing a pair of electrons from the O on the top or on the right, but it is better to borrow it from the O on the top, which only has one bond so far, than the O to the right, which already has two bonds.

$H-C\equiv N:$



Note: if you have an odd total number of electrons, in the end you will end up with one atom that has only seven total electrons around it. That's OK; such a compound is called a *free radical,* and its reactivity is characterized by the fact that one of its atoms is electron-deficient.

(5) Assign *formal charges*. Because C, N, O, and H and the halogens require four, three, two, and one electrons to complete their valence shells, respectively, they *usually* make four, three, two, and one bonds to other atoms, respectively. An atom that is making an “unusual” number of bonds must have a formal charge assigned. For methanol, HCN, and methyl acetate, no formal charges need to be assigned, but for NH_2^- and for NH_4^+, they must be assigned. The formal charge for any atom is calculated by:

(eq. 1) formal charge = valence electrons – number of bonds – number of unshared electrons

A quick way of assigning formal charges to electronegative atoms such as N, O, and halogens comes from the fact that electronegative atoms in organic compounds almost always have their octet. If an atom has an octet, then the sum of the number of unshared electrons and twice the number of bonds equals eight. Then the formula for formal charge for an octet-bearing atom becomes:

(eq. 2) formal charge (octet-bearing atom) = valence electrons + number of bonds – 8

For N or P (five valence electrons), the formal charge is number of bonds – 3. For O or S, it is number of bonds – 2. For halogens, it is number of bonds – 1. In other words, the formal charge for an *electronegative* octet-bearing atom is usually:

(eq. 3) formal charge (octet-bearing atom) = number of bonds – "usual" number of bonds

This formula does not hold for C, which, as an electropositive element, often lacks an octet. In fact, C can have a formal charge of +1, 0, or –1, depending on whether it has no, one, or two unshared electrons. Even more electropositive elements like B and Al have a formal charge of 0 when they have three bonds (because they have a sextet), and they have a formal charge of –1 when they have four bonds (when they have an octet). The formula also does not hold if the electronegative atom lacks an octet. For example, in hydroxyl radical, HO·, the O atom has only seven electrons and has no formal charge. In any of these situations, you must use eq. 1. But, most of the time, for elements such as N, O, P, S, and the halogens, you can use eq. 3.

In any case, *the sum of all the formal charges in a compound must add up to the total charge on that compound.*

We need to distinguish strongly between *formal charge* and *electron deficiency*. An atom is electron-deficient when it lacks an octet (or for H, a duet). An atom has a formal charge if the total number of electrons in its bonds and lone pairs is different from its number of valence electrons. The two properties are orthogonal, i.e. an atom with one may or may not have the other. For example, consider NH_3 and NH_4^+. In both of these compounds, N is electron-sufficient, but in one it has a formal charge and the other it doesn't. Now consider CH_3 and CH_4. In both of these compounds, C has no formal charge, but in one it is electron-deficient and in the other it is not. One way to think about it is as follows. Formal charge is a bookkeeping mechanism that we use to keep track of the number of electrons, it is in our mind. Electron deficiency is a *real* property that has *real* consequences for the behavior of organic compounds.

This is illustrated by the fact that O atoms with a formal positive charge (e.g., H_3O^+) are quite commonly seen in organic chemistry, despite O's strong electronegativity; yet an electron-deficient O atom with only six electrons around it is extremely rare.

1.4 Common Bonding Situations.

We've seen that C "normally" makes 4 bonds, N 3, O 2, and H and halogens 1. But there are a lot of ways that these valences can be fulfilled. Here are some of the most common.

C normally makes four bonds. The four bonds can be made to four different atoms, as in CH_4. Or two can be to one atom and the other two to two others, as in formaldehyde or ethylene. Or three can be to one atom and the fourth to another, as in acetylene or HCN. Occasionally one sees molecules where C makes two bonds to one atom and two bonds to another, as in CO_2.

Sometimes C makes only three bonds. There are three kinds of trivalent C: free radicals, carbanions, and carbocations, depending on whether the C has a total electron count of 6, 7, or 8 electrons. Compounds containing trivalent C are usually very reactive compounds that exist only fleetingly as intermediates; that is, they rapidly are converted to other species containing tetravalent C.

O normally makes two bonds. The two bonds can be to two different atoms, as in water, or to the same atom, as in acetone. Sometimes we see O with only one bond, and in this case it almost always has a formal minus charge, as in HO^-, because it must have a total electron count of 8 being very electronegative. Sometimes we see O with three bonds, as in H_3O^+, and here it must have a formal + charge and a total electron count of 8.

N normally makes three bonds. Ammonia, pyridine, and HCN are three examples. Sometimes N is divalent, as in NH_2^-, and here it has a formal minus charge. Sometimes N is tetravalent, as in NH_4^+, and here it has a formal + charge.

H and the halogens normally make one bond. Sometimes H is bonded to nothing else. It may have an empty outer shell, as in H^+, or a filled outer shell, as in H^-. A halogen bound to nothing else may be neutral, with seven electrons in its outer shell, but more often it has 8 electrons and a formal minus charge.

Normally P and S are perfectly analogous to N and O. But sometimes they are “hypervalent”, and a lone pair can be replaced by a double bond to O. So we have phosphoric acid, DMSO, and mesyl chloride.

Organic chemists usually omit lone pairs or unshared electrons when drawing organic structures, but it is important for you to know how many they are there. How do you tell how many unshared electrons an atom has? Simple: we already know that,

(eq. 1) formal charge = valence electrons – number of bonds – number of unshared electrons

Therefore,

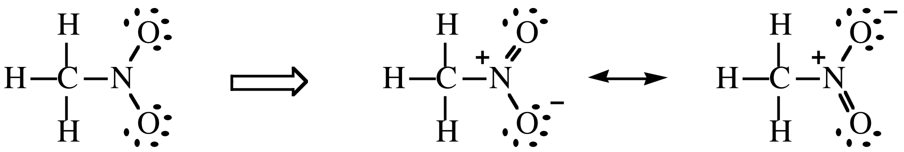
(eq. 4) number of unshared electrons = valence electrons – number of bonds – formal charge

So a neutral halogen or negative O with one bond has three lone pairs, a neutral O or negative N with two bonds has two lone pairs, and a neutral N or positive O with three bonds has one lone pair.

Warning: Before you apply this formula to C, make sure that you have drawn in as many C–H bonds as appropriate for that atom! A C atom that is indicated by a vertex (not by the letter C) makes three bonds if a charge or a single unshared electron is indicated. It makes four if nothing special is indicated.

1.5 Resonance Structures.

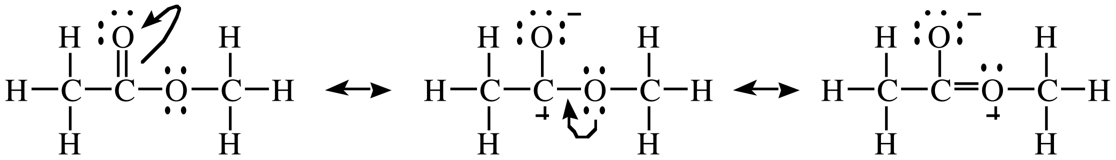
Sometimes, after you have assigned all the electrons to a structure and you start sharing heteroatom lone pairs with electron-deficient atoms, you find that there is more than one way to arrange the electrons. The structures that are obtained thereby are called *resonance structures*. Two structures are resonance structures if they differ *only* in the location of *double and triple bonds and non-bonding electrons*. They must not differ in the location of single bonds, i.e. in which atoms are bound to which other atoms. For example, let's look at nitromethane, H_3CNO_2. In this compound, N is bound to two O's and one C. After we compute the total number of valence electrons and assign them all to the various atoms, we obtain the structure shown. We can borrow a pair of electrons from either the top O or the bottom one. Which should it be?



In fact, either one is OK. The fact that we can borrow from either O means that after assignment of formal charges, we have two possible structures. In one of them, the top O is doubly bound and neutral and the bottom O is singly bound and has a formal positive charge; in the other, the situation is reversed. Does this mean that the two O atoms in nitromethane are different? N–O bond lengths and all spectroscopic properties show that the two O atoms are exactly identical. We rationalize this by saying that the two structures are *resonance structures* that each contribute an equal weight toward the description of the compound. Two resonance structures are drawn with a double-headed arrow (↔) between them.

Students sometimes have trouble understanding the concept of resonance structures. The double-headed arrow doesn't mean that the compound is going back and forth between the two resonance descriptions. Think of it like this. There is a real compound, out there in the real world. We construct diagrams called Lewis structures to *describe* the real compound in concepts that a person can understand. Lewis structures, in other words, are like adjectives in a language called chemistry, and as is true in all languages, sometimes just a single word does not suffice to describe the compound. In the case of nitromethane, the two resonance descriptions of nitromethane are two equally good descriptions of what is going on out there in the real world, but each one alone is inadequate. To really describe what is going on in the real compound, we need to transform the two resonance descriptions into mathematical equations and average the two equations. The equation we get is a better description of the real nitromethane.

In nitromethane, the two resonance structures are equally good descriptions of one another. This is not always true. Sometimes, one resonance structure is sometimes a *better* description of the compound than the others. For example, let's take our drawing for methyl acetate and move the pair of electrons in the second bond between C and the top O back up to O. (Remember, resonance structures differ only in the placement of lone pairs and double and triple bonds.) We use a curved arrow to show the change in location of the electrons. After we assign formal charges, we get a new resonance structure. The central C is electron-deficient now, so we can generate the old resonance structure by moving a pair of electrons from the top O to between C and O, or we can make a new resonance structure by borrowing a pair of electrons from the O on the right. Again we need to assign formal charges.



Three resonance structures, or three adjectives. Which is the *best* description of the real methyl acetate? Use the following rules in the order shown to determine the best resonance structure.

1. Resonance structures in which any atom has more than an octet (duet for H) are *not* acceptable.
2. It *is* acceptable to draw a resonance structure in which electron-deficient atoms are present, but the fewer the electron-deficient atoms, the better the resonance structure. (Cf. structures 1 and 2 of methyl acetate above.) If there must be electron-deficient atoms, they should be relatively electropositive ones (C, B) rather than electronegative ones (N, O).
3. Structures with fewer formal charges are better than those with more formal charges, unless this violates rule #2.
4. If there must be formal charges, the negative charges should be located on atoms that are as electronegative as possible, and the positive charges should be located on atoms that are as electropositive as possible.

Using these rules, we deduce that the left-hand structure for methyl acetate is the best. This does not mean that the other resonance structures have no contribution to the electronic nature of the compound, i.e., that they are worthless adjectives. Au contraire! Often a *minor* resonance structure gives us an insight into the reactivity of a compound. We will see this for methyl acetate when we discuss the reactivity of carbonyl compounds later.

To generate resonance structures, use the following techniques.

1. Look for an electron-deficient atom. If you find one, see if its next-door neighbor has a lone pair that it can share or if the neighbor has a π bond to yet another atom from which it can take one or two electrons to share with the electron-deficient atom. $H_2\ddot{N}–BH_2 \leftrightarrow H_2\overset{+}{N}=\overset{-}{B}H_2$, $Me_2C=CH–\overset{+}{C}H_2 \leftrightarrow Me_2\overset{+}{C}–CH=CH_2$, $Me_2C=CH–\dot{C}H_2 \leftrightarrow Me_2\dot{C}–CH=CH_2$.
2. Look for an atom with a lone pair. If you find one, see if it can share its lone pair with a neighbor, either because the neighbor is electron-deficient or because the neighbor makes a π

bond to yet another atom. In the latter case, the π bond breaks and the electrons go to the distal atom. $H_2\ddot{N}{-}CH{=}CH_2 \leftrightarrow H_2\overset{+}{N}{=}CH{-}\bar{C}H_2$, and $O{=}CH{-}\bar{C}H_2 \leftrightarrow \bar{O}{-}CH{=}CH_2$.

3. Look for a ring of alternating double bonds. The double bonds can be moved around to generate a new structure that is different from the original one.
4. Look for a π bond. Both electrons in that bond may be given to either atom of the π bond, or one electron may be given to one atom and one to the other. In either case, the π bond is broken. $H_2C{=}CH_2 \leftrightarrow H_2\overset{+}{C}{-}\bar{C}H_2 \leftrightarrow H_2\dot{C}{-}\dot{C}H_2 \leftrightarrow H_2\bar{C}{-}\overset{+}{C}H_2$.
5. A C or N atom bonded to four different atoms does *not* participate in resonance. N bound to three atoms or O bound to two atoms can *donate* a pair of electrons to a neighbor, but it cannot *accept* a pair of electrons.

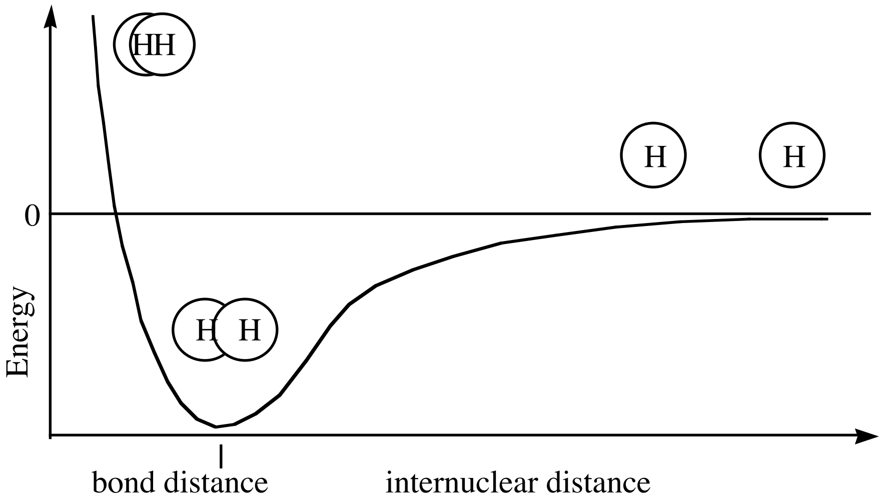
Why are resonance structures important? As we have seen, a single Lewis structure is often not sufficient to give us a good description of a compound. Just as important, though, is the fact that *the more low-energy resonance structures can be drawn for a compound, the lower in energy that compound is*. This is especially true of structures in which one or more atoms is eletron-deficient. E.g., $\overset{+}{C}H_2CH_3$ is very high in energy, but $\overset{+}{C}H_2CH{=}CH_2 \leftrightarrow CH_2{=}CH\overset{+}{C}H_2$ is much lower in energy.

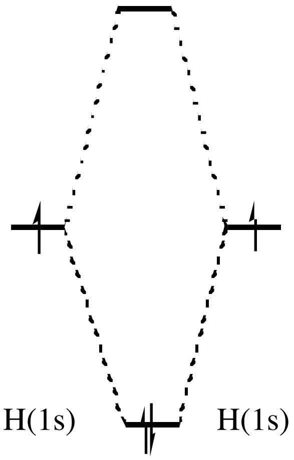
Another important reason for understanding resonance structures: *The lowest energy structure is the best description of a compound, but it is usually the second-best resonance structure that tells you about the reactivity of a compound.* E.g. Carbonyl compounds, CH_2N_2, $CH_2{=}\overset{+}{O}Me$.

1.6 Atomic and Molecular Orbitals.

We can use *molecular orbital (MO) theory* to describe the structure of molecules in more detail. MO theory also provides a means of predicting the shapes of molecules. In MO theory, our first hypothesis is that bonding occurs by the overlap of singly occupied atomic orbitals. So if we look at H_2, we see that two singly occupied *s* orbitals, each with a spherical shape, come together in space to form a new MO with an oblong shape. Electrons in this new MO have less energy than electrons in either of the two atomic orbitals with which we started. As a result, energy is released, and the molecule that is formed is more stable than the individual atoms form which it was formed. You might think that the atoms could keep coming together until they were merged, but at a certain distance the repulsion between the positively charged nuclei becomes important. The balance point is called the *bond distance*. At this point the energy of the system is at a minimum. We can draw diagrams like the ones below.

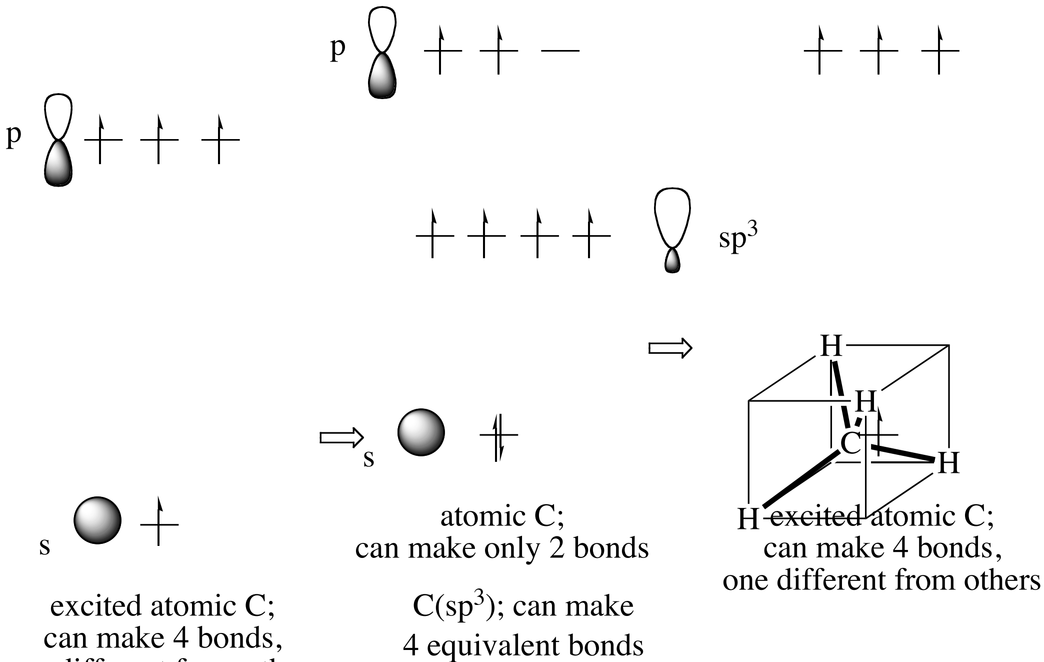
The diagram on the right shows how two atomic orbitals come together to form a bonding orbital of lower energy than either constituent orbital. It also shows that an anti-bonding orbital of correspondingly higher energy is formed. If two He atoms come together, we can draw exactly the same picture, except that we would have to put the two extra electrons in the anti-bonding orbital. Then we would have equal amounts of loss and gain in energy. The net result would be no gain in energy for the system, and the two He atoms would be happier to fly apart than they would be to stick together.





1.7 sp³ Hybridization.

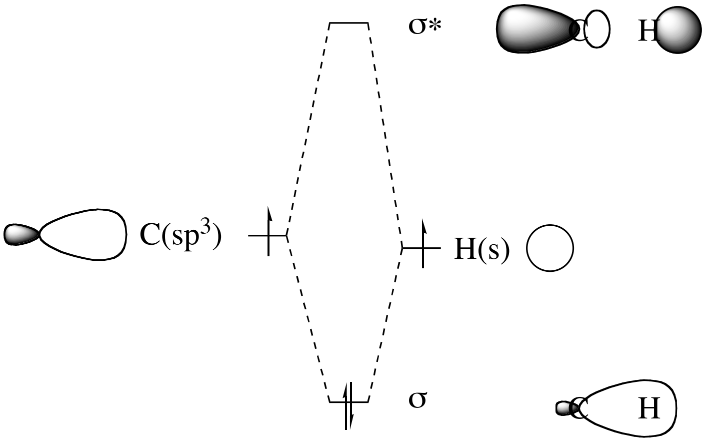
Remember that C has four valence electrons in the configuration $2s^2 2p_x{}^1 2p_y{}^1$, where p_x and p_y are two of the three p atomic orbitals (AOs) in shell 2. Since C has two singly occupied AOs, we might expect that it would form two bonds. In fact, C almost always likes to form four bonds, as in methane, CH_4. What can we do? The first thing we can do is promote one electron from 2s to $2p_z$. Then we have the configuration $2s^1 2p_x{}^1 2p_y{}^1 2p_z{}^1$, with four singly occupied AOs. This helps a lot. Now we can say that each AO is used to form one bond to H in CH_4.



There is still a problem, though. The angle between each of the *p* orbitals is 90°, so we might guess that three of the four C–H bonds in methane are 90° apart. In fact every bit of evidence shows that all four C–H bonds are equivalent. Something must be done. What we do is to average the four *s* and *p* AOs mathematically. This gives us four equivalent AOs. We call them sp^3 orbitals, because they consists of 1 part *s* orbital and 3 parts *p* orbital. Their energy is 3/4 of the distance between *s* and *p*. They point at 109.5° angles from each other, that is, to the four corners of a tetrahedron. C can use each hybrid AO to overlap with a H(*s*) orbital to make two new MOs.

[How do we derive 109.5°? Look at the depiction of the CH_4 tetrahedron within the octahedron. Consider the midpoint, M, of the line connecting any two H atoms. If the length of a side of the octahedron is 1, the distance from M to either H must be (√2)/2, and the distance from M to C must be ½. The H-M-C angle is 90°, so we can use trigonometry (remember SOHCAHTOA?) to conclude that the H–C–M angle is $\tan^{-1}(\sqrt{2})$, or 54.74°. The H–C–H angle is twice this number, or close to 109.5°.]

The concept of hybridization is very different from that of bond-making, even though both involve mixing orbitals to make new orbitals. In hybridization, a single atom takes its AOs and uses mathematics to convert them into the same number of new AOs. No physical change has taken place; the total energy of the AOs is the same, and the amount of space covered by those AOs is the same. In bonding, two *different* atoms come together, and one AO from each overlap to form new *MOs*. When two AOs come together in this way, one new MO is lower in energy, and one is higher in energy. If each constituent AO contained one electron, then two electrons go into the bonding MO, and a bond is formed because the two electrons have lower energy than they would if the two atoms were far apart. That is, the new hybrid AOs are used to make bonds just as the individual "pure" AOs might have done.

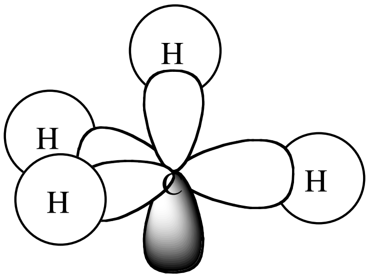


1.8 Hybridization in Alkenes.

We can hybridize orbitals in other ways, too. If we combine the *s* orbital with *two p* orbitals and leave the third one unaltered, we have *sp*^{2} *hybridization*. An *sp*^{2}-hybridized atom has three equivalent *sp*^{2} orbitals, each with 1/3 *s* and 2/3 *p* character, and one unadulterated *p* orbital. The *sp*^{2} orbitals are 120° apart. If we combine the *s* orbital with *one p* orbital and leave the other two unaltered, we have *sp hybridization*. An *sp*-hybridized atom has two equivalent *sp* orbitals, each with 1/2 *s* and 1/2 *p* character, and two unadulterated *p* orbitals. The *sp* orbitals are 180° apart. The two *p* orbitals are perpendicular to each other and to the line containing the *sp* orbitals. Cartoons of sp^3, sp^2, and *sp* orbitals all look like a fishy, although in fact they have slightly different shapes.

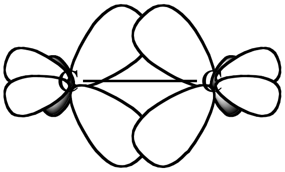
Under what circumstances do we find C(sp^3), C(sp^2), and C(*sp*) hybridization, and how does C "choose" a particular hybridization? Suppose CH_4 were sp^2-hybridized. Three H atoms would be coplanar, and the fourth, whose *s* orbital overlapped with the *p* orbital, would have a 90° angle with respect to the other three. Moreover, half the *p* orbital's bonding density would be wasted on the side of the C atom opposite the unique H atom. So we can see that sp^3 hybridization is best for a C atom that is bound to four different atoms.

CH_4 with C(sp^2)



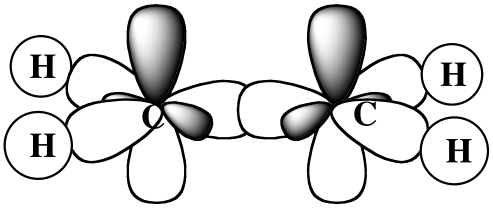
However, when a C atom is bound to three different atoms, the situation changes. Consider ethene (ethylene, $H_2C{=}CH_2$). If the C atoms were sp^3-hybridized, we would need to use two hybrid orbitals to construct the double bond. They would need to be canted with respect to the C–C axis, thus putting only a small amount of electron density between the two C nuclei. Not a good situation!

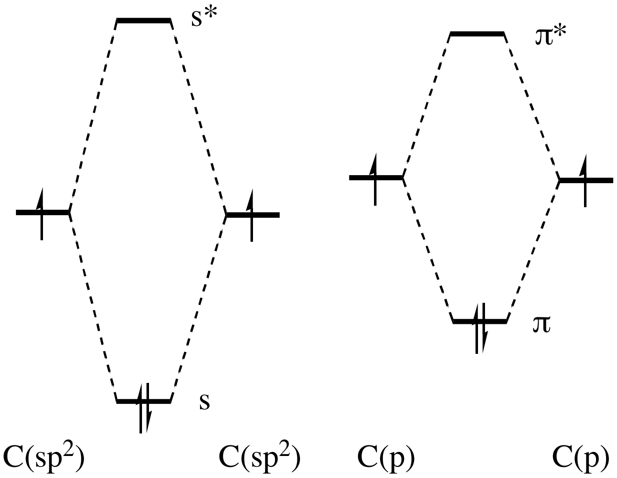
$H_2C{=}CH_2$ with C(sp^3)



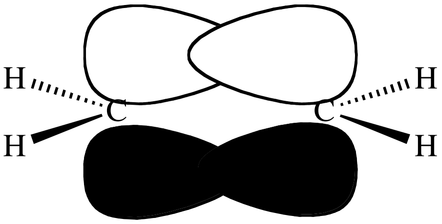
To put maximum density between the two C nuclei, the C atom must place an orbital in the same plane as the C–H bonds. This arrangement is achieved by sp^2 hybridization. The three C(sp^2) orbitals on one C atom are used to form two σ bonds to H atoms and one σ bond to the other C. The *p* orbital is used to form the second bond to the other C atom. The C(*p*) orbitals overlap with each other lengthwise, giving a bond that does not look like the σ bonds we have seen already. This bond is a π bond. It has a node, i.e., a plane in which no electron density resides.

The C(p) orbital has a higher energy than the C(sp^2) orbital used to make the σ bond, and the C(p)–C(p) overlap is poorer than the C(sp^2)–C(sp^2) overlap, so the energy of the C–C π bond is higher than the energy of the C–C σ bond. Whenever you have a double bond between two atoms, there is one σ MO and one π MO. The energy of the C(sp^2)–C(sp^2) σ bond is lower than the energy of the C(sp^3)–C(sp^3) bond of ethane, because the C(sp^2) orbitals are lower in energy than a C(sp^3) orbital.

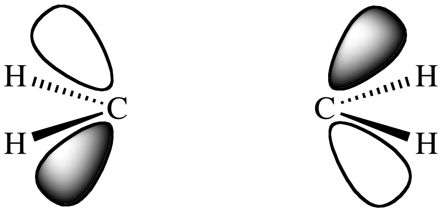




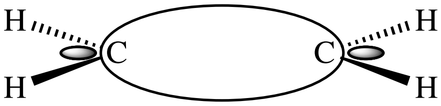
Just like there is a σ* orbital associated with a σ orbital in the H–H bond, so there are anti-bonding orbitals associated with the C(sp^2)–C(sp^2) σ bond and the C(p)–C(p) π bond. *A C atom that makes one double bond and two single bonds is sp^2-hybridized.*



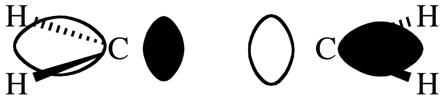
π orbital



π* orbital



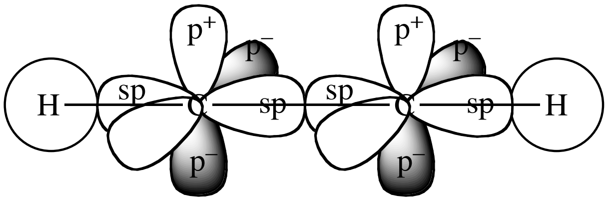
σ orbital



σ* orbital

1.9 Hybridization in Alkynes.

The same logic that told us that the C atoms in ethylene cannot be sp^3-hybridized tells us that the C atoms in ethyne (acetylene, $HC\equiv CH$) cannot be sp^3- or sp^2-hybridized. Instead, each C atom is *sp*-hybridized. The *s* orbital is averaged with just one *p* orbital to make two new hybrid *sp* orbitals that are pointing 180° from one another. The energy of the sp orbital is halfway between that of an *s* orbital and that of a *p* orbital. One of the *sp* orbitals is used to make a σ bond with the other C, and the other is used to make a σ bond with H. The two remaining, unhybridized *p* orbitals are used to overlap with two *p* orbitals on the other C atoms to make two π bonds. Whenever you have a triple bond between two atoms, there are one filled σ MO and two filled π MOs (and the corresponding empty anti-bonding MOs). Again, there are anti-bonding orbitals associated with the C(*sp*)–C(*sp*) σ bond and the C(*p*)–C(*p*) π bonds. *A C atom that makes one triple bond and one single bond is sp-hybridized.*



Even though it's hard to tell, the π electrons around the C≡C bond form a hollow cylinder of electron density.

1.10 Hybridization in Heteroatoms.

Heteroatoms also hybridize. We treat most lone pairs as if they were groups to which the heteroatom was bound; usually they reside in hybrid orbitals. If a heteroatom has only σ bonds to its neighbors, it is sp^3-hybridized. (Examples: dimethyl ether, ammonia.) If a heteroatom has one π bond to one neighbor, it is sp^2-hybridized. (Examples: pyridine, acetone, protonated acetone.) If a heteroatom has two π bonds to its neighbors, it is *sp*-hybridized. (Acetonitrile.) These hybridizations have consequences for both *structure* (bond angles and lengths) and *reactivity* (lone pairs with certain energies).

To summarize: *Hybrid orbitals are used to form σ bonds and to contain lone pairs. Unhybridized p orbitals are used to form π bonds or are empty.* To determine the hybridization of an atom, count the number of σ bonds and lone pairs not used in resonance; you need that many hybrid orbitals.

We said that lone pairs are put in hybrid orbitals. If the lone pair can be used in resonance, however, it must be in a *p* orbital for maximum overlap to occur. Therefore: *Hybrid orbitals are used to form σ bonds and to contain lone pairs not used in resonance. Unhybridized p orbitals are used to form π bonds, hold lone pairs used in resonance, or are empty.*

Be careful when determining hybridization of heteroatoms in cyclic compounds. Pyridine, pyrrole, furan all have sp^2-hybridized heteroatoms. In pyrrole and furan one lone pair is involved in resonance; in pyridine the lone pair is not involved in resonance.

1.11 Bond Strengths.

Bonds can be broken homolytically (one electron to each atom) or heterolytically (two electrons to one atom, none to the other). Bond strengths A—B are defined as the ability to separate A—B into A· and ·B.

Bonds differ in strength. Some are strong, some weak. How to tell?

1) Bonds between two electronegative elements are weak. E.g., O—O (35).
2) Bonds between two elements of different size are weaker than bonds between elements of the same size. E.g., cf. C—F (116), C—Cl (79), and C—I (52).
3) Bonds between two small elements are usually strong. E.g., C—H (98), C—O (79), C—C (81), C—N (66), O—H (109).
4) Double bonds are stronger than single bonds. But the C=C bond (145) is not twice as strong as the C—C bond (81); on the other hand, the C=O bond (173) is more than twice as strong as the C—O (79) bond, and the C≡N bond (204) is just about thrice as strong as the C—N (66) bond.

Why does size matter? It has to do with overlap between orbitals. Overlap between two small orbitals is much better than overlap between a big orbital and a small orbital.

A strong bond is one in which the bonding MO is much lower in energy than the component AOs. This terminology is a little counterintuitive: a high-energy bond is weak, and a low-energy bond is strong. (More on this in a moment.)

Heterolytic cleavage of bonds is typical of acids and bases, as is the reverse reaction, the formation of bonds from an acid and a base. Here, a filled orbital comes together with an empty orbital to make two new orbitals, one of which is lower in energy than either partner.

1.12 Bond Polarity.

Electronegativity. Nonpolar bonds have Δ(electronegativity) ≤ 0.4. C has electronegativity near center of scale, so most of its bonds are covalent. Bond polarity has very important effect on reactivity. Compare C—H and C—C bonds to C—O, C—Cl, C—Mg bonds. But electronegativity is not the only thing important in reactivity!