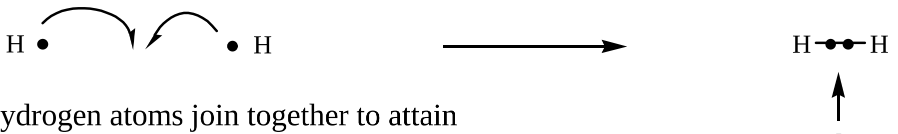
Lecture 2

Simple Molecular Orbitals - Sigma and Pi Bonds in Molecules

An atomic orbital is located on a single atom. When two (or more) atomic orbitals overlap to make a bond we can change our perspective to include all of the bonded atoms and their overlapping orbitals. Since more than one atom is involved, we refer to these orbitals as molecular orbitals. Quantum mechanics uses higher mathematics to describe this mixing, but we can use symbolic arithmetic and descriptive pictures of the mathematical predictions. The total number of atomic orbitals mixed is always the same as the number of molecular orbitals generated. At this point we just want to show how to create the two most common types of bonds used in our discussions: sigma bonds and pi bonds. You very likely remember these bonds from your earlier chemistry course, but it's usually good to take a quick review.

The first covalent bond between two atoms is always a sigma bond. We will use hydrogen as our first example, because of its simplicity. Later we will use this approach to generate a sigma bond between any two atoms. Recall our earlier picture of two hydrogen atoms forming a bond, becoming molecular diatomic hydrogen.



Two hydrogen atoms join together to attain the helium Noble gas configuration by sharing electrons and form a molecule.

Two electron, pure covalent bond

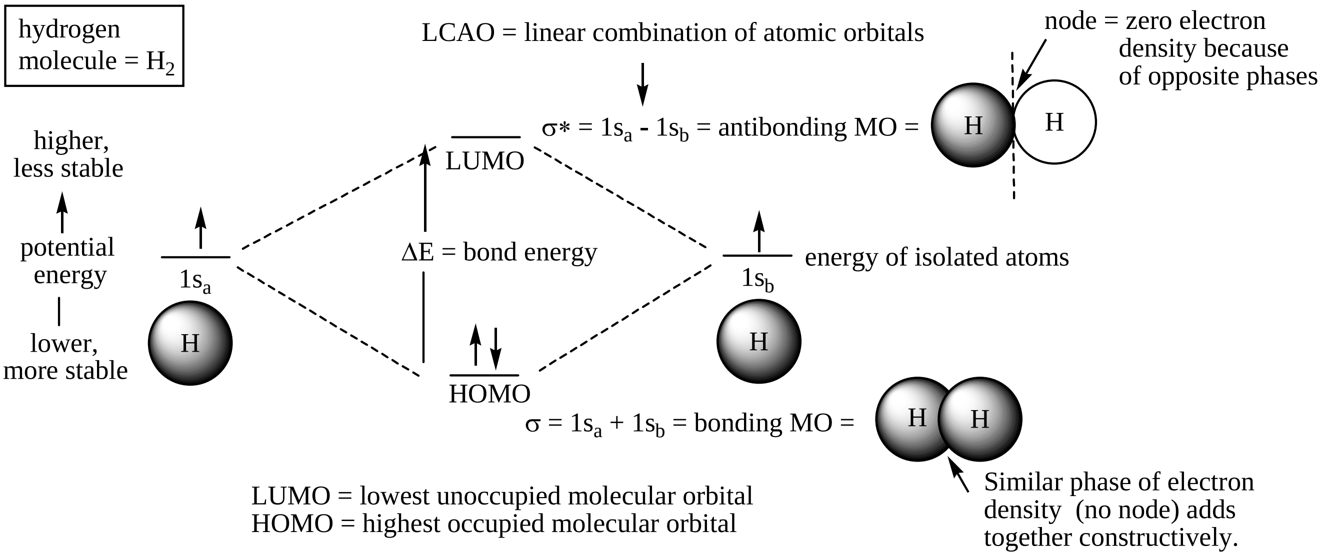
Each hydrogen atom brings a single electron in its 1s atomic orbital to share electron density, thus acquiring two electrons in its valence shell. This shared electron density lies directly between the bonding atoms, along the bonding axis. The interaction of the two bonded atoms with the bonding electrons produces a more stable arrangement for the atoms than when they are separated and the potential energy is lowered by an amount referred to as the bond energy (lower potential energy is more stable). Using our simplistic mathematics we will indicate this by adding the two atomic 1s orbitals together to produce a sigma molecular orbital $[\sigma = (1s_a + 1s_b)]$. Since the electrons in this orbital are more stable than on the individual atoms, this is referred to as a bonding molecular orbital. A second molecular orbital is also created, which we simplistically show as a subtraction of the two atomic 1s orbitals $[\sigma^* = (1s_a - 1s_b)]$. This orbital is called sigma-star (σ^*) and is less stable than the two separated atoms. Because it is less stable than the two individual atoms, it is called an anti-bonding molecular orbital. This adding and subtracting of atomic orbitals is referred to as a linear combination of atomic orbitals and abbreviated as LCAO. (Study the figure on the next page.)

We now have two molecular orbitals (MO's), created from two atomic orbitals. We also have two electrons to fill into these orbitals, so the lower energy molecular orbital (σ) will be filled and the higher energy molecular orbital (σ^*) will be empty (recall the Aufbau Principle). While there are only two molecular orbitals in this example, in a more general example there may be many molecular orbitals. Of all the possible molecular orbitals in a structure, two are so special they get their own names. One is called the highest occupied molecular orbital (HOMO), because it is the highest energy orbital holding electrons. The other is called the lowest unoccupied molecular orbital (LUMO), because it is the lowest energy orbital without any electrons. These orbitals will be crucial in understanding certain classes of reactions, some of which we study later. For right now, we just want to be familiar with the terms.

Bond order is a simple calculation, based on the number of bonding versus antibonding electrons that shows us the net bonding between the two atoms. In this calculation the number of anti-bonding electrons is subtracted from the number of bonding electrons and divided by two, since two electrons make a bond.

$$\text{bond order} = \frac{\text{(number of bonding electrons) - (number of antibonding electrons)}}{2} = \text{amount of bonding}$$

The following figure illustrates our sigma and sigma-star molecular orbitals pictorially and energetically for a hydrogen molecule. The bond order calculation equals one, which is what we expect for diatomic hydrogen.



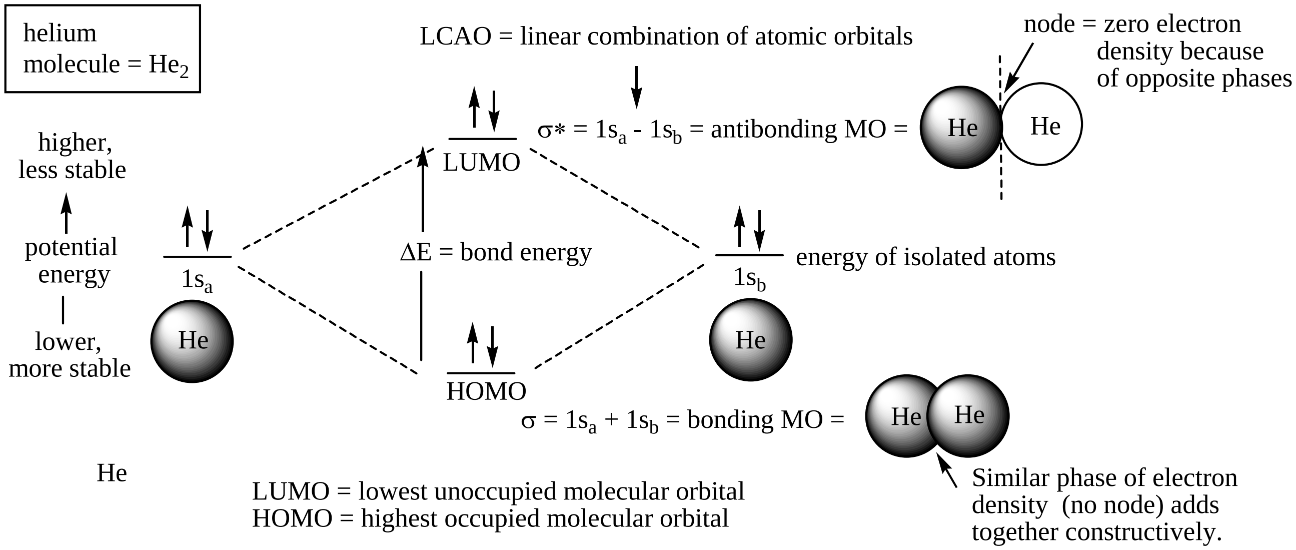
$$\text{bond order } (H_2 \text{ molecule}) = \frac{(2) - (0)}{2} = 1 \text{ bond}$$

There is a big energy advantage for a hydrogen molecule over two hydrogen atoms.

Sigma (σ) bonding molecular orbital - Shared electron density is directly between the bonding atoms, along the bonding axis. The interaction of the two bonded atoms with the bonding electrons produces a more stable arrangement for the atoms than when separated. Electrons usually occupy these orbitals. A sigma bonds is always the first bond formed between two atoms.

Sigma star (σ*) antibonding molecular orbital – Normally this orbital is empty, but if it should be occupied, the wave nature of electron density (when present) is out of phase (destructive interference) and canceling in nature. There is a node between the bonding atoms (zero electron density). Nodes produce repulsion between the two interacting atoms when electrons are present. Normally, because this orbital is empty, we ignore it. There are a number of reactions where electron density is transferred into the LUMO antibonding orbital. To understand those reactions, it is essential to have knowledge of the existence of this orbital.

What would happen if two helium atoms tried to form a bond by overlapping their two 1s orbitals? The bonding picture is essentially the same as for the hydrogen molecule, except that each helium atom brings two electrons to the molecular orbitals. There would be four electrons to fill into our molecular orbital diagram and that would force us to fill in the bonding sigma MO and the anti-bonding sigma-star MO. What we gain in the bonding sigma MO, we lose in the anti-bonding sigma-star MO. There is no advantage for two helium atoms to join together in a molecule, and so they remain as isolated atoms (note that He_2 is not a condensed version of humor, as in HeHe). The bond order calculation equals zero, as expected for a diatomic helium molecule.



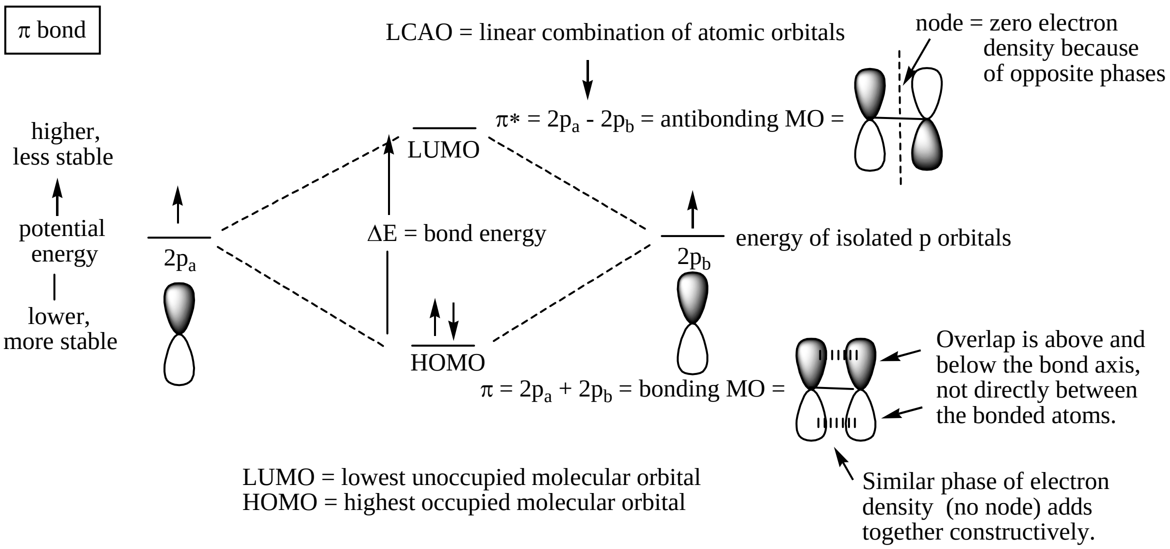
bond order (H$_2$ molecule) = $\frac{(2) - (2)}{2}$ = 0 bond

There is no energy advantage for a helium molecule over two helium atoms.

Problem 1 – What would the MO pictures of H_2^+, H_2^- and He_2^+ look like? Would you expect that these species could exist? What would be their bond orders?

When double and triple bonds are present between two atoms, there is additional bonding holding the atoms together. While a sigma bond is always the first bond between two atoms, a pi bond is always the second bond between two atoms (…and third bond, if present). Pi bonds use 2p orbitals to overlap in a bonding and anti-bonding way, generating a pi bonding molecular orbital [$\pi = (2p_a + 2p_b)$] and a pi-star anti-bonding molecular orbital [$\pi^* = (2p_a - 2p_b)$]. The simplistic mathematics (add the 2p orbitals and subtract the 2p orbitals) and qualitative pictures generated via a similar method to the sigma molecular orbitals discussed above.

A really big difference, however, is that there is NO electron density directly between the bonding atoms since 2p orbitals do not have any electron density at the nucleus (there is a node there). The overlap of 2p orbitals is above and below, if in the plane of our paper, or in front and in back, if perpendicular to the plane of our paper. The picture of two interacting 2p orbitals looks something like the following.



bond order of a pi bond = $\frac{(2) - (0)}{2}$ = 1 bond

There is a big energy advantage for a pi bond over two isolated p orbitals.

Pi bond (π): bonding molecular orbital –The bonding electron density lies above and below, or in front and in back of the bonding axis, with no electron directly on the bonding axis, since 2p orbitals do not have any electron density at the nucleus. The interaction of the two bonded atoms with the bonding electrons produces a more stable arrangement for the 2p orbitals than for the atoms than when separated. Electrons usually occupy these orbitals, when present. These are always second or third bonds overlapping a sigma bond formed first. The HOMO of a pi system is especially important. There are many reactions that are explained by a transfer of electron density from the HOMO to the LUMO of another reactant. To understand these reactions, it is essential to have knowledge of the existence of this orbital, and often to know what it looks like.

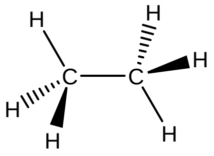
Pi star (π*): antibonding molecular orbital – Normally this orbital is empty, but if it should be occupied, the wave nature of electron density is out of phase (destructive interference) and canceling in nature. There is a second node between the bonding atoms, in addition to the normal 2p orbital node at the nucleus (nodes have zero electron density). This produces repulsion between the two interacting atoms, when electrons are present. Normally, because this orbital is empty, we ignore it. As with sigma bonds, there are a number of reactions where electron density is transferred into the LUMO antibonding orbital. To understand those reactions, it is essential to have knowledge of the existence of this orbital, and often to know what it looks like.

Atoms gain a lot by forming molecular orbitals. They have more stable arrangement for their electrons and the new bonds help them attain the nearest Noble gas configuration.

In more advanced theory, every single atomic orbital can be considered, to some extent, in every molecular orbital. However, the molecular orbitals are greatly simplified if we only consider "localized" atomic orbitals around the two bonded atoms, ignoring the others (our approach above). An exception to this approach occurs when more than two 2p orbitals are adjacent and parallel (…3, 4, 5, 6…etc.). Parallel 2p orbitals interact strongly with one another, no matter how many of them are present. As was true in forming sigma and pi molecular orbitals, the number of 2p orbitals that are interacting is the same as the number of molecular orbitals that are formed. We will develop this topic more when we discuss concerted chemical reactions. The old fashion way of showing interaction among several 2p orbitals is called resonance, and this is the usual approach in beginning organic chemistry. Resonance is yet another topic for later discussion.

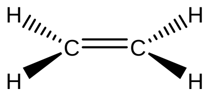
The Hybridization Model for Atoms in Molecules

The following molecules provide examples of all three basic shapes found in organic chemistry. In these drawings a simple line indicates a bond in the plane of the paper, a wedged line indicates a bond coming out in front of the page and a dashed line indicates a bond projecting behind the page. You will have to become a modest artist to survive in organic chemistry.



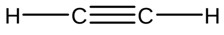
ethane
tetrahedral carbon atoms

HCH bond angles ≈ 109^o
HCC bond angles ≈ 109^o



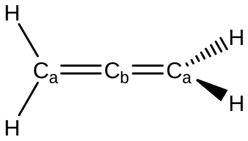
ethene
trigonal planar carbon atoms

HCH bond angles ≈ 120^o (116^o)
CCH bond angles ≈ 120^o (122^o)



ethyne
linear carbon atoms

HCC bond angles = 180^o



allene
trigonal planar carbon atoms at the ends and a linear carbon atom in the middle

HC_aH bond angles ≈ 120^o
HC_aC_b bond angles ≈ 120^o
$C_aC_bC_a$ bond angles = 180^o

Our current task is to understand hybridization. Even though you probably already studied hybridization, this topic is way too important to assume you know it from a previous course. Hybrids are new creations, resulting from mixtures of more than one thing. In organic chemistry our orbital mixtures will be simple combinations of the valence electrons in the 2s and 2p orbitals on a single carbon atom. Though not exactly applicable in the same way for nitrogen, oxygen and the halogens, this model will work fine for our purposes in beginning organic chemistry. We will mix these orbitals three ways to generate the three common shapes of organic chemistry: linear (2s+2p), trigonal planar (2s+2p+2p) and tetrahedral (2s+2p+2p+2p).

We will first show how the three shapes can be generated from the atomic orbitals, and then we will survey a number of organic structures, using both two-dimensional and three dimensional drawings to give you abundant practice in using these shapes. You should be able to easily manipulate these shapes, using only your imagination and, perhaps, pencil and paper, if a structure is a little more complicated. If you have molecular models, now is a good time to get them out and assemble them whenever you are having a problem visualizing or drawing a structure. Your hands and your eyes will train your mind to see and draw what you are trying to understand and explain.

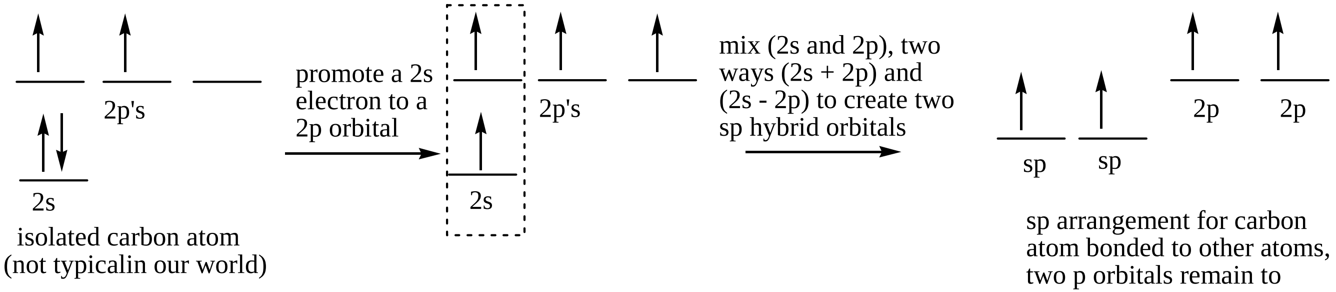
Organic chemistry and biochemistry are three dimensional subjects. Just like you don't look at every letter in a word while you are reading, you can't afford to struggle with the shape of every atom while examining a structure. If you are struggling to comprehend "shapes", you will never be able to understand more complicated concepts such as conformations, stereochemistry or resonance as stand-alone topics, or as tools for understanding reaction mechanisms. You have to practice (correct your errors), practice (correct your errors), practice (correct your errors) until this skill is second nature, and the pictures and terminology are instantly comprehended when you see a structure…and you have to do it quickly, because there's a lot more material still to be covered. However, anyone reading these words can do this – and that includes you!

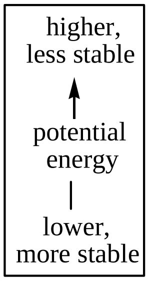
Carbon as our first example of hybridization

1. sp hybridization – carbon and other atoms of organic chemistry

Our first example of hybridization is the easiest and merely mixes a 2s and a 2p atomic orbital to form two sp hybrid orbitals. Remember that when we mix atomic orbitals together, we create the same number of new "mixture" orbitals. This is true for molecular orbitals on multiple atoms, as shown just above (σ, σ^*, π and π^*), and for hybrid orbitals on a single atom, as shown below (sp, sp^2 and sp^3). We might expect that our newly created hybrid orbitals will have features of the orbitals from which they are created…and that's true. The 2s orbital has no spatially distinct features, other than it fills up all three dimensions in a spherical way. A 2p orbital, on the other hand, is very directional. Its two oppositely phased lobes lie along a single axis, in a liner manner. Newly created sp hybrid orbitals will also lay along a straight line in a linear fashion, with oppositely phased lobes, because of the 2p orbital's contribution. The two new sp hybrid orbitals point in opposite directions, having 180^o bond angles about the sp hybridized atom.

The scheme below shows a hypothetical process to change an isolated "atomic" carbon atom into an sp hybridized carbon atom having four unpaired electrons, ready for bonding. The vertical scale in the diagram indicates potential energy changes as electrons move farther from the nucleus. Unpairing the 2s electrons allows carbon to make two additional bonds and acquire the neon Noble gas configuration by sharing with four other electrons. There is an energy cost to promote one of the 2s electrons to a 2p orbital, but this is partially compensated by decreased electron/electron repulsion when one of the paired electrons moves to an empty orbital. The really big advantage, however, is that two additional highly directional sigma bonds can form, each lowering the energy of the carbon atom by a considerable amount (lower potential energy is more stable). The combination of all the energy changes is quite favorable for carbon atoms, whether sp, sp^2 or sp^3 hybridized. It's important that you understand the qualitative ideas presented here with two orbitals (2s + 2p), because we are going to do it all over again with three orbitals (2s + 2p + 2p = three sp^2 hybrid orbitals) and four orbitals (2s + 2p + 2p + 2p = four sp^3 hybrid orbitals).





Overall, this would be a favorable trade.

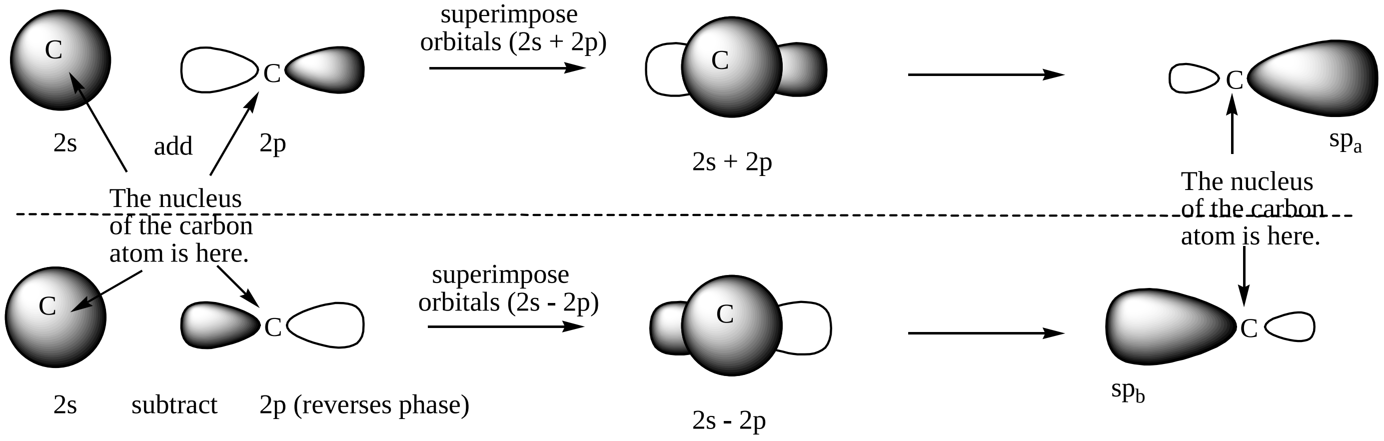
- cost = promotion energy ≈ 100 kcal/mole
- gain = electron/electron repulsion in s ortibal is removed ≈ 20-40 kcal/mole
- gain = two additional bonds are possible ≈ 150-200 kcal/mole
- gain = more directional orbitals form, that have better overlap of electron density between the bonding atoms, thus forming stronger bonds

The energy diagram shows that 2s electrons are held more tightly than 2p electrons (because they are closer to the nucleus, on average). Because sp electrons have 50% s orbital contribution, they are also held more tightly than 2p electrons [2s (100% s) > sp (50% s) > sp^2 (33% s) > sp^3 (25% s) > 2p (0% s)]. The greater the percent 2s contribution in a hybrid orbital, the more tightly the electrons are held by the atom. In a sense, this is a property similar to electronegativity, except that changes occur within the same kind of atom, based on hybridization, instead of in different types of atoms based on $Z_{effective}$ or distance from the nucleus. This idea will be developed more fully in our acid/base topic.

Creating the sp hybrid orbitals

We can show the orbital mixing to create sp hybrid orbitals pictorially by using images of 2s and 2p orbitals. We simplistically represent the mathematics of the mixing by showing addition of the two orbitals and subtraction of the two orbitals. This is close to what happens, but not exactly correct. It does serve our purpose of symbolically changing the phase of the 2p orbital in the subtraction, generating the second sp hybrid orbital pointing 180^o in the opposite direction from the first sp hybrid orbital. Phase is important here and adds constructively when it is the same (bonding) and destructively when it is opposite (antibonding). This will produce a larger lobe on the bonding side of the sp hybrid orbital (more electron density to hold the atoms together) and a smaller lobe on the antibonding side of the sp orbital (less electron density). Greater electron density between the bonded atoms will produce a stronger bond.

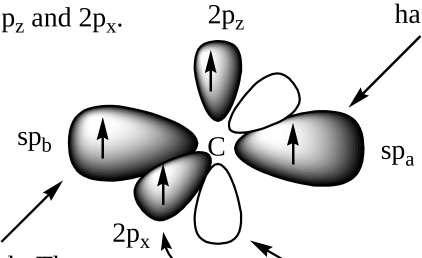
The 2s and 2p orbitals are artificially separated in the first part of the scheme for easier viewing. Even though the orbitals are drawn separately, remember that the center of the carbon atom is at the middle of the 2s orbital and at the node of all of the hybrid and p orbitals.



The Complete Picture of an sp Hybridized Carbon Atom

An isolated sp hybridized carbon atom for viewing. A bonded carbon atom would need orbital overlap for each orbital present, sp_a, sp_b, $2p_z$ and $2p_x$.

This represents the sp_a hybrid orbital. The small, opposite phase lobe on the backside has been left off to simplify the picture.



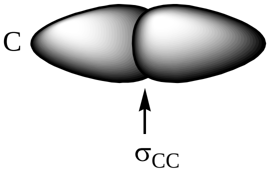
Carbon has one electron available for each orbital to share with bonding partners.

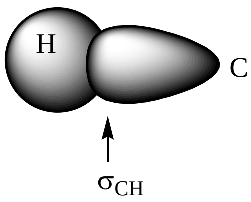
This represents the sp_b hybrid orbital. The small, opposite phase lobe on the backside has been left off to simplify the picture.

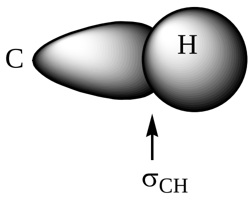
There remain two 2p orbitals which are perpendicular to the two sp hybrid orbitals and to each other. Each 2p orbital extends along its entire axis with opposite phase in each lobe.

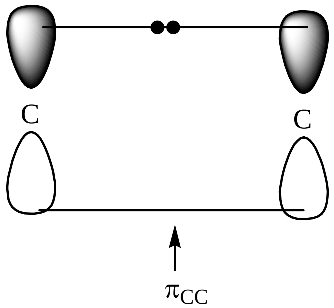
Two sp carbon atoms bonded in a molecule of ethyne (…its common name is acetylene)

The simplest possible way to place our sp hybridized carbon into a neutral molecule is to bring another sp hybridized carbon up to bond with three of its atomic orbitals: one sp hybrid sigma bond, along the bonding axis of the two carbon atoms and two pi bonds. One of the pi bonds will lie above and below the sigma bonded carbon atoms in the plain of the page. The other pi bond will lie in front and in back of the carbon atoms, perpendicular to the plane of the page. On the other side of each carbon atom, 180^o away from the other carbon atom, we can attach a simple hydrogen atom, using its 1s atomic orbital to overlap in a sigma bond along the bonding axis (a first bond is always sigma bond).

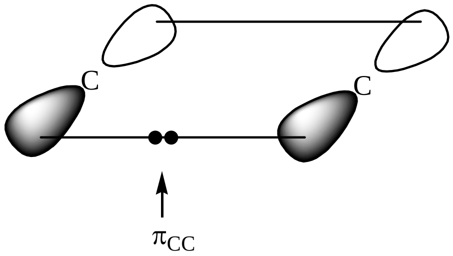








top and bottom



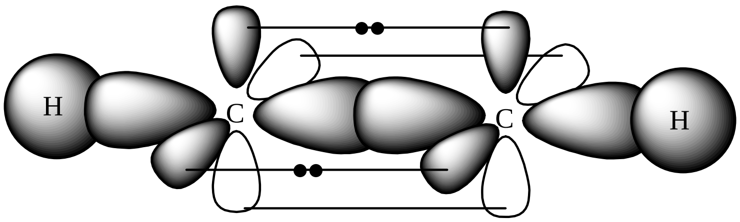
front and back

Ethyne has five total bonds: three sigma bonds and two pi bonds.

The shape of each sp carbon atom is linear and allows the electrons in the σ bonds and the atoms they are bonded to, to be as far apart in space as possible, minimizing the electron/electron repulsion. The small backside lobe of each sp orbital has been omitted for clarity, since the bond on the side of the large lobe has the bulk of the electron density and determines where the bonded atom will be.

In organic chemistry sigma bonds (σ) are always the first bond between two atoms, resulting from overlap along the bonding axis (of hybrid orbitals), while pi bonds (π) are second and third bonds resulting from the overlap of p orbitals, above and below (or in front and back of) the bonding axis. (I'm repeating myself on purpose.)

Our molecule of ethyne now looks as shown, including all of the lobes of the orbitals (except for the small backside lobes of the hybrid orbitals). However, it looks a little too congested with details to see everything clearly, and it's way too much work to draw routinely. If we tried to add other non-hydrogen atoms, it would get too messy, as well.



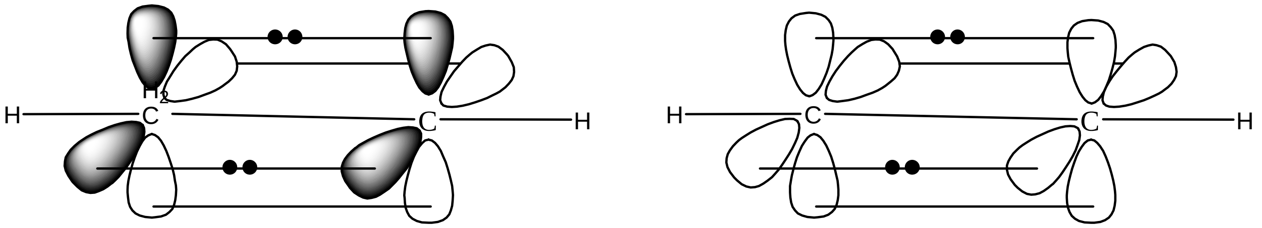
These terms all go together. For neutral sp carbon, knowing any one of them, implies all of the others.

sp hybridized carbon
carbon atom shape = linear
bond angles about sp carbon = 180^{o}
number of sigma bonds = 2
number of pi bonds = 2

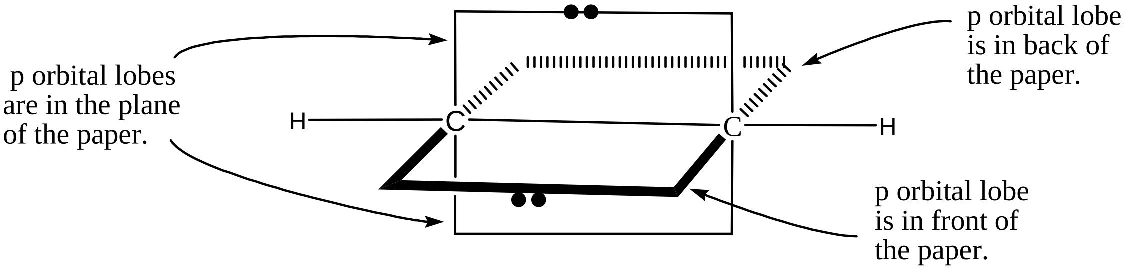
We rarely draw our 3D structures like this, preferring simpler ways of representing the details. Over the years students have convinced me that it is easier for them to see the details if the p orbitals are also drawn as straight lines (same 3D conventions: simple, wedged and dashed lines). Connecting lines are still drawn on both sides between overlapping 2p orbitals (i.e. top and bottom) to show the pi bonding (these two lines represent only one bond).

I explicitly include two dots for the pi electrons, because I want you to think of those electrons the way you think of lone pair electrons (for example, in acid/base reactions where a proton transfers from lone pair to lone pair). Much of the chemistry of pi bond compounds (alkenes, alkynes and aromatics) begins with these pi electrons. Most of our arrow pushing mechanisms, for these classes of compounds, will begin with a curved arrow moving from the pi electrons, just as we begin much of the chemistry of heteroatoms (nitrogen, oxygen and halogens) with an arrow moving from their lone pair electrons.

Alternative ways of drawing 3D structures that are simpler than the above drawing at showing the 3D details.



3D ethyne drawn with p orbitals as lobes (p orbitals with phase shown in the left structure and without phase in the right structure.



3D ethyne drawn with p orbitals as lines and pi electrons explicitly drawn in, in a manner similar to showing lone pair electrons. In this book I will usually draw pi bonds this way in 3D structures.

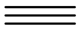
We will practice drawing many 3D structures to train our minds to imagine in three dimensions, and to help us understand a topic under discussion, such as parallel p orbitals in resonance, or understanding a mechanism we are learning for the first time. However, even our simplified 3D structures are too complicated for drawing structures in typical discussions of organic molecules. Most of the time our organic structures will be condensed to very simple representations that are quick to draw and easy to see at a glance. Sometimes we will include letters to symbolically represent the atoms and sometimes we will merely have lines on the page, almost to the point where the structures become a foreign language writing system. Some additional ways of drawing ethyne are shown below. Each subsequent representation puts a greater burden on you to interpret its meaning. Your advantage is that every non-hydrogen atom you view (carbon, nitrogen, oxygen and halogens) has to be one of the three shapes we are developing in this topic, so your choices are pretty limited (sp, sp^2 or sp^3).

$H-C\equiv C-H$

Each line represents a bond. While the three simple lines of the triple bond appear equivalent, we know that the first bond formed is a sigma bond of overlapping sp hybrid orbitals. The second and third bonds are overlapping 2p orbitals, above and below and in front and in back. Since the C-H bonds are single bonds, we know that they are sigma bonds too, using hybrid orbitals. This is how you will determine the hybridization of any atom in a structure. Knowing how many pi bonds are present will tell you how many 2p orbitals are being used in those pi bonds. The remaining s and 2p orbitals must be mixed together in hybrid orbitals (in this example, only an s and a 2p remain to form two sp hybrid orbitals).

HCCH

The connections of the atoms are implied by the linear way the formula is drawn. You have to fill in the details about the number of bonds and where they are from your understanding of each atom's bonding patterns. A C-H bond can only be a single bond so there must be three bonds between the carbon atoms to total carbon's normal number of four bonds. This means, of course, that the second and third bonds are pi bonds, using 2p orbitals, leaving an s and p orbitals to mix, forming two sp hybrid orbitals.



A bond line formula only shows lines connecting the carbon atoms and leaves off the hydrogen atoms. Every end of a line is a carbon (two in this drawing) and every bend in a line is a carbon (none in this drawing). You have to figure out how many hydrogen atoms are present by substracting the number of lines shown (bonds to non-hydrogen atoms) from four, the total number of bonds of a neutral carbon (4 - 3 = 1H in this drawing). The shape of the carbon atoms must be linear, because we know the hybridization is sp.

C_2H_2

This is the ultimate in condensing a structure. Merely writing the atoms that are present and how many of them there are provides no details about the connectivity of the atoms. It only works for extremely simple molecules that have only one way that they can be drawn. Ethyne is an example of such molecule. Other formulas may have several, hundreds, thousands, millions, or more ways for drawing structures. Formulas written in this manner are usually not very helpful.

carbon atom shape = linear
hybridization = sp
bond angles about sp carbon = 180°
number of sigma bonds = 2
number of pi bonds = 2

All of the details in this group go together. If you have any one of them, you should be able to fill in the remaining details.

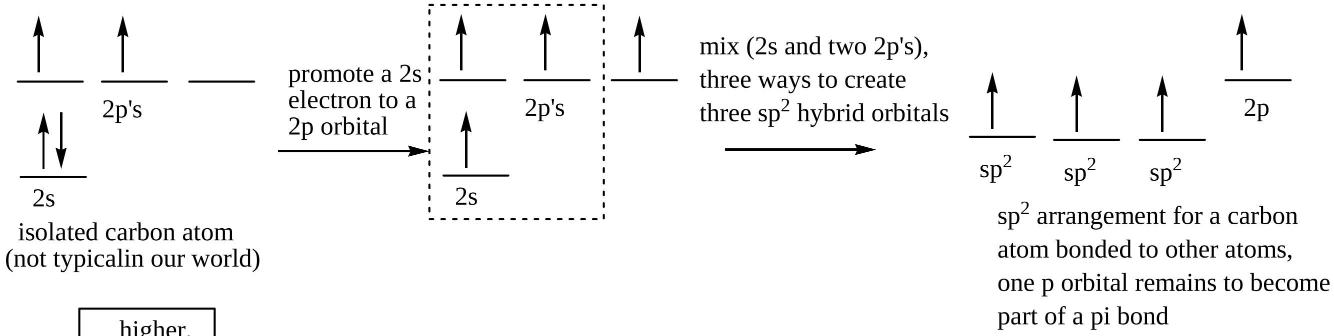
Problem 2 – Draw a 3D representation or hydrogen cyanide, HCN. Show lines for the sigma bond skeleton and the lone pair of electrons. Show two dots for the lone pair. Also show pi bonds represented in a manner similar to above. What is different about this structure compared with ethyne above?

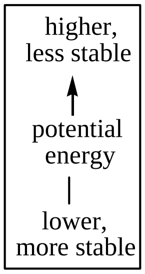
Show lines for the sigma bond skeleton and the lone pairs of electrons with two dots for each lone pair. Also show pi bonds represented in a manner similar to above. What is different about this structure compared with ethene above?

This represents 1/3 of the bonding pictures you need to understand. I hope it wasn’t too painful. We need to extend this approach two more times for sp^2 and sp^3 hybridized atoms.

2. sp^2 hybridization

Our second hybridization example mixes the 2s orbital with two 2p atomic orbitals, creating three new sp^2 hybrid orbitals. One 2p orbital remains unchanged, and it will help form a pi bond. The relative energy scheme showing electron promotion and orbital mixing is almost the identical to the sp hybrid example above. The major difference is the mixing of a second 2p orbital, which alters our hybrid creations from linear to planar. As above, promoting a 2s electron allows for four bonds to form and allows the carbon atom to acquire the neon Noble gas configuration. As mentioned in the example of sp hybridization, electrons in sp^2 orbitals are held more tightly than electrons in 2p orbitals, but less tightly than electrons in 2s orbitals. Among atoms of the same type, an atom's relative electronegativity is dependent on the amount of 2s character [2s (100% s) > sp (50% s) > sp^2 (33% s) > sp^3 (25% s) > p (0% s)].



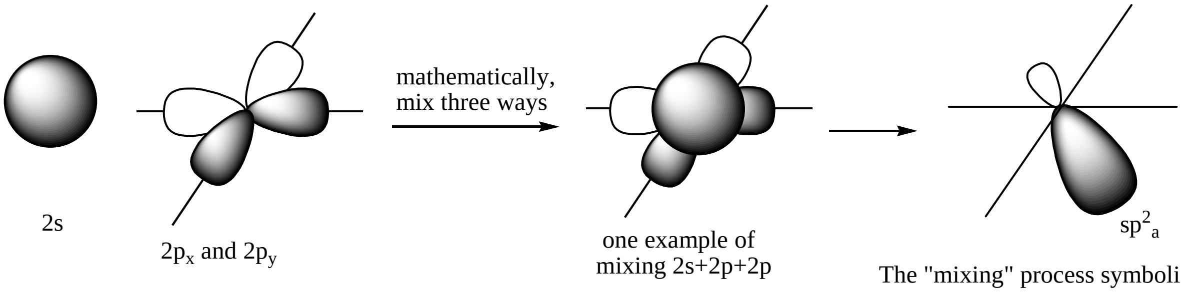


Overall, this would be a favorable trade.

cost = promotion energy ≈ 100 kcal/mole
gain = electron/electron repulsion in s ortibal is removed ≈ 20-40 kcal/mole
gain = two additional bonds are possible ≈ 150-200 kcal/mole
gain = more directional orbitals form, that have better overlap of electron density between the bonding atoms, thus forming stronger bonds

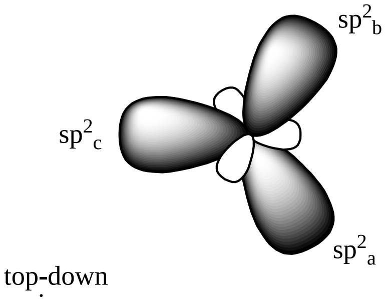
Creating the sp^2 hybrid orbitals

Because two 2p orbitals lie in a plane, the three sp^2 hybrid creations will also lie in a plane. The picture below shows one possible example of orbital mixing. Two additional combinations are necessary (not shown). Dividing a plane (same as a circle = 360°) into three equal divisions forms 120° bond angles between the orbitals, where the sigma bonds will be. This allows the electrons in the sigma bonds to be as far apart in space as possible and minimizes the electron/electron repulsion. The descriptive term for this shape is trigonal planar. The hybrid orbitals will form sigma bonds and the p orbital will usually form a pi bond.

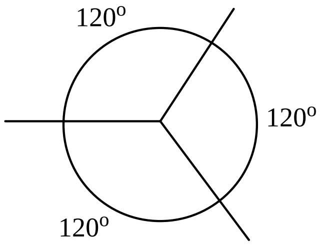


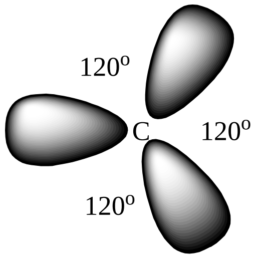
Similar phase mixes constructively in the right front quadrant

The "mixing" process symbolized here is repeated two additional ways, creating three sp_2 hybrid orbitals.



All three sp^2 hybrid orbitals lie in a plane and divide a circle into three equal pie wedges of 120°. The descriptive term for the shape is trigonal planar.



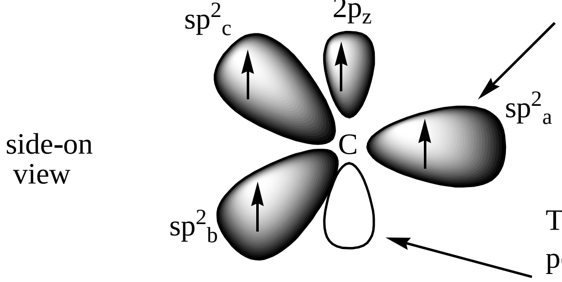


This picture shows the sp^2 hybrid orbitals without their small backside lobes and no p orbital is shown. These hybrid orbitals will form sigma bonds.

The complete picture of an sp^2 hybridized carbon atom

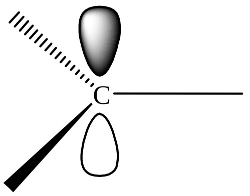
An isolated sp^2 hybridized carbon atom for viewing. A bonded carbon atom would need orbital overlap for each orbital present, $sp^2{}_a$, $sp^2{}_b$, $sp^2{}_c$ and $2p_z$.

These represent $sp^2{}_a$ hybrid orbitals. The small, opposite phase lobe on the backside has been left off to simplify the picture.

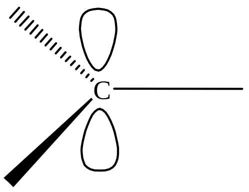


There remains one 2p orbital perpendicular to the three sp^2 hybrid orbitals. The 2p orbital extends along the entire axis with opposite phase in each lobe.

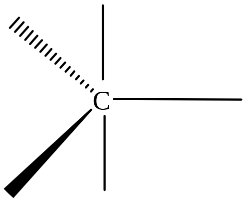
There are more convenient alternative methods of drawing a three dimensional sp^2 carbon atom, using simple lines, dashed lines and wedged lines. The first drawing below shows the lobes of the 2p orbital with its relative phases. The second drawing shows the lobes, but not the phases. The third drawing uses only simple lines instead of lobes for the p orbitals. It is quicker to draw, obscures less background, yet still shows the directionality of the 2p orbitals, which is an important feature of resonance.



sp^2 hybridized carbon atom



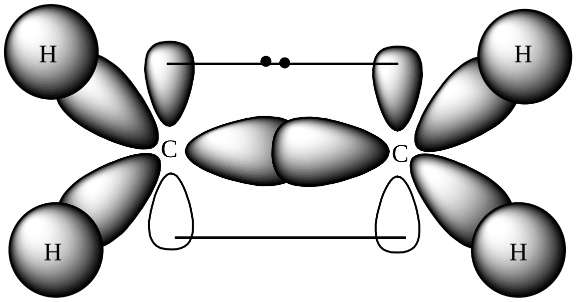
sp^2 hybridized carbon atom



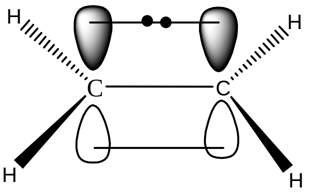
sp^2 hybridized carbon atom
We will use this approach.

Two sp^2 carbon atoms bonded in a molecule of ethene (…its common name is ethylene)

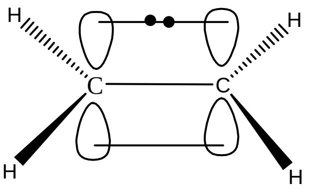
As in our sp example, the simplest possible way to place our sp^2 carbon atom into a neutral molecule is to bring another sp^2 carbon atom up to overlap with two of its atomic orbitals: a sigma bond using an sp^2 hybrid orbital, along the bonding axis of the atoms and a pi bond, using the 2p orbital. The pi bond lies above and below the carbon-carbon sigma bond, in the plane of the paper, the way we have drawn it. Four additional sigma bonds can form around the outside of the two carbons using the remaining sp^2 hybrid orbitals. The easiest bonding arrangement is to bond four hydrogen atoms, using their 1s atomic orbitals. As with ethyne, this way of drawing a three dimensional structure is too cumbersome for routine use.



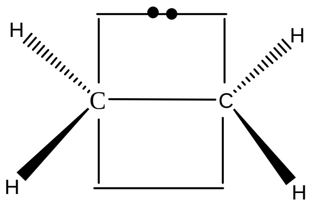
We will draw our 3D structures using more simplified representations. Each sp^2 carbon atom has trigonal planar geometry, with 120° bond angles. Our 3D representations include simple lines to indicate bonds in the plane of the page, wedges to indicate bonds extending in front of the page and dashed lines to indicate bonds extending behind the page. Possible 3D drawings are shown below.



2p orbitals drawn as lobes, with phase indicated



2p orbital drawn as lobes, without phase indicated

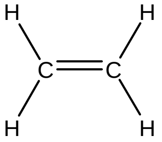
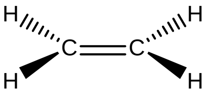
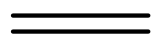


2p orbitals drawn as lines, no phase indicated. This will be our method of drawing 3D structures

carbon atom shape = trigonal planar
hybridization = sp^2
bond angles about sp carbon = 120°
number of sigma bonds = 3
number of pi bonds = 1

All of the details in this group go together. If you have any one of them, you should be able to fill in the remaining details.

As with ethyne, some additional ways of drawing ethene are shown below. Each subsequent representation puts a greater burden on you to interpret its meaning. Your advantage is that every non-hydrogen atom you view (carbon, nitrogen, oxygen and halogens) has to be one of the three shapes we are developing in this topic, so your choices are pretty limited (sp, sp^2 or sp^3).

 ...or... 	Each line represents a bond. While the two simple lines of the double bond appear equivalent, we know that the first bond formed is a sigma bond of overlapping sp^2 hybrid orbitals. This means, of course, that the second bond is a pi bond, using a 2p orbital, leaving an s and two 2p orbitals to mix, forming three sp^2 hybrid orbitals.
H_2CCH_2 or CH_2CH_2	The connections of the atoms are implied by the linear way the formula is drawn. You have to fill in the details about the number of bonds and where they are from your understanding of each atom's bonding patterns. A CH_2 forms two single bonds, so there must be two bonds between the carbon atoms for carbon's normal number of four bonds. The second bond has overlapping 2p orbitals, above and below the bonding axis and means the carbon must be sp^2 hybridized.
	A bond line formula only shows lines connecting the carbon atoms and leaves off the hydrogen atoms. Every end of a line is a carbon (two in this drawing) and every bend in a line is a carbon (none in this drawing). You have to figure out how many hydrogens are present by substracting the number of lines shown (bonds to non-hydrogen atoms) from four (the total number of bonds of a neutral carbon (4 - 2 = 2H in this drawing).
C_2H_4	This is the ultimate in condensing a structure. Merely writing the atoms that are present and how many of them there are provides no details about the connectivity of the atoms. It only works for extremely simple molecules that have only one way that they can be drawn. Ethene is an example of such molecule.

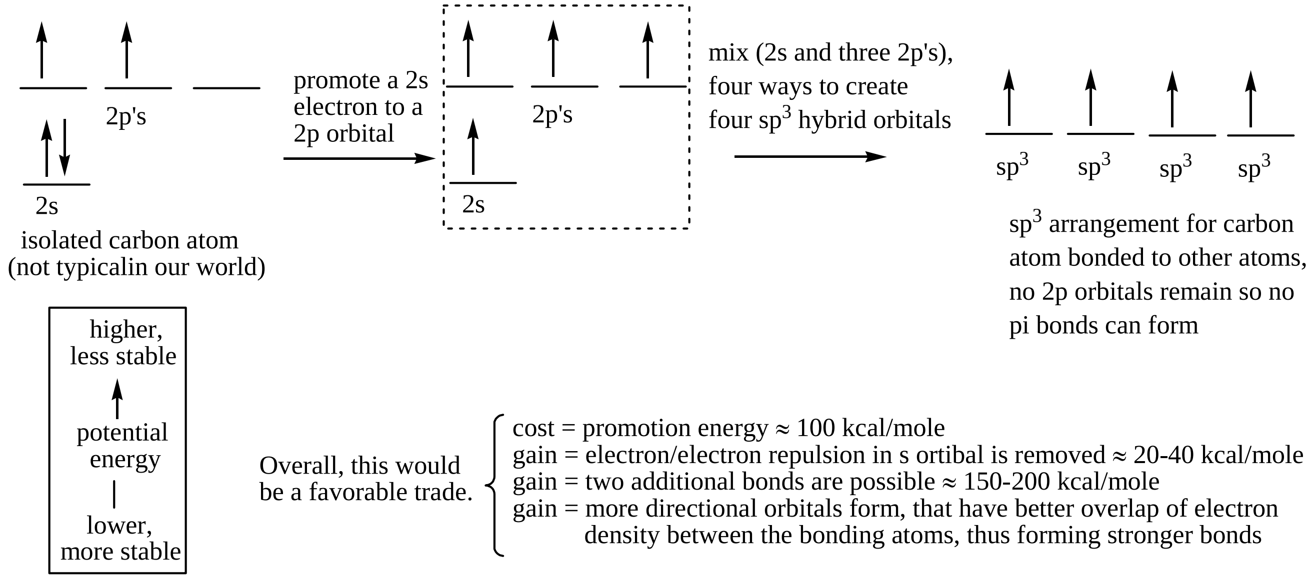
Problem 3 – Draw a 3D representation of methanal (common name = formaldehyde), $H_2C{=}O$. Show lines for the sigma bond skeleton and the lone pairs of electrons with two dots for each lone pair. Also show pi bonds represented in a manner similar to above. What is different about this structure compared with ethene above?

This completes the second of our three bonding pictures you need to understand. We need to extend this approach one more time with sp^3 hybridized atoms.

3. sp^3 hybridization

Our final example of hybridization mixes the 2s orbital with all three 2p atomic orbitals, creating four new, equivalent sp^3 hybrid orbitals. The three 2p orbitals fill all three dimensions and the four sp^3 hybrid orbitals created from them also fill all three dimensions. There are no π bonds, since no 2p orbitals remain to make them. All of the bonds are sigma bonds, because all of the bonding orbitals are hybrid orbitals. Your intuition about the bond angles probably fails you in this example (it fails me), so we'll just accept that the bond angle between sp^3 orbitals is approximately 109^o (…and if you are really good at trigonometry, you can figure the exact bond angle out for yourself). We won't worry about the exact bond angle (109^o 28' = 109.5^o) since there is a considerable amount of variation about the 109^o value in different molecules. The atomic shape of sp^3 carbon atoms is described as tetrahedral, but not because of the shape about the carbon atom, as was the case in our previous two examples. The descriptive term for the shape of an sp^3 atom is based on a geometric figure drawn by connecting the ends of the sigma bonds. A four sided figure of equilateral triangles is generated, called a tetrahedron. The energy scheme below is a hypothetical process to get sp^3 hybridized carbon from atomic carbon.

As mentioned in the examples of sp and sp^2 hybridization, electrons in sp^3 orbitals are held more tightly than electrons in 2p orbitals, but less tightly than electrons in 2s orbitals. Among atoms of the same type, an atom's relative electronegativity is dependent on the amount of s character [2s (100% s) > sp (50% s) > sp^2 (33% s) > sp^3 (25% s) > 2p (0% s)]. The relative electronegativity of hybridized carbon increases with increasing percent 2s contribution: sp > sp^2 > sp^3.

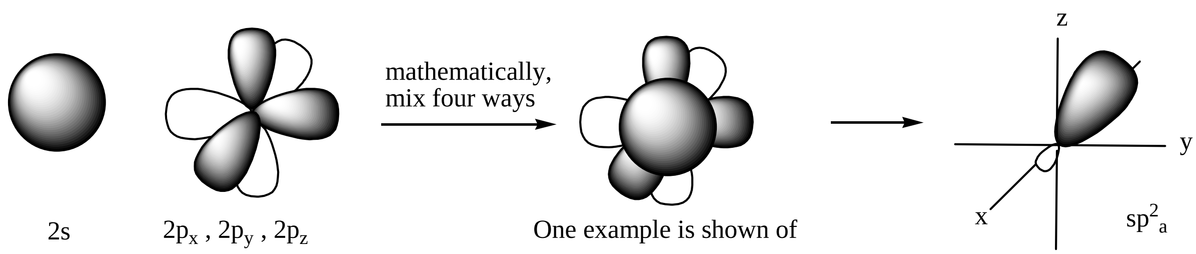


Overall, this would be a favorable trade.

cost = promotion energy ≈ 100 kcal/mole
gain = electron/electron repulsion in s ortibal is removed ≈ 20-40 kcal/mole
gain = two additional bonds are possible ≈ 150-200 kcal/mole
gain = more directional orbitals form, that have better overlap of electron density between the bonding atoms, thus forming stronger bonds

Creating the sp^3 hybrid orbitals

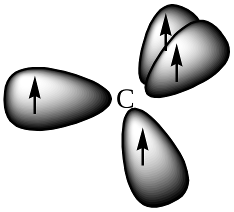
One example of a picture of orbital mixing is provided. Three additional combinations are used to create the other three sp^3 hybrid orbitals, but it is more difficult to show this with our simplistic representations than it was for sp hybridization. The bottom line is that four atomic orbitals are mixed four ways to generate four equivalent sp^3 hybrid orbitals. An example of all four sp^3 orbitals is shown using our simple 3D conventions: a simple line indicates a bond in the plane of the page, a wedged line indicates a bond extending in front of the page and a dashed line indicates a bond behind the page. A tetrahedral figure is also drawn to show where the descriptive geometric term comes from.



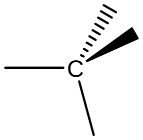
One example is shown of mixing 2s+2p+2p+2p to form an sp^3 hybrid orbital.

Similar phases interact constructively in the front, right, upper octant where the large lobe will be located.

The "mixing" process symbolized here is repeated three additional ways, creating four sp^3 hybrid orbitals.



sp^3 orbitals minus the small backside lobes



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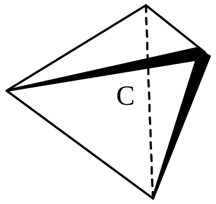
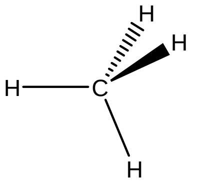
sp^3 orbitals drawn using our 3D conventions



A tetrahedron has four equivalent triangular sides. The atoms at the ends of the bonds with carbon define the vertices of the tetrahedron. The carbon is sitting in the middle of the tetrahedron.

One sp^3 carbon atom bonded in methane and two sp^3 carbon atoms bonded in ethane

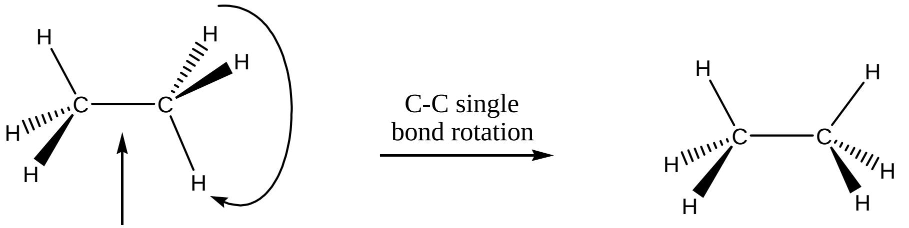
In both of our previous examples, we needed two carbons in order to form a pi bond, using the unhybridized 2p orbitals. Hydrogen atoms don't have available p orbitals in the n = 1 shell and cannot form pi bonds. Since sp^3 carbon atoms only make single bonds, this is our first example of hybridization where we can surround a carbon atom with only hydrogen atoms (four of them).. This forms a molecule of methane, CH_4, one of the simplest organic molecules we will encounter. Notice there is only one type of bond now (σ_{CH}) and the HCH bond angles about the central carbon atom are **109°** (plus a little bit that we ignore). This angle allows the electrons in the sigma bonds to be as far apart in space as possible, minimizing the electron/electron repulsion. The atomic shape is designated as tetrahedral. Since sp^3 atoms fill all three dimensions, there is no choice but to use our 3D drawing conventions (simple lines, dashed lines and wedged lines).



carbon atom shape = tetrahedral
hybridization = sp^3
bond angles about sp carbon = 109°
number of sigma bonds = 4
number of pi bonds = 0

All of the details in this group go together. If you have any one of them, you should be able to fill in the remaining details.

If we remove one of the hydrogen atoms of methane and replace it with the simplest possible carbon atom, CH_3, we would form molecular ethane. Ethane has two sp^3 carbons connected by a single, sigma bond. The six hydrogen atoms in ethane occupy all three dimensions. The single bond between the two carbons allows rotation to occur and the three hydrogen atoms on one carbon atom can rotate past the three hydrogen atoms on the other carbon, like the spokes on a wheel. If you have models, why not build ethane and rotate the C-H bonds about the carbon-carbon axis to see how they move? The different shapes have slightly different potential energies, and this will be important to us in a later topic (conformational analysis).

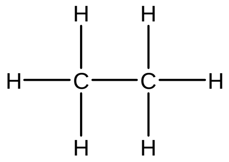


A single bond allows rotation to occur about the carbon-carbon bond, which alters the shape and the energy of the molecule.

carbon atom shape = tetrahedral
hybridization = sp^3
bond angles about sp carbon = 109^o
number of sigma bonds = 4
number of pi bonds = 0

All of the details in this group go together. If you have any one of them, you should be able to fill in the remaining details.

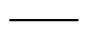
As with ethyne and ethene, there are some additional ways of drawing ethane. Some of these are shown below. Each subsequent representation puts a greater burden on you to interpret its meaning. Your advantage is that every non-hydrogen atom you view (carbon, nitrogen, oxygen and halogens) has to be one of the three shapes we are developing in this topic, so your choices are pretty limited (sp, sp^2 or sp^3).



Each line represents a bond. Since there are only single bonds, we know that they must be sigma bonds. There cannot be any pi bonds becasue there are no second or third bonds between the same two atoms. The 2s and all three 2p orbitals must all be mixed, meaning that the hybridization has to be sp^3 and all of the terms that go along with sp^3 hybridization.

H_3CCH_3
or
CH_3CH_3

The connections of the atoms are implied by the linear way the formula is drawn. You have to fill in the details about the number of bonds and where they are located from your understanding of each atom's bonding patterns. A CH_3 has three single bonds between carbon and hydrogen, so there can only be one additional bond between the carbon atoms to total carbon's normal number of four bonds. This means, of course, that there is no pi bond, using a 2p orbital, leaving the 2s and all three 2p orbitals to mix, forming four sp^3 hybrid orbitals.



A bond line formula only shows lines connecting the carbon atoms and leaves off the hydrogen atoms. Every end of a line is a carbon (two in this drawing) and every bend in a line is a carbon (none in this drawing). You have to figure out how many hydrogens are present by substracting the number of lines shown (bonds to non-hydrogen atoms) from four (the total number of bonds of a neutral carbon (4 - 1 = 3H on each carbon atom in this drawing).

C_2H_6

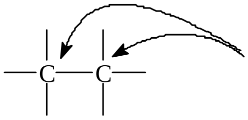
This is the ultimate in condensing a structure. Merely writing the atoms that are present and how many of them there are provides no details about the connectivity of the atoms. A structure can be generated only for extremely simple molecules that have only one way that they can be drawn. Ethane is an example of such molecule.

Problem 4 – Draw a 3D representation or hydrogen methanol, H_3COH and methanamine, H_3CNH_2. Show lines for the sigma bond skeleton and a line with two dots for lone pairs, in a manner similar to above. What is different about this structure compared with ethene above?

This represents the last of our bonding pictures that you need to understand. Almost every example of hybridization used in this book, whether carbon, nitrogen, oxygen or the halogens will use one of these three shapes. I hope you can see how important this is to your organic career (…and your biochemistry career).

Summary – Key features to determine hybridization of atoms in organic chemistry.

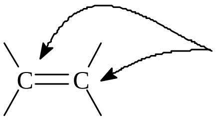
Use multiple bonds to determine the hybridization state of an atom. A second bond between two atoms is always made up of 2p orbitals, as part of a π bond, which leaves 2s+2p+2p to hybridize as sp^2. If a third bond is present between the same two atoms, or if a second pi bond is present with a second atom, it also is made up of 2p orbitals, which leaves 2s+2p to hybridize as sp. If there are only single bonds, then all four atomic orbitals (2s+2p+2p+2p = sp^3) must be mixed together. Essentially, the hybridization state is determined by subtracting any p orbitals of pi bonds from the three 2p orbitals available for hybridization. Whatever is left over is mixed with the 2s to form hybrid orbitals. If you know the hybridization, then you know the bond angles, the shape and how many sigma and pi bonds are present. What you need now is lots of practice.



There are no second or third bonds between the same two atoms so no 2p orbitals are used to make any pi bonds. The hybridization must be sp^3 (2s + 2p + 2p + 2p = sp^3) and all four atomic orbitals are mixed to form four sp^3 hybrid orbitals.

2s 2p 2p 2p

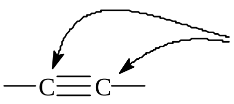
No pi bonds so all atomic orbitals are used in hybridization = sp^3



There is a second bond between the two carbon atoms. This must be a pi bond and uses 2p orbitals. The hybridization must be sp^2 (2s + 2p + 2p = sp^2) and three atomic orbitals are mixed to form three sp^2 hybrid orbitals

2s 2p 2p $\cancel{2p}$

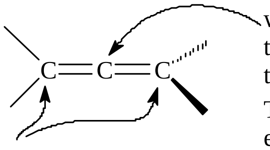
One pi bond, so only the 2s and two of the 2p's are used in hybridization = sp^2



There is a second and a third bond between the same two atoms. There must be two pi bonds using two 2p orbitals. The hybridization must be sp (2s + 2p = sp) and two atomic orbitals are mixed to form two sp hybrid orbitals.

2s 2p $\cancel{2p}$ $\cancel{2p}$

Two pi bonds, so only the 2s and one of the 2p's are used in hybridization = sp



There is a second bond with the atom on the left and again with the atom on the right. There must be two pi bonds using two 2p orbitals. The hybridization must be sp (2s + 2p = sp) and two atomic orbitals are mixed to form two sp hybrid orbitals. The hybridization of the end carbons, is sp^2 (see the second example above). The planar shapes of the atoms of the two end carbons are twisted 90° relative to one another because the 2p orbitals on the middle carbon making the pi bonds with them are angled at 90° relative to one another.

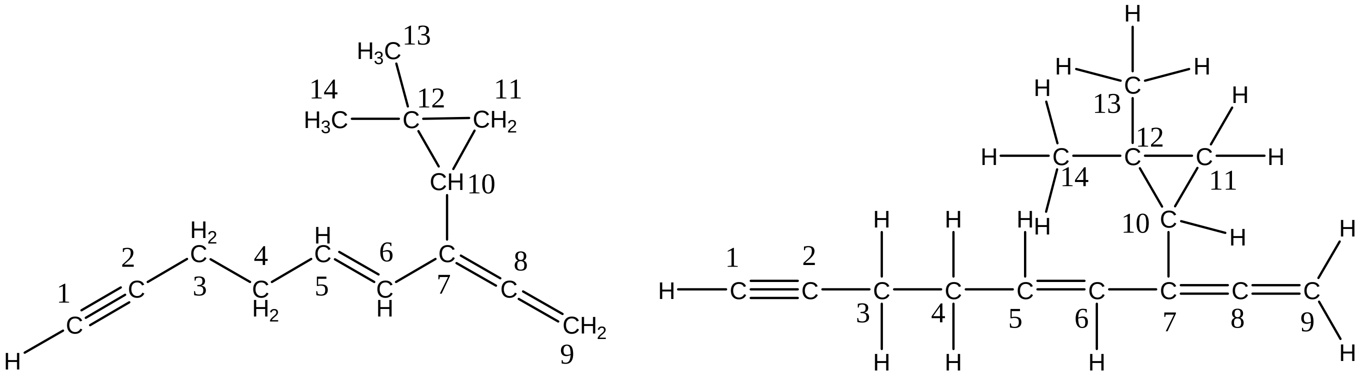
2s 2p $\cancel{2p}$ $\cancel{2p}$

Two pi bonds on center carbon, so only the 2s and one of the 2p's are used in hybridization = sp

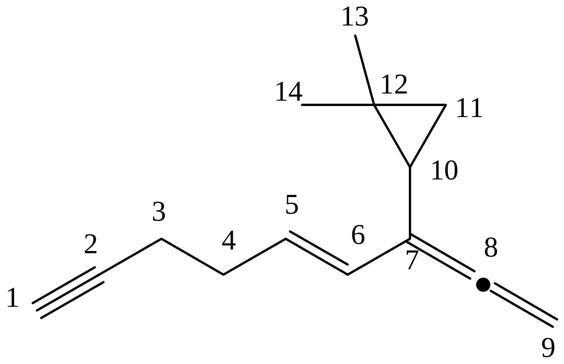
We will be viewing and drawing many complicated structures in this book, as we work on problems and try to understand organic chemistry. To simplify this process, we will often use bond-line formulas. We have mentioned bond-line formulas, very briefly above, but now we will examine how they work using all of the features just discussed. The first structure drawn below shows all of the carbon atoms and hydrogen atoms. The second structure is a 2D Lewis structure. It takes some time to include such detail. Bond-line formulas allow us to more quickly draw such a structure without all of those atoms. The down side is that your organic knowledge has to be more sophisticated to interpret what they mean. Recall that every end of a line and every bend in a line is a carbon atom. We will also use the convention that a large "dot" in the structure is a carbon atom (see the structure below). Since hydrogen atoms are deliberately left out, for drawing convenience, you must determine the number of hydrogen atoms present in bond-line formulas by subtracting the number of bonds shown from four, the usual number of bonds on a neutral carbon atom.

Number of hydrogen atoms on a carbon (you don't see these) = (4) - (number of bonds shown)

See if your interpretation of the bond-line structure is the same as the more detailed structures provided. As an experiment, time yourself drawing this structure all three different ways, then multiply the difference in time by the number of structures you will draw during your organic career. I'm sure you'll agree that it's worth the effort to understand bond-line formulas.



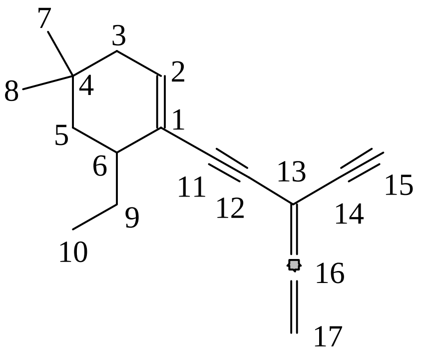
Two structures showing all of the atoms. It's a lot of work to draw structures this way.



Same molecule using a bond-line structure showing only non-hydrogen bonds. A carbon atom is implied at every bend and every end of a line and every dot. This one is a lot easier and faster to draw.

Carbon #	**hybridization**	**bond angles**	**shape**	**number of hydrogen atoms**
1	sp	180^o	linear	1
2	sp	180^o	linear	0
3	sp^3	109^o	tetrahedral	2
4	sp^3	109^o	tetrahedral	2
5	sp^2	120^o	trigonal planar	1
6	sp^2	120^o	trigonal planar	1
7	sp^2	120^o	trigonal planar	0
8	sp	180^o	linear	0
9	sp^2	120^o	trigonal planar	2
10	sp^3	109^o	tetrahedral	1
11	sp^3	109^o	tetrahedral	2
12	sp^3	109^o	tetrahedral	0
13	sp^3	109^o	tetrahedral	3
14	sp^3	109^o	tetrahedral	3

Problem 5 - What is the hybridization of all carbon atoms in the structure below? What are the bond angles, shapes, number of sigma bonds, number of pi bonds and number's of attached hydrogen atoms? Bond line formulas are shorthand, symbolic representations of organic structures. Each bend represents a carbon, each end of a line represents a carbon and each dot represents a carbon. All carbon/carbon bonds are shown. The number of hydrogen atoms on a carbon is determined by the difference between four and the number of bonds shown.

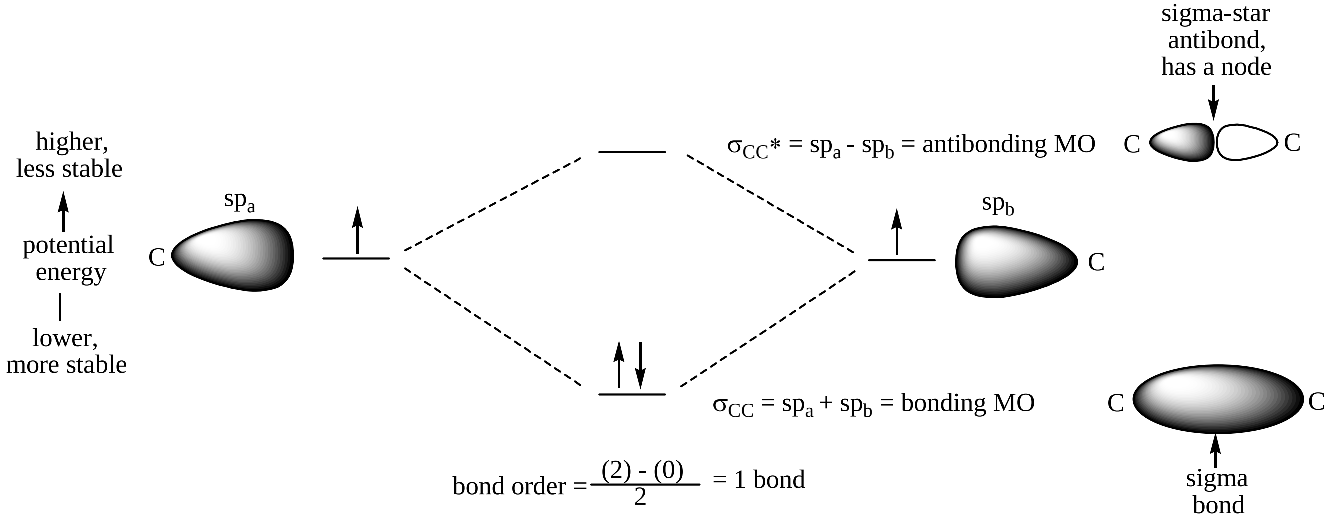


atom	hybridization	angles	# H's	shape
1				
2				
3				
4				
5				
6				
7				
8				
9				
10				
11				
12				
13				
14				
15				
16				
17				

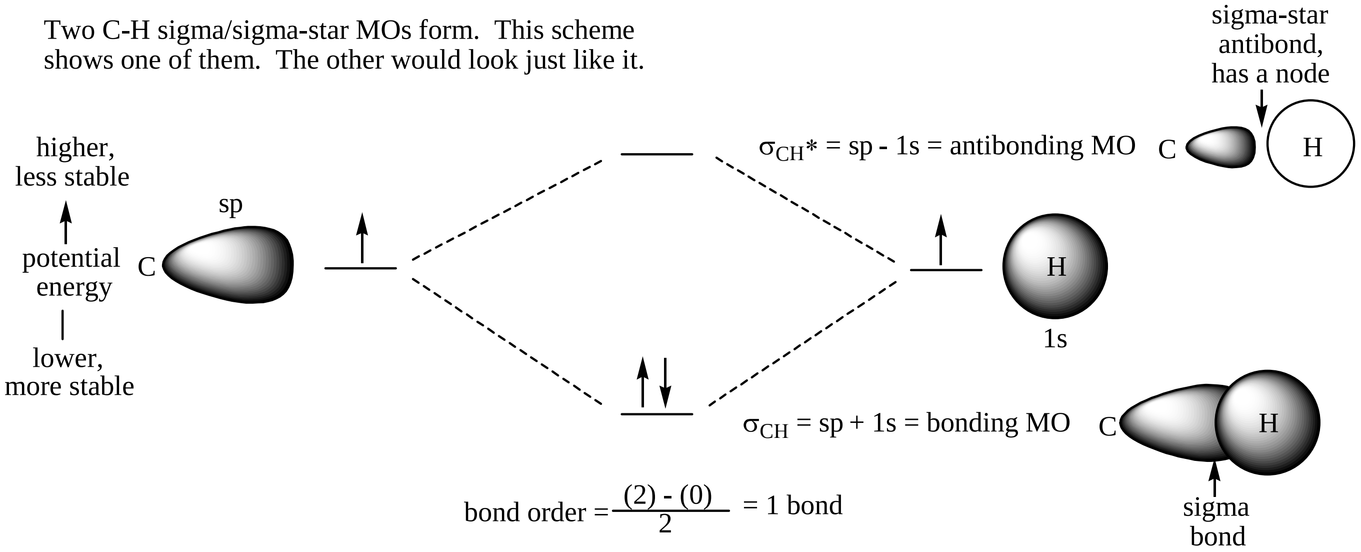
Molecular Orbital Diagrams

Ethyne MOs

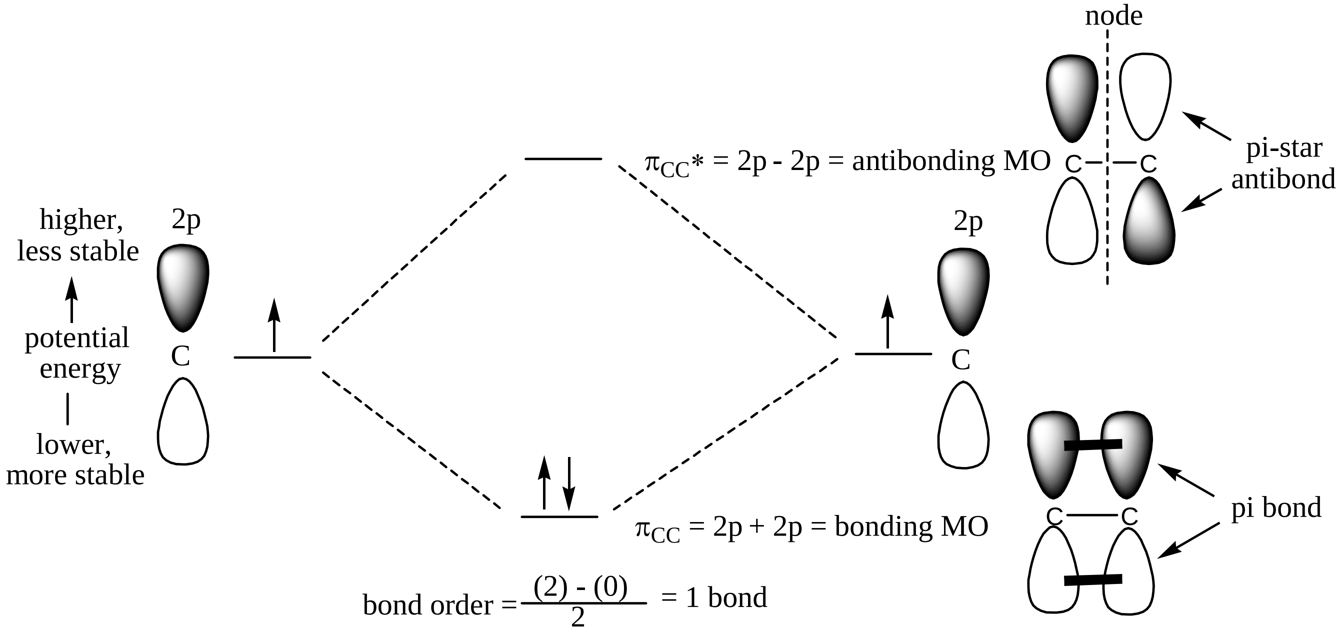
We made two very simple molecular orbitals using hydrogen atoms (σ and σ*) and p orbitals (π and π*) above. The process works pretty much the same when we are making bonds using carbon and hydrogen atoms (…and nitrogen, oxygen and halogen atoms). Let's quickly develop the molecular orbitals for ethyne. First we need to form the sigma and sigma-star MOs between the two carbon atoms using their sp hybrid orbitals (σ_{cc} and σ^*_{cc}). The vertical scale represents relative potential energy among the various orbitals. Lower is more stable.



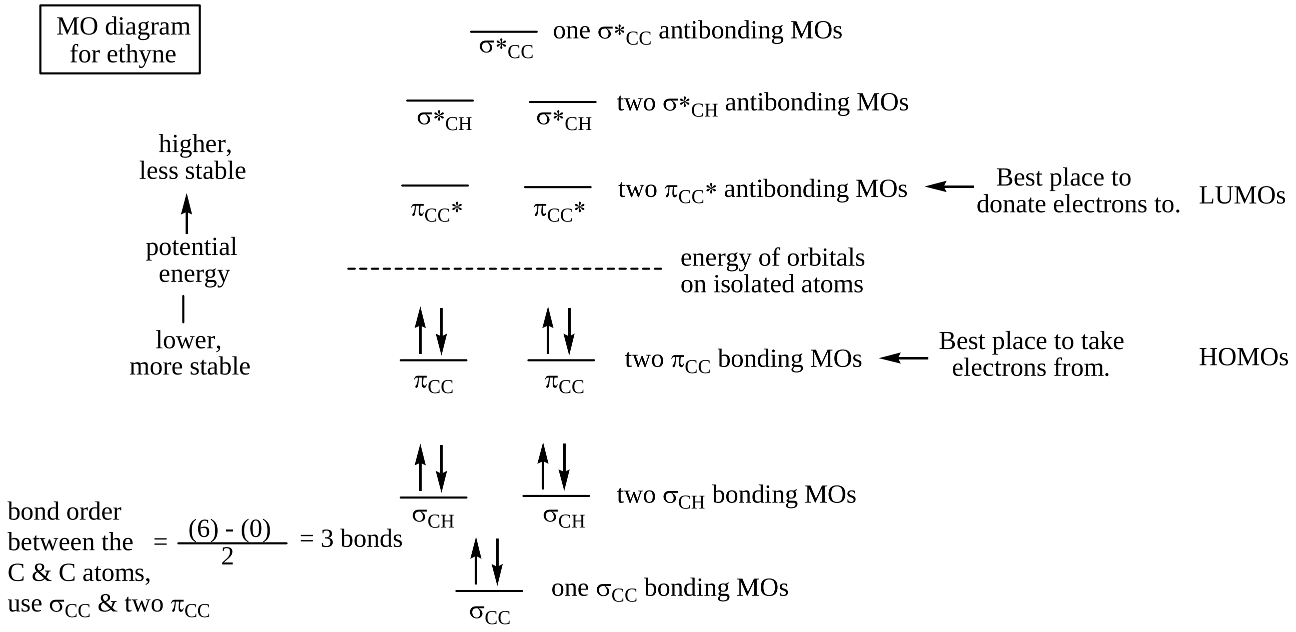
Next we need to form sigma and sigma-star MOs between each carbon atom and a hydrogen atom using each carbon atom's other sp hybrid orbital and a hydrogen atom's 1s atomic orbital (σ_{CH} and σ^*_{CH}). We'll just show one MO diagram and you can imagine doing it twice.


Two C-H sigma/sigma-star MOs form. This scheme shows one of them. The other would look just like it.

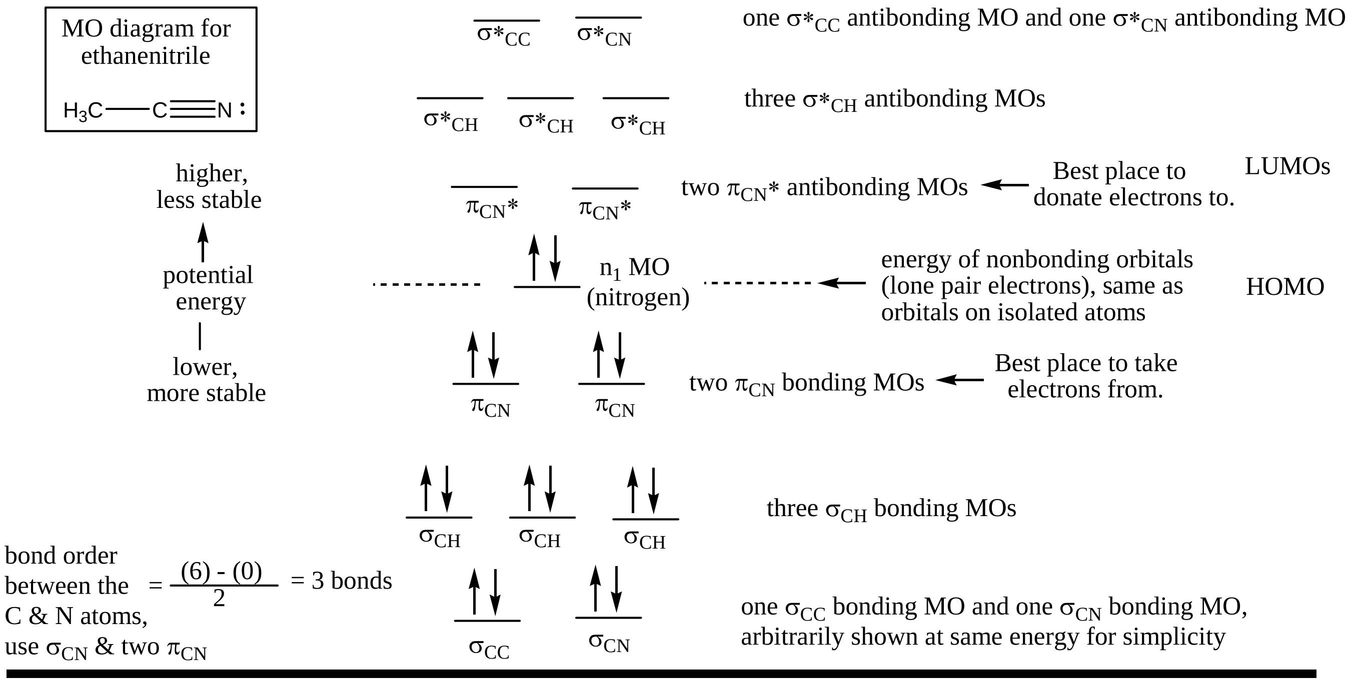
Finally we need to form two pi and pi-star MOs between the carbon atoms using carbon 2p orbitals (π_{CC} and π^*_{CC}). We'll just show one MO diagram and you can imagine doing it a second time. This is going to look almost exactly like our example of a pi bond presented earlier.



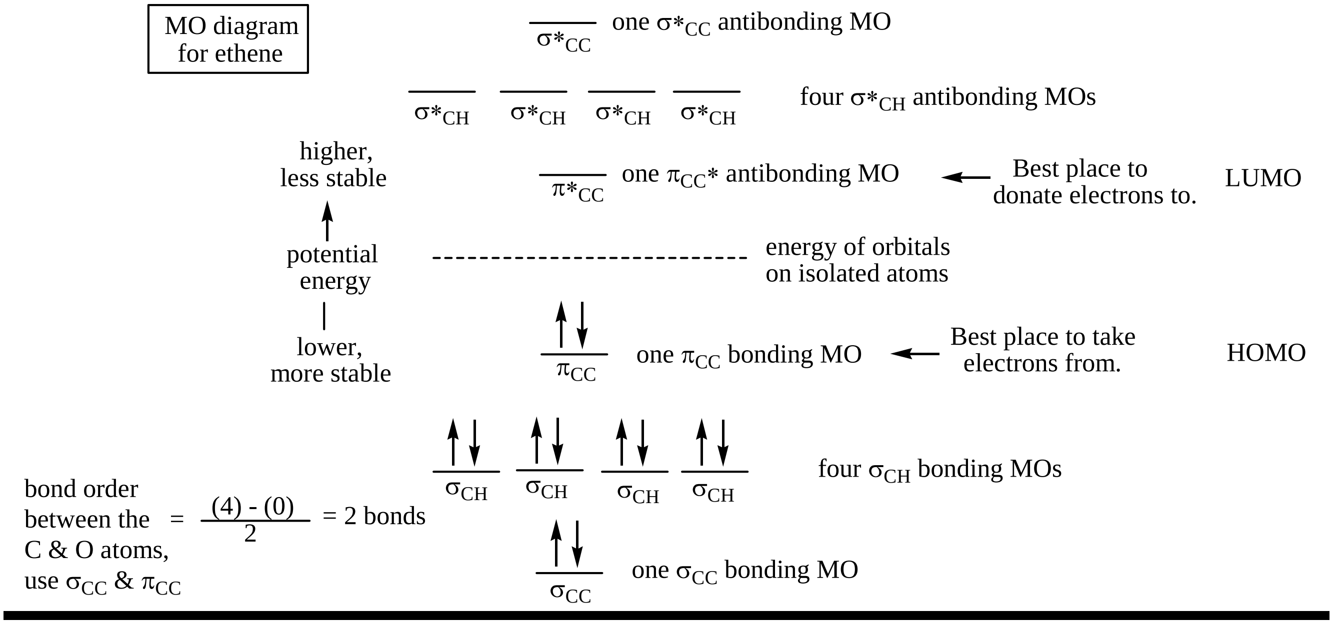
If we put all of the molecular orbitals of ethyne together, in a single energy diagram, it would look as follows. The pi MOs determine the *highest occupied molecular orbital (HOMO)* and *lowest unoccupied molecular orbital (LUMO)*. The 2p orbital overlap is the least bonding and the least antibonding. The HOMO electrons are the easiest place to donate electrons from (least tightly held) and the LUMO orbital is the best place to accept electrons, if accepted into the molecular orbitals (lowest potential energy empty orbital = most stable of the empty orbitals). The pi molecular orbitals determine much of the chemistry of alkynes.



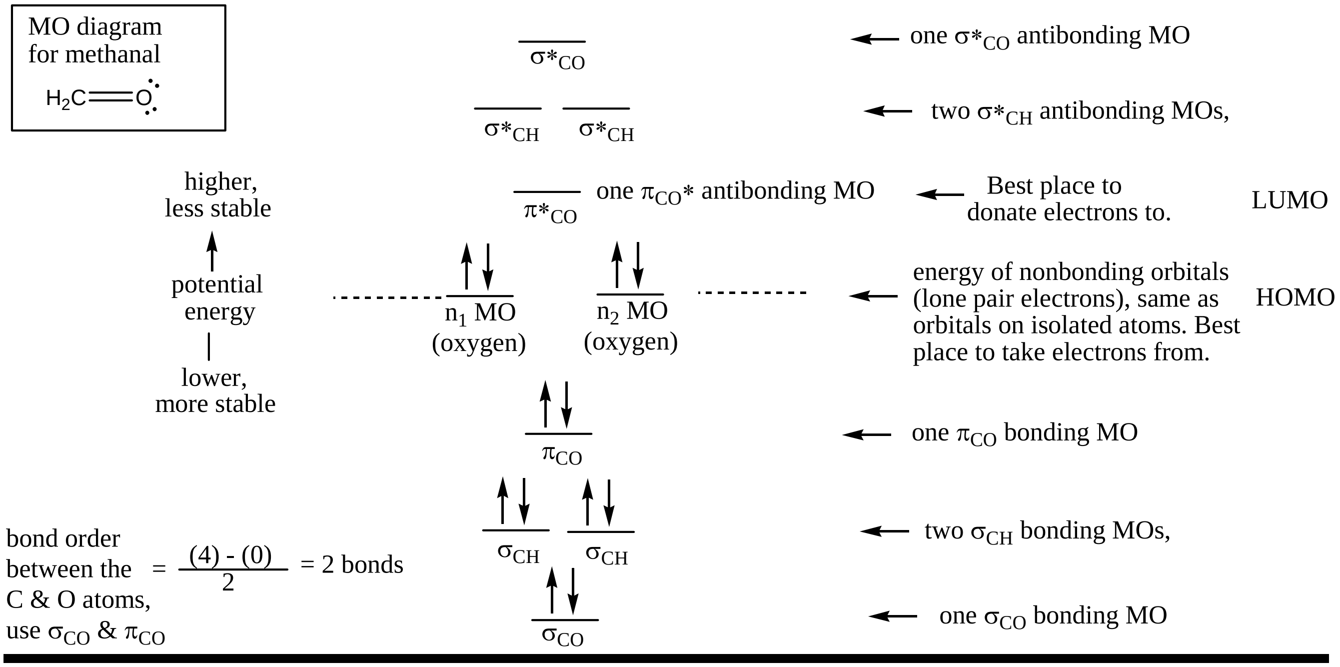
Problem 6 – Use ethyne (H-CC-H) as a model to draw an MO diagram for hydrogen cyanide (H-CN) and propanenitrile (CH_3CH_2CN). Lone pairs of electrons belong to a single atom and are found at middle energies (they do not form bonding and antibonding orbitals). Label lone pair orbitals with the letter “n” for nonbonding electrons. Notice there is one fewer bond for each lone pair in the structures above. Ethanenitrile (common name = acetonitrile),is shown below as an example.



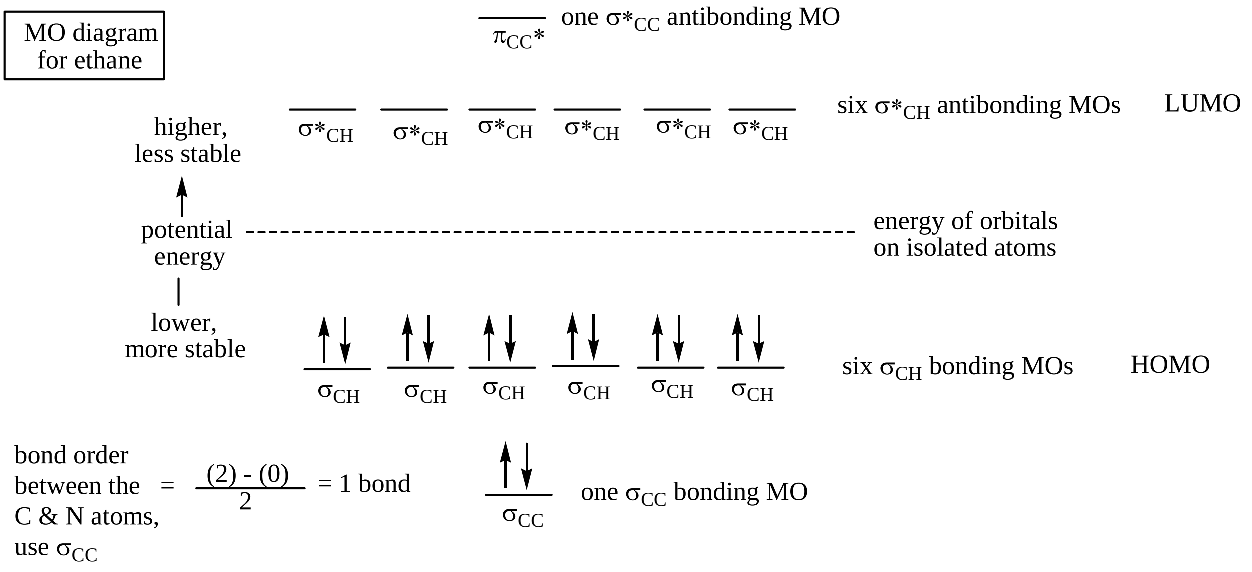
We won't build all of the molecular orbitals for ethene from scratch since the process is essentially the same as that used for ethyne. However, we will provide a complete molecular orbital energy diagram, showing all of the sigma and sigma-star MOs and the pi and pi-star MOs. There are now five sigma bonds (four C-H and one C-C) and one pi bond (C=C). As is usually the case when a pi bond is present, the pi / pi-star orbitals form the important HOMO / LUMO molecular orbitals. The 2p orbital overlap is the least bonding (HOMO) and the least antibonding (LUMO). The HOMO electrons are the easiest place to donate electrons from (it holds the highest potential energy electron pair = most reactive of the full orbitals), and the LUMO orbital is the best place to accept electrons into (it is the lowest potential energy empty orbital = least unstable of the empty orbitals). Most of the chemistry of alkenes uses these orbitals.



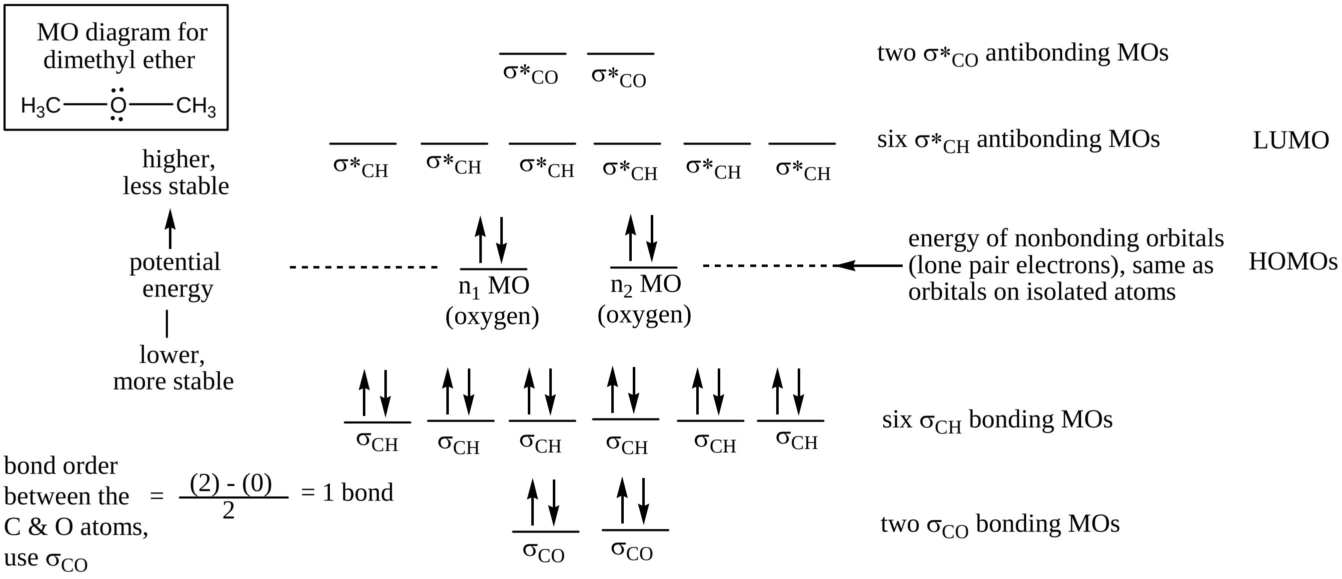
Problem 7 – Use ethene ($H_2C{=}CH_2$) as a model to draw an MO diagram for ethanal ($CH_3CH{=}O$) and 2-propanone (CH_3COCH_3). Lone pairs of electrons belong to a single atom and are found at middle energies (they do not form bonding and antibonding orbitals). Label lone pair orbitals with the letter “n” for nonbonding electrons. If there is more than one lone pair label them as n_1 and n_2. And show them at the same energy. Notice there is one fewer bond for each lone pair in the structures above. Methanal (common name = formaldehyde) is shown below as an example.



As with ethene, we won’t build all of the molecular orbitals for ethane from scratch, but we will provide a qualitative molecular orbital energy diagram, showing all of the sigma and sigma-star MOs. There are no pi and pi-star MOs in ethane. There are now seven sigma bonds (six C-H and one C-C) and zero pi bonds. The important HOMO / LUMO orbitals have to be sigma and sigma-star MOs in this example (our designation of relative sigma energies is arbitrary). Because there are no pi / pi-star HOMO / LUMO molecular orbitals, ethane is much less reactive than ethyne and ethene.

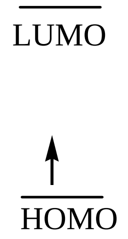


Problem 8 – Use ethane (CH_3-CH_3) as a model to draw an MO diagram for methyl amine (CH_3NH_2) and methanol (CH_3-OH). Lone pairs of electrons belong to a single atom and are found at middle energies (they do not form bonding and antibonding orbitals). Label lone pair orbitals with the letter “n” for nonbonding electrons. If there is more than one lone pair label them as n_1 and n_2. And show them at the same energy. Notice there is one fewer bond for each lone pair in the structures above. Dimethyl ether is shown below as an example.



Lecture 2
Possible Solutions

Problem 1 – What would the MO pictures of H_2^+, H_2^- and He_2^+ look like? Would you expect that these species could exist? What would be their bond orders?

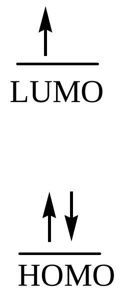


$\sigma* = 1s_a - 1s_b$ = antibonding MO

$\sigma = 1s_a + 1s_b$ = bonding MO

bond order (H_2^+) molecule) = $\frac{(1) - (0)}{2}$ = 1/2 bond

There is some energy advantage
for H_2^+ over two hydrogen atoms.

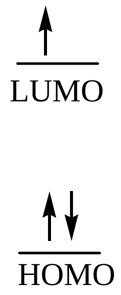


$\sigma* = 1s_a - 1s_b$ = antibonding MO

$\sigma = 1s_a + 1s_b$ = bonding MO

bond order (H_2^-) molecule) = $\frac{(2) - (1)}{2}$ = 1/2 bond

There is some energy advantage
for H_2^- over two hydrogen atoms.



$\sigma* = 1s_a - 1s_b$ = antibonding MO

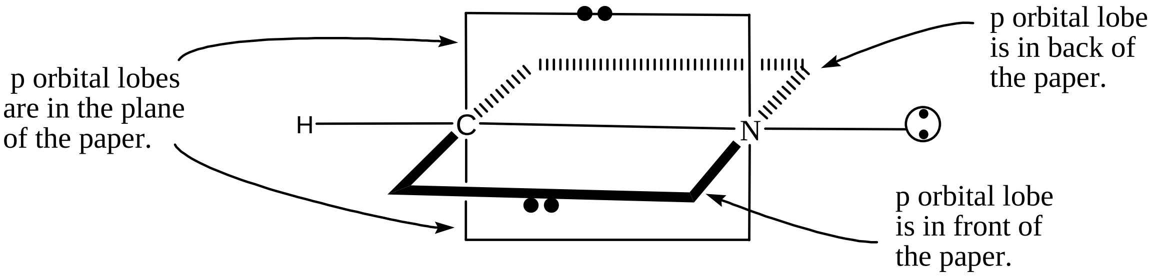
$\sigma = 1s_a + 1s_b$ = bonding MO

bond order (He_2^+) molecule) = $\frac{(2) - (1)}{2}$ = 1/2 bond

There is some energy advantage
for He_2^+ over two helium atoms.

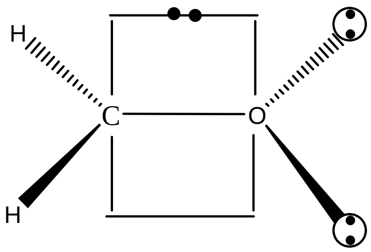
Problem 2 – Draw a 3D representation or hydrogen cyanide, HCN. Show lines for the sigma bond skeleton and the lone pair of electrons. Show two dots for the lone pair. Also show pi bonds represented in a manner similar to above. What is different about this structure compared with ethyne above?

Ethyne and hydroge cyanide look similar except for the lone pair on nitrogen.



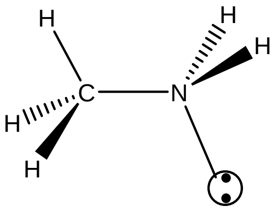
Problem 3 – Draw a 3D representation of methanal (common name = formaldehyde), $H_2C=O$. Show lines for the sigma bond skeleton and the lone pairs of electrons with two dots for each lone pair. Also show pi bonds represented in a manner similar to above. What is different about this structure compared with ethene above?

Ethene and methanal look similar except for the two lone pairs on oxygen.

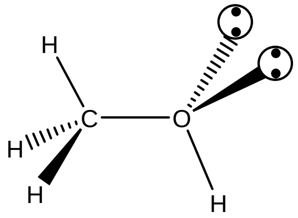


Problem 4 – Draw a 3D representation or hydrogen methanol, H_3COH and methanamine, H_3CNH_2. Show lines for the sigma bond skeleton and a line with two dots for lone pairs, in a manner similar to above. What is different about this structure compared with ethene above?

Ethane, methanamine and methanol look similar except for the number of lone pairs of electrons.

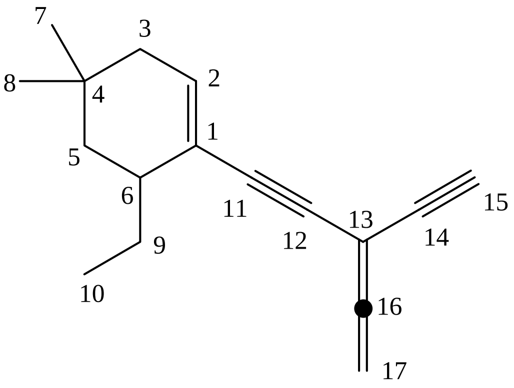


methanamine



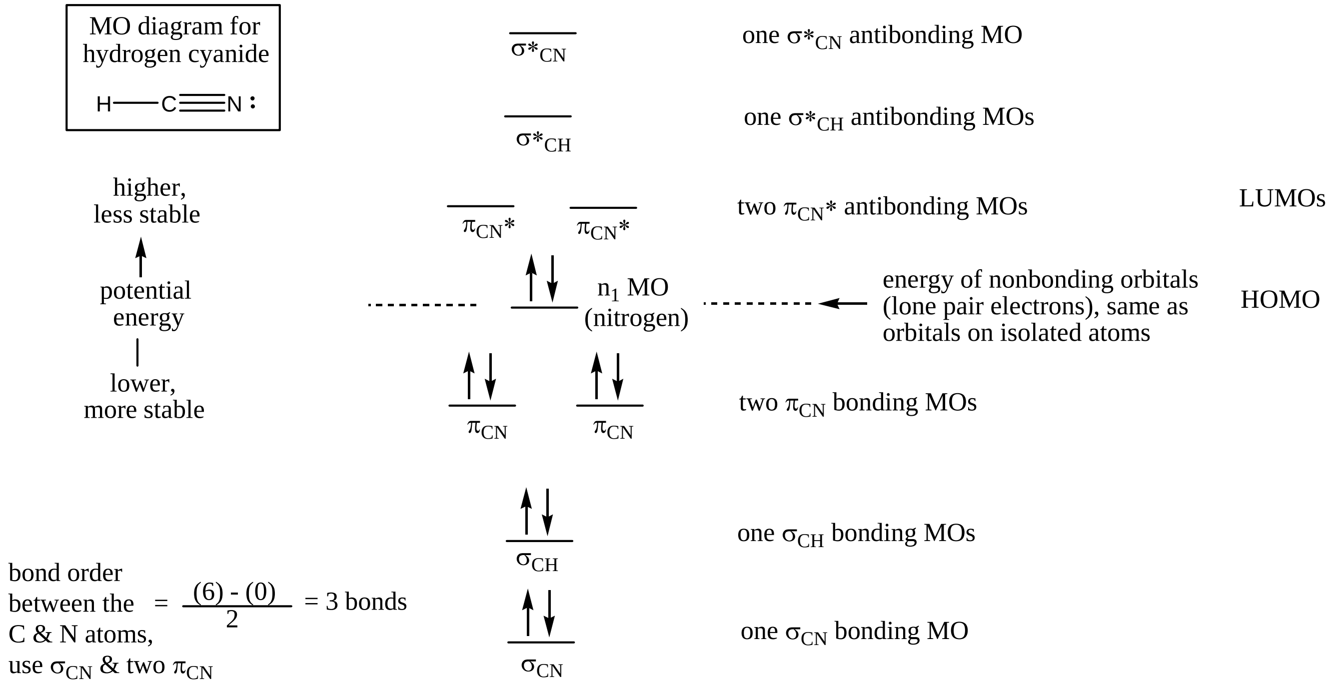
methanol

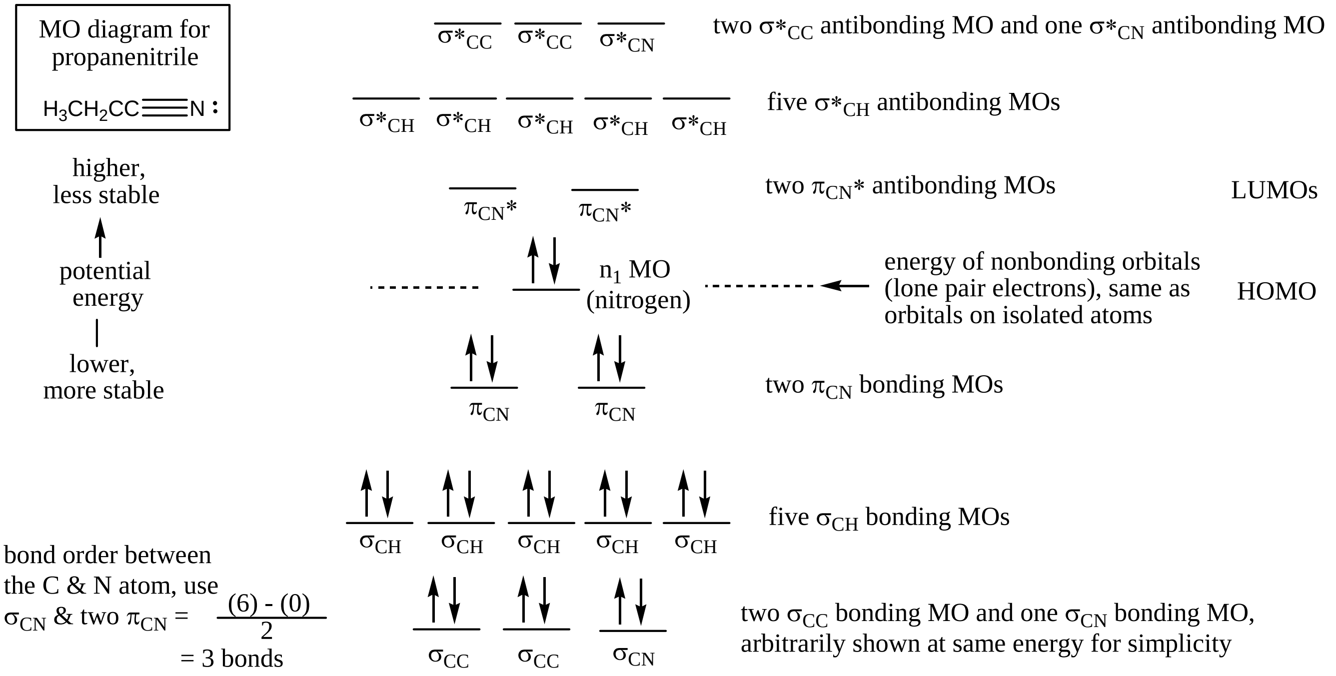
Problem 5 - What is the hybridization of all carbon atoms in the structure below? What are the bond angles, shapes, number of sigma bonds, number of pi bonds and number's of attached hydrogen atoms? Bond line formulas are shorthand, symbolic representations of organic structures. Each bend represents a carbon, each end of a line represents a carbon and each dot represents a carbon. All carbon/carbon bonds are shown. The number of hydrogen atoms on a carbon is determined by the difference between four and the number of bonds shown.



Carbon #	hybridization	bond angles	shape	number of hydrogen atoms
1	sp^2	120^o	trigonal planar	0
2	sp^2	120^o	trigonal planar	1
3	sp^3	109^o	tetrahedral	2
4	sp^3	109^o	tetrahedral	0
5	sp^3	109^o	tetrahedral	2
6	sp^3	109^o	tetrahedral	1
7	sp^3	109^o	tetrahedral	3
8	sp^3	109^o	tetrahedral	3
9	sp^3	109^o	tetrahedral	2
10	sp^3	109^o	tetrahedral	3
11	sp	180^o	linear	0
12	sp	180^o	linear	0
13	sp^2	120^o	trigonal planar	0
14	sp	180^o	linear	0
15	sp	180^o	linear	1
16	sp	180^o	linear	0
17	sp^2	120^o	trigonal planar	2

Problem 6 – Use ethyne (H-CC-H) as a model to draw an MO diagram for hydrogen cyanide (H-CN) and propanenitrile (CH_3CH_2CN). Lone pairs of electrons belong to a single atom and are found at middle energies (they do not form bonding and antibonding orbitals). Label lone pair orbitals with the letter "n" for nonbonding electrons. Notice there is one fewer bond for each lone pair in the structures above. Ethanenitrile (common name = acetonitrile),is shown below as an example.





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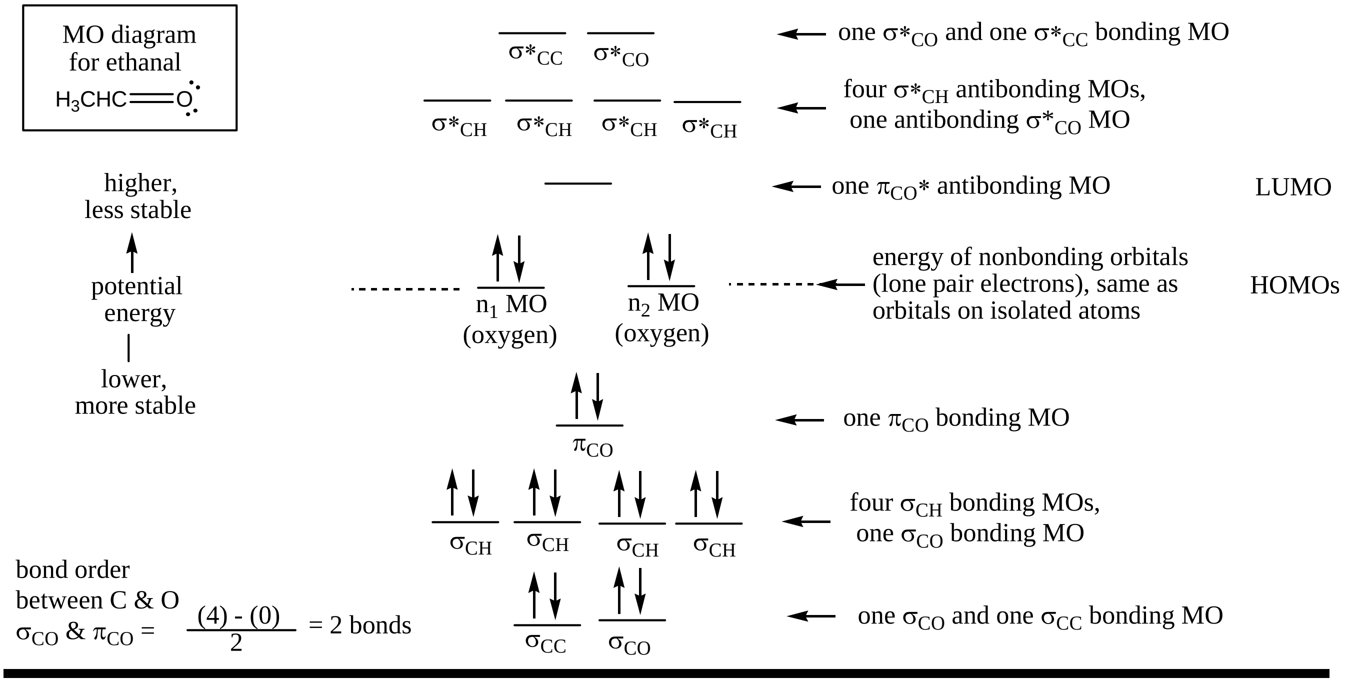

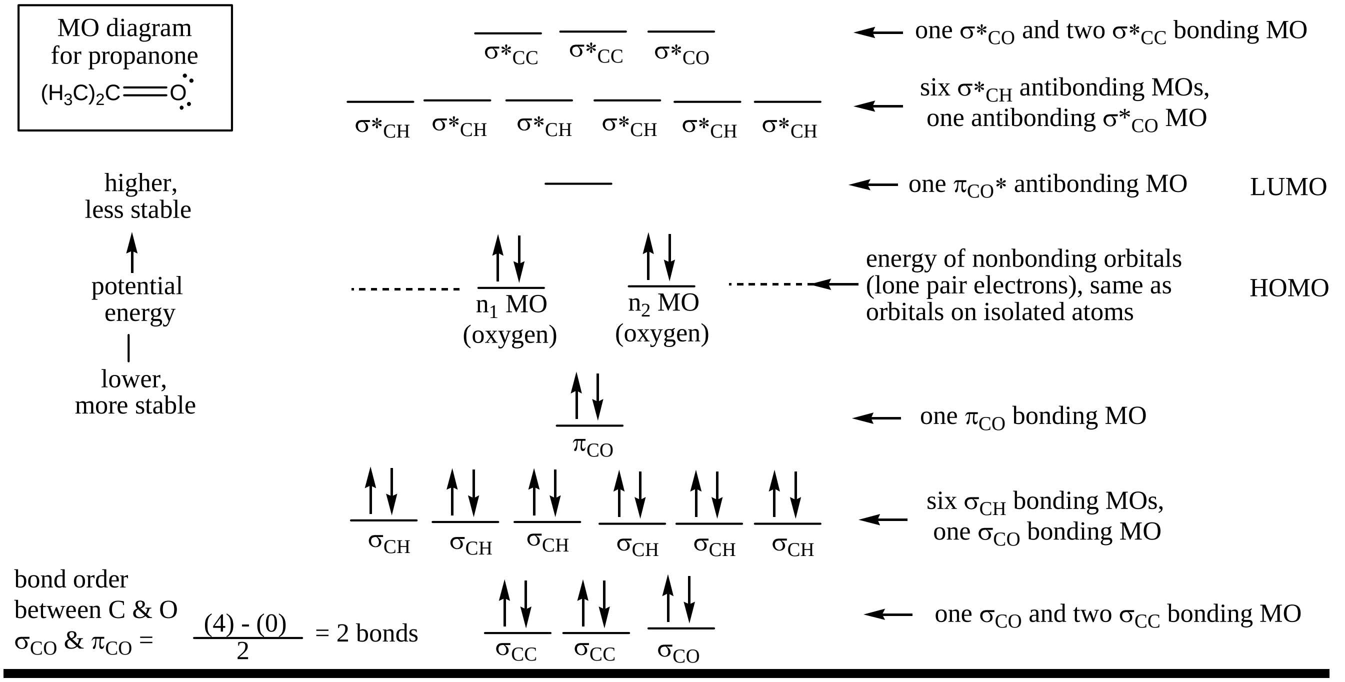

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