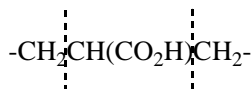
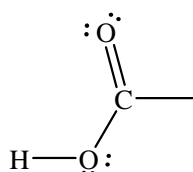
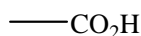
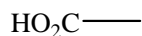
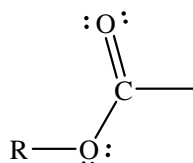
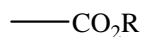
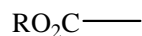


Lecture 4

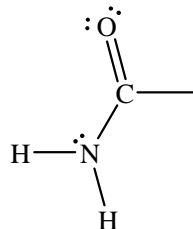
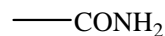
carboxylic acid group



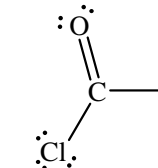
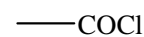
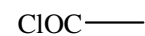
ester group



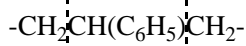
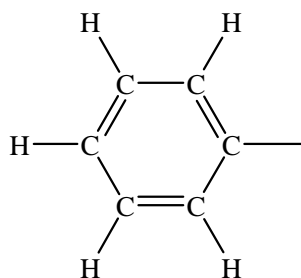
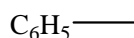
amide group



acid chloride group

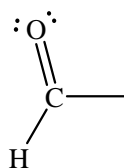
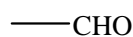
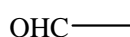


phenyl group

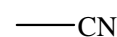
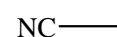


(six carbon ring present)

aldehyde group

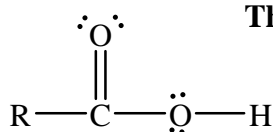
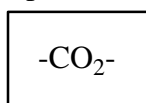


nitrile group



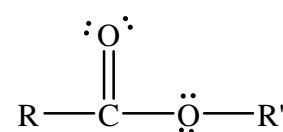
Common Error 2 – The following patterns show up frequently, and are often misdrawn. The first pattern is found in esters (RCO₂R) and carboxylic acids (RCO₂H). The two oxygen atoms are both connected to the same carbon atom and one of the oxygen atoms continues the chain to R or H. I have inserted each “O₂” pattern in between two atoms (R and/or H) to show how it should look. “R” represents a generic continuation of a carbon chain.

confusing pattern



carboxylic acid
(example h, below)

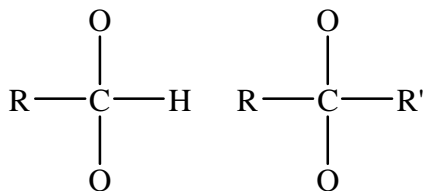
These are "correct".



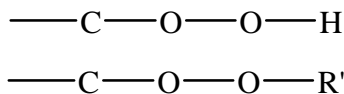
ester
(example i, below)

Lecture 4

Common errors. These are "incorrect".



The chain (H or R') is incorrectly connected to the carbon atom instead of being connected to an oxygen atom. The oxygen atoms, as drawn here, cannot form two bonds without exceeding the carbon atom's octet and the oxygen atoms look like they need negative formal charge.



The incorrectly drawn carbon atom only has two bonds and there is no way to form more bonds. The peroxide linkage (-O-O-) is a possible functional group, but not common and very reactive.

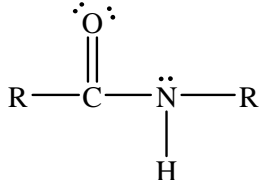
Related problems are common with amides, acid chlorides, aldehydes and ketones, and are shown below. "R" symbolizes the rest of the structure.

Correctly drawn functional group structures.

(example k, below)



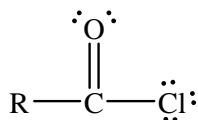
amides



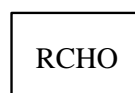
(example c, below)



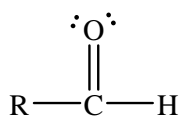
acid chlorides



(example f and l, below)



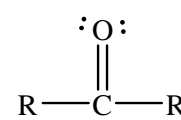
aldehydes



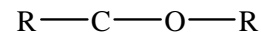
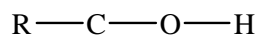
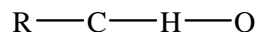
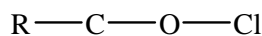
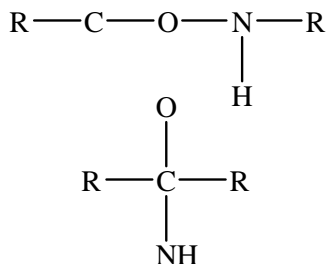
(example g, below)



ketones



These drawings of functional groups are **incorrect**, but they are **common student errors**.



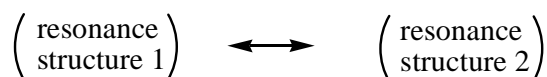
These are **wrong!**

Lecture 4

Concise Mechanical Rules for Drawing 2D Lewis Structures, including resonance structures.

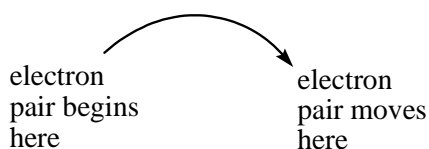
(Good intuition can substitute for all of these rules.)

1. Draw a sigma skeletal framework showing all of the sigma bonds from the condensed line formula.
2. Sum all of the valence electrons available for bonding and lone pairs. Reduce this number by 1 for each positive charge and increase this number by 1 for each negative charge.
3. Each sigma bond counts for two electrons. Subtract this number of electrons from the total number of electrons to determine how many electrons are available for lone pairs and pi bonds.
4. Use any remaining electrons as lone pairs to fill in octets on electronegative atoms first ($F > O > N > \text{other halogens} > C$). If the electrons are still not used up, add the additional electrons to carbon atoms at alternate positions to maximize charge separation where possible (minimize electron-electron repulsion) until all electrons have been used. It is sometimes helpful for you to write in the formal charge at this point. Formal charge will suggest the best way to group lone pair electrons used to make pi bonds. However, it is a lot of extra work to do this.
5. A lone pair of electrons on an atom next to a neighbor with an incomplete octet can be shared to form a second (double) or third (triple) bond with the neighbor atom (these will be pi bonds). If this can be done to a particular electron deficient atom by more than one neighbor atom, then resonance structures are present. The best resonance structure will have the maximum number of bonds and full octets. If two structures have the same number of bonds, then a secondary consideration is to minimize charge separation (the formal charge from rule 4 will help here). If residual charge is necessary, it is better to be consistent with electronegativity (e.g. negative formal charge is better on oxygen than on carbon). Your goals, in this order, are
 1. to maximize the number of bonds and full octets and
 2. to minimize formal charge and
 3. keep formal charge consistent with electronegativity, if the other two goals have been met.
6. Resonance structures require a specific use of arrows.
 - a. Double headed arrows are placed between resonance structures.



A double headed resonance arrow shows that these structures both contribute to an actual structure that can be drawn as more than one reasonable Lewis structure.

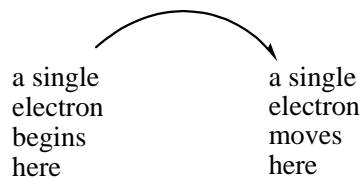
- b. A full headed curved arrow indicates two electron movement.



A full headed curved arrow indicates two electron movement to show where an electron pair will be located in the "next" structure, whether used in resonance structures or used in a reaction equation.

Lecture 4

c. A half headed curved arrow indicates one electron movement.

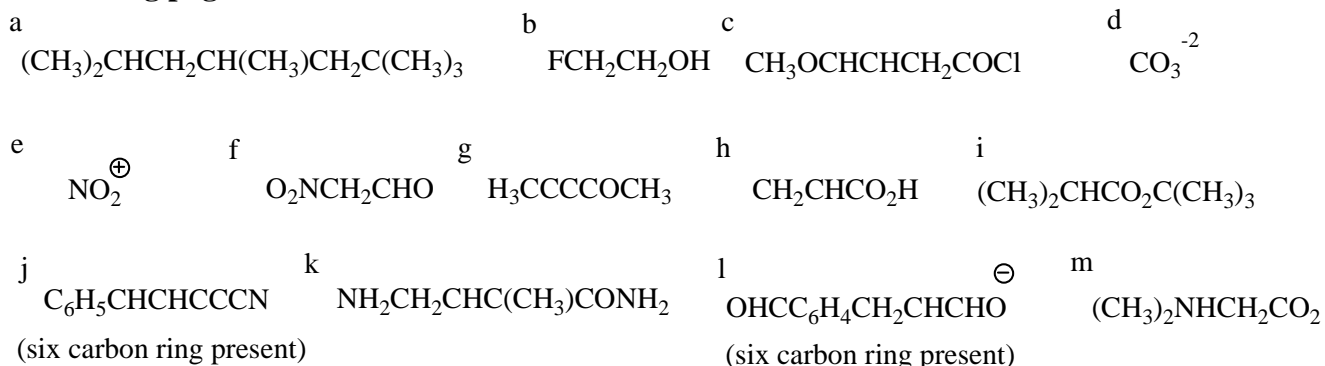


A half headed curved arrow indicates one electron movement to show where an electron will be located in the "next" structure (as in free radicals), whether used in resonance structures or used in a reaction equation.

We will work through several example structures to show how these rules work. At the same time, we will also illustrate many of the functional groups that we will study. After studying these examples, you can practice on your own by working problems. If you feel really daring, why not try and generate these 2D structures on your own before you look at the worked examples, and then use the structures below to check your work.

Two of your most important tools for learning organic chemistry are a pencil and paper (lots of it). Use them frequently. After your 2D practice, we'll practice drawing some simple to medium sized organic structures in three dimensions.

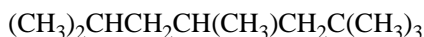
13 Examples of 2D Lewis structures from condensed line formulas. These are explained in detail in the following pages.



Lecture 4

a. This structure is an alkane. There are no pi bonds, only sigma bonds, and no lone pairs of electrons. When all of the sigma bonds are drawn, the structure is complete.

condensed bond-line formula

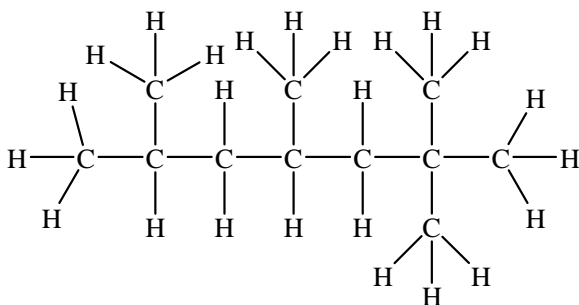


break into pieces



↓ No excess electrons
to add in.

2D sigma skeleton



Rule 1

Draw the 2D sigma skeleton.

Rule 2

total available electrons

$$11 \times \text{C} = 44 \text{ electrons}$$

$$24 \times \text{H} = 24 \text{ electrons}$$

$$+/- \text{ charge} = \text{none}$$

$$\text{total} = 68 \text{ electrons}$$

Rule 3

There are 34 sigma bonds using 68 electrons.

Rule 4

There are zero electrons left over for lone pairs and pi bonds. All of the carbon atoms have full octets. The structure is complete. There is no formal charge present.

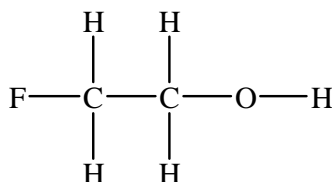
At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .

b. This structure has an alcohol (R-OH) and a "fluoro" substituent (R-F). "R" is used to indicate a generic carbon portion. There are no pi bonds, only sigma bonds. We know there will be lone pairs of electrons, because there are heteroatoms (oxygen and fluorine). The 2D sigma skeleton is not complete, because there are more electrons to add in. Once the lone pairs are added, the structure is complete.

condensed bond-line formula



2D sigma skeleton



↓ add in excess electrons
a. to electronegative atoms (O, F)
b. to alternate carbon atoms (none)

Continued on the next page.

Rule 1

2D sigma skeleton

Rule 2

total available electrons

$$2 \times \text{C} = 8 \text{ electrons}$$

$$5 \times \text{H} = 5 \text{ electrons}$$

$$1 \times \text{O} = 6 \text{ electrons}$$

$$1 \times \text{F} = 7 \text{ electrons}$$

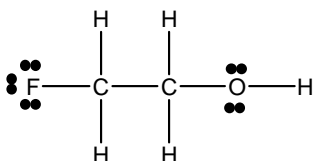
$$+/- \text{ charge} = \text{none}$$

$$\text{total} = 26 \text{ electrons}$$

Rule 3

There are 8 sigma bonds using 16 electrons.

Lecture 4



Rule 4

There are ten electrons left over for lone pairs and pi bonds. After placing two lone pairs on oxygen and three lone pairs on fluorine, zero electrons are left over. All atoms have full octets, so no pi bonds are present. The structure is complete. There is no formal charge present.

At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .

c. This structure has an acid chloride ($RCOCl$), an alkene ($C=C$) and an ether (ROR). There are atoms with fewer than the expected number of bonds in the 2D sigma skeleton, so pi bonds are likely present. We know there will be lone pairs of electrons, because there are heteroatoms (two oxygen atoms and a chlorine atom).

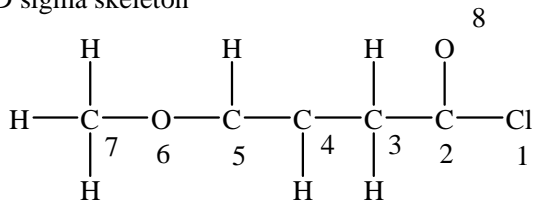
condensed bond-line formula



break into pieces

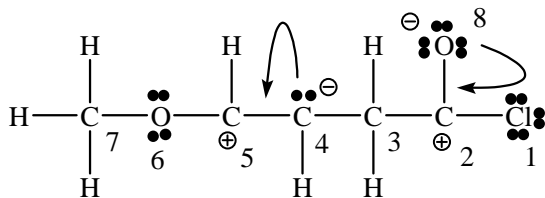


2D sigma skeleton

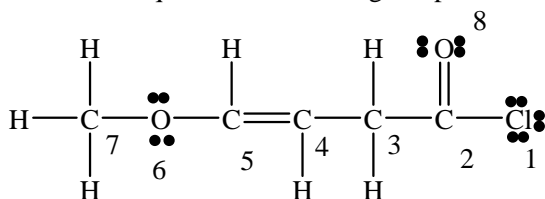


add in excess electrons

- to electronegative atoms ($2 \times O$)
- to alternate carbon atoms (1 pair)
- indicate formal charge



- share electrons to make pi bonds and complete any octets
- quench formal charge, if possible



Rule 2

total available electrons

$$5 \times C = 20 \text{ electrons}$$

$$7 \times H = 7 \text{ electrons}$$

$$2 \times O = 12 \text{ electrons}$$

$$1 \times Cl = 7 \text{ electrons}$$

$$+/- \text{ charge} = \text{none}$$

$$\text{total} = 46 \text{ electrons}$$

Rule 3

There are 14 sigma bonds using 28 electrons.

Rule 4

There are 18 electrons left over for lone pairs and pi bonds. Place two lone pairs on the O6, three lone pairs on O8 and three lone pairs on Cl-1 (a total of 16 electrons). There are two electrons left over and two adjacent carbon atoms without full octets (C4 and C5). Place the two electrons on the C4, farthest from the oxygen lone pairs. The structure is not complete because there are incomplete octets.

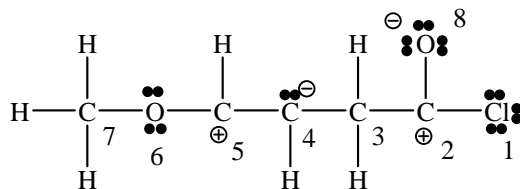
Rule 5

If you add in the formal charges (more work), they will provide clues as to the best resonance structure(s). Borrowing from the atoms that have negative charge (C4 and O8) quenches the positive charge (C5 and C2). Other resonance structures are possible, but this is the best one because it maximizes the number of bonds and quenches all formal charge. **Good intuition can do this without the formal charge.**

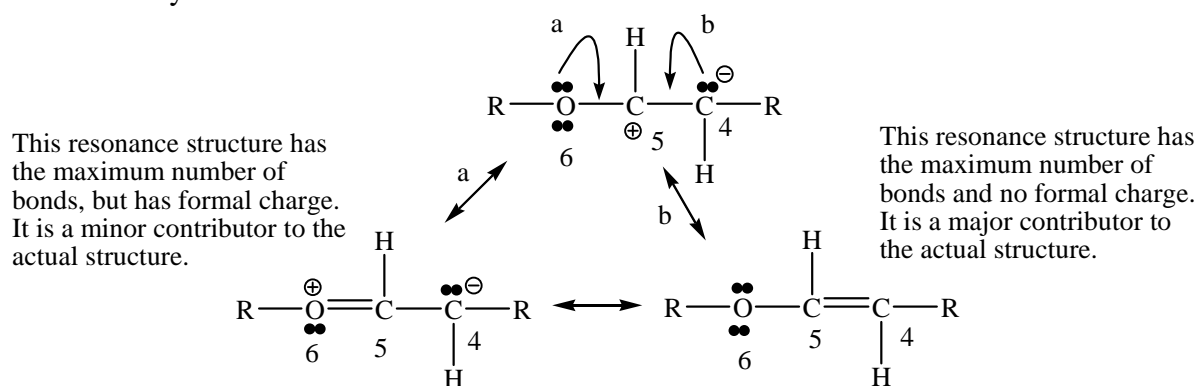
At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .

Lecture 4

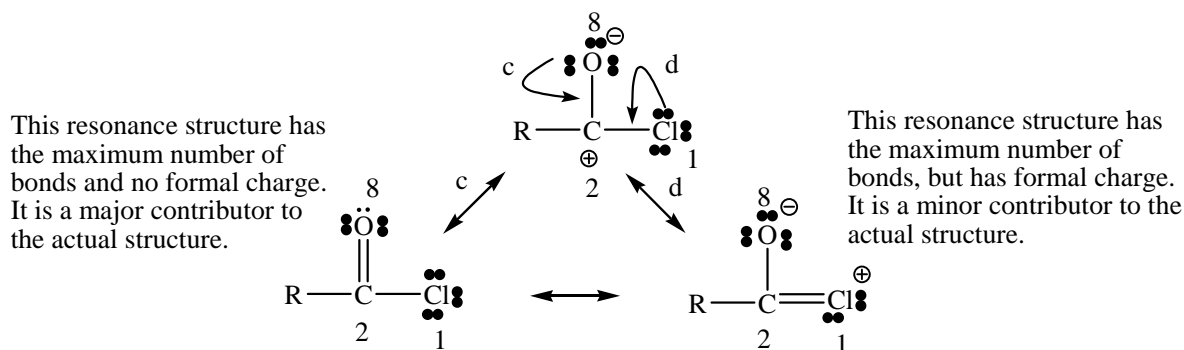
Example c, continued – A detailed look at possible resonance structures.



Two carbon atoms remain without an octet (C2 and C5). Both of them are next to two atoms with lone pairs that could be shared in a pi bond. These will be resonance structures. If C5 borrows an electron pair from C4 both atoms will have four bonds, full octets and zero formal charge will remain. This will be an important resonance structure. If C5 borrows an electron pair from O6, both atoms will have full octets, but formal charge is created. Also, C4 will not have four bonds. This will be a less important resonance structure, though it still provides useful information about the possible chemistry of this functionality.



A similar situation exists for C2. It is easy to recognize which atom is better to borrow an electron pair from when the formal charge is indicated. Both C2 and O8 need one more bond to reach their normal number of bonds (four and two) and they have opposite formal charge. Cl-1 already has its normal number of bonds (one) and is neutral. Borrowing from the O8 is a better choice because it has negative formal charge and will quench the positive formal charge of C2. No residual formal charge remains. Borrowing from Cl-1 creates a less important resonance contributor because formal charge remains. However, all of these possibilities are partial resonance contributors.



As we go through the remaining examples, we will not be so thorough in our analysis of the possible resonance structures. We will show minor resonance contributors, when they help provide insight into the chemistry of a functional group.

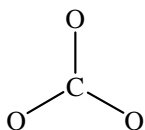
Lecture 4

d. Carbonate is an inorganic anion (CO_3^{-2}). There is no clue about the connection of the atoms in this formula. This example is included to make a point about multiple oxygen atoms grouped together near another atom. Rarely will we find oxygen atoms connected to other oxygen atoms (only in molecular diatomic oxygen, peroxides and ozone in this book). Oxygen loves to bond with less electronegative atoms so it can steal away extra electron density. There are a number of bonding patterns where multiple oxygen atoms are gathered about a central atom ($-\text{CO}_2^-$, $-\text{NO}_2^-$, $-\text{SO}_2^-$, etc.). This will usually be the case for us. Typically (but not always), one of the oxygen atoms will have a double bond with another atom. For us this is usually a carbon atom, but can also be nitrogen (NO_2^- , NO_3^-), sulfur (SO_3^{-2} , SO_4^{-2}), phosphorous (PO_4^{-3}) or a metal atom (CrO_3^{-2} , MnO_4^- , OsO_4). This is confusing at first, but you will get better as you become familiar with the functional groups of organic chemistry. After rule 4, the carbonate structure is still lacking something. Carbon has fewer than the expected bonds, so a pi bond is likely present. We can borrow a lone pair from any of the three oxygen atoms that will quench some charge and complete the structure by giving the carbon atom a full octet. These three possibilities are equivalent resonance structures and show that the -2 charge is divided among three oxygen atoms. Each oxygen atom carries $-2/3$ of the charge and this helps to stabilize the carbonate anion by spreading out electron density and minimizing electron-electron repulsion.

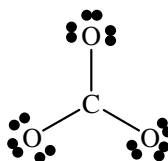
condensed bond-line formula



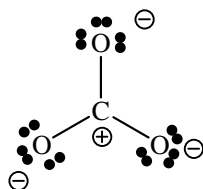
2D sigma skeleton



add in excess electrons
a. to electronegative atoms (3xO)
b. to alternate carbon atoms (none)



Add in formal charge



Rule 2

total available electrons

1xC = 4 electrons

0xH = 0 electrons

3xO = 18 electrons

-2 charge = 2 electrons

total = 24 electrons

Rule 3

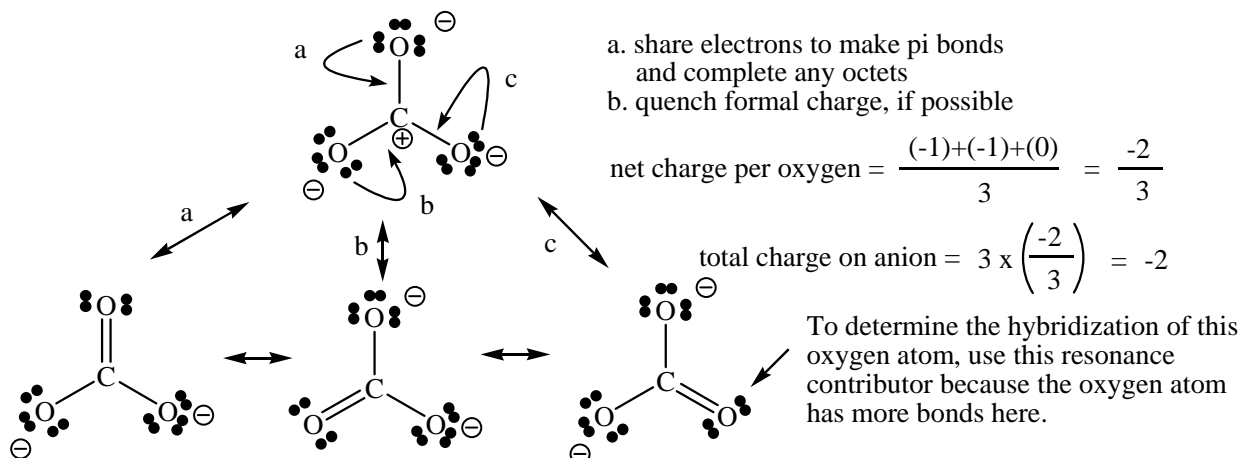
There are 3 sigma bonds using 6 electrons.

Rule 4

There are 18 electrons left over for lone pairs and pi bonds. Place three lone pairs on each oxygen atom. There are no electrons left over. Carbon remains without a full octet. The structure is not complete.

Rule 5

If you add in the formal charges (extra work vs. intuition), they will provide clues as to the best resonance structure(s). Borrowing from the atoms that have negative charge quenches the positive charge. This can be done three equivalent ways in carbonate. Generally, resonance is most important when this is the case.



At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp, sp² or sp³.

In this example, it's a little tricky to determine the hybridization of the oxygen atoms from a single resonance structure. When the oxygen atoms are written with the negative charge, they look like they are sp³, but when they are written with the double bond, they look like they are sp². They can't be both. They have to be sp² if there is a pi bond, and if they are sp² in one structure, then they have to be sp² in all of the structures. 2D Lewis structures do not show this clearly, because all you see are two dots, whether the orbital is a 2p orbital (used in resonance) or a hybrid orbital. If you always decide an atom's hybridization based on the resonance structure where it has the greatest number of bonds, you will be correct. The problem with this is that you have to draw all of the 2D resonance structures to decide an atom's hybridization, and you may miss a key resonance contributor that shows more bonds for a particular atom. The solution to this problem only comes with practice and experience to decide where resonance is important.

e. The nitronium ion (NO₂⁺) is a reactive intermediate that we will study later in the book. It is similar to the carbonate example above in that nitrogen has multiple oxygen atoms attached, but with a positive charge. Connect both of the oxygen atoms to nitrogen, not to one another. The nitrogen has fewer than the expected number of bonds, so pi bonds are likely present. We know there will be lone pairs of electrons, because there are heteroatoms (two oxygen atoms and a nitrogen). Once the lone pair electrons and formal charges are written in, we can see the various possible ways to complete the structure and judge which among them is the major contributor.

condensed bond-line formula

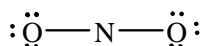


2D sigma skeleton



add in excess electrons

- a. to electronegative atoms (2xO, N)
b. to alternate carbon atoms (none)



Add in formal charge

Rule 2

total available electrons

0xC = 0 electrons

0xH = 0 electrons

1xN = 5 electrons

2xO = 12 electrons

+ charge = -1 electrons

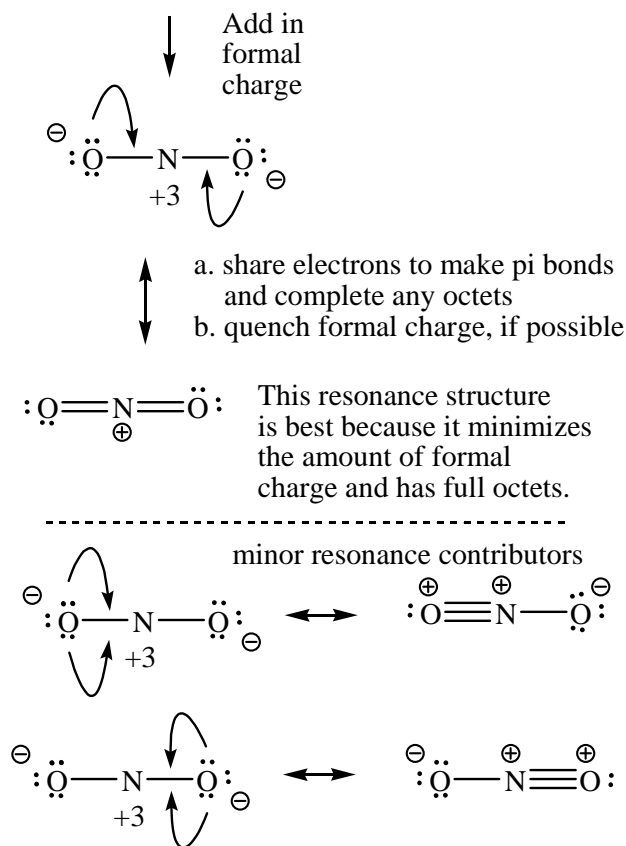
total = 16 electrons

Rule 3

There are 2 sigma bonds using 4 electrons.

Continued on the next page.

Lecture 4



Rule 4

There are 12 electrons left over for lone pairs and pi bonds. Place three lone pairs on each oxygen atom. There are no electrons left over. Nitrogen remains without a full octet. The structure is not complete.

Rule 5

If you add in the formal charges (more work), they will provide clues as to the best resonance structure(s). Borrowing from the atoms that have negative charge quenches the positive charge. Borrowing a lone pair from each oxygen atom quenches the most formal charge. This forms the best resonance contributor. Borrowing two lone pairs from a single oxygen also fills the octets, but creates more formal charge. Those structures are minor resonance contributors.

At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .

As with the carbonate example, it's a little tricky to determine the hybridization of the oxygen atoms from a single resonance structure. When the oxygen atoms are written with the positive charge and a triple bond, they look like they are sp , but when they are written with the double bond, they look like they are sp^2 and when they are written with a single bond they look like they are sp^3 . They have to be sp if there is a triple bond, and if they are sp in one structure, then they have to be sp in all of the structures. 2D Lewis structures do not show this clearly, because all you see are two dots, whether the orbital is a $2p$ orbital (used in resonance) or a hybrid orbital. Base your decision about an atom's hybridization on the resonance structure where it has the greatest number of bonds and you will be correct. It would be easy to overlook the two extra resonance structures where one oxygen atom has a triple bond and one oxygen atom has a single bond. If you see them, it's easy to decide that the nitrogen atom is sp because it has four bonds in all of the resonance structures. Each example you see will make you better at recognizing these subtleties.

f. This structure has an aldehyde (RCHO) and a "nitro" substituent (R-NO_2). The most confusing part of this formula are the two ends, $-\text{CHO}$ and $-\text{NO}_2$. On the $-\text{CHO}$ end, the hydrogen atom cannot be bonded to both the carbon atom and the oxygen atom because hydrogen only makes 1 bond. Both the oxygen atom and the hydrogen atom are bonded to the carbon atom, but we can only write one of them after the carbon atom. If we switched the order (RCOH), it would be more confusing since this is a possible connection (see the alcohol in b above). Writing it this would leave the carbon atom deficient by two bonds in this example. On the $-\text{NO}_2$ end, we expect that both of the oxygen atoms are connected to the nitrogen atom (and that's correct). In the 2D sigma skeleton there are atoms with fewer than the expected number of bonds, so pi bonds are present. In the $-\text{CHO}$ group, carbon and oxygen are each lacking one bond and have opposite formal charge. The oxygen atom can share a lone pair of electrons with the carbon, which will quench all formal charge and make the needed bond. This is the best for the resonance structure. The other resonance structure has one fewer bond and formal charge, but it is very informative

Lecture 4

about how aldehydes behave in chemical reactions. In the $-\text{NO}_2$ group, the nitrogen atom needs to borrow a pair of electrons and can do so equally well from either oxygen atom. This will force a fourth bond to the nitrogen atom and require a positive formal charge on the nitrogen. In one resonance structure, one oxygen atom will be neutral and the other will have a negative formal charge, while in the other resonance structure the roles are reversed. Overall, the opposite charges will cancel one another, and there is no net charge on the nitro group. However, a nitro group will always have to be drawn with formal charge, positive on the nitrogen atom and negative split evenly between the two oxygen atoms.

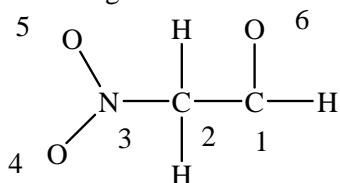
condensed bond-line formula



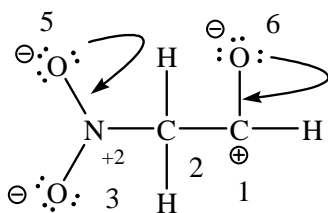
break into pieces



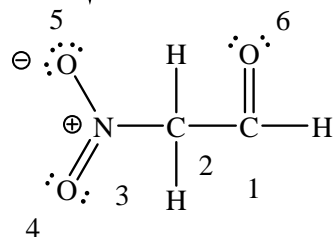
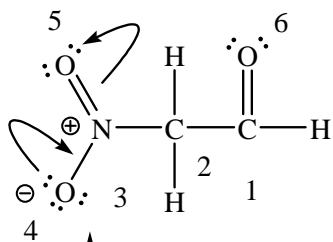
2D sigma skeleton



Add in excess electrons
 a. to electronegative atoms (3xO, N)
 b. to alternate carbon atoms (none)
 c. indicate formal charge



a. share electrons to make pi bonds and complete any octets
 b. quench formal charge, if possible



These last two resonance structures minimize the amount of formal charge and has provide full octets for all of the nonhydrogen atoms. Each oxygen atom has a double bond in one of the resonance structures, so the hybridization of the oxygen atoms must therefore be sp^2 . This is hard to see when oxygen is drawn with a single bond.

Rule 2

total available electrons
 $2 \times \text{C} = 8$ electrons
 $3 \times \text{H} = 3$ electrons
 $1 \times \text{N} = 5$ electrons
 $3 \times \text{O} = 18$ electrons
 $-/+ \text{ charge} = 0$ electrons
 total = 34 electrons

Rule 3

There are 8 sigma bonds using 16 electrons.

Rule 4

There are 18 electrons left over for lone pairs and pi bonds. Place three lone pairs on each of the oxygen atoms. There are no electrons left over. C1 and N3 remain without a full octet. The structure is not complete.

Rule 5

If you add in the formal charges (more work vs. intuition), they will provide clues as to the best resonance structure(s). Borrowing from the atoms that have negative charge quenches the positive charge. Only the O6 can supply electrons to the C1 in this example, which also provides an additional bond for each atom. N3 needs two electrons and can get them equally well from either O4 or O5. This means there are two equivalent resonance structures for the nitro end of the molecule. Formal charge is unavoidable, with N3 having positive formal charge and the negative charge split evenly between O4 and O5.

At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .

Lecture 4

g. This structure has a ketone (RCOR) and an alkyne (CC triple bond). The oxygen atom cannot be between the two carbon atoms because the left carbon would then be left with only two bonds (see Common Errors 2 on pages 3-4). Both the oxygen atom and the methyl group (CH₃) on the right are attached to the C2. Three carbon atoms and the oxygen atom lack the normal number of bonds. C2 can borrow a lone pair from the O6 and quench charge and satisfy the bond requirement of both atoms. C3 and C4 can each share their lone pair with one another, forming a triple bond between them and the normal number of four bonds for carbon. This forms the best resonance structure, because it maximizes the number of bonds and minimizes formal charge.

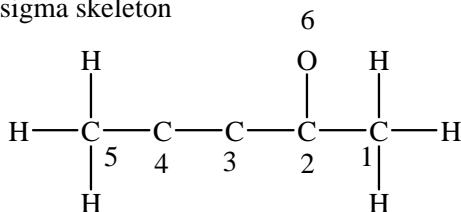
condensed bond-line formula



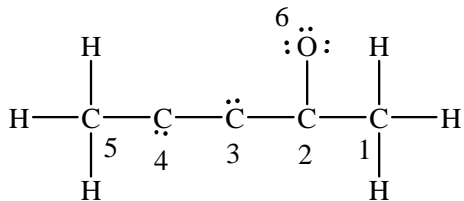
break into pieces



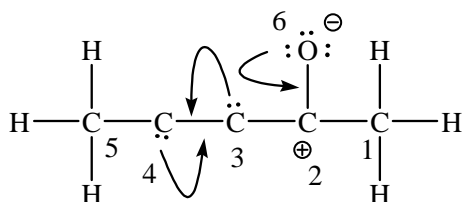
2D sigma skeleton



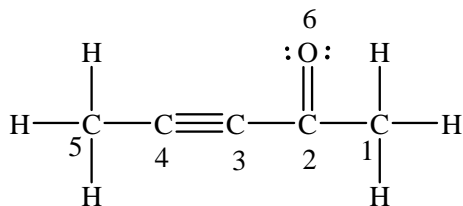
↓ add in excess electrons
a. to electronegative atoms (1xO)
b. to alternate carbon atoms (2 pairs)



↓ Add in formal charge



↑ a. share electrons to make pi bonds and complete any octets
b. quench formal charge, if possible



Rule 2

total available electrons

$$5 \times \text{C} = 20 \text{ electrons}$$

$$6 \times \text{H} = 6 \text{ electrons}$$

$$1 \times \text{O} = 6 \text{ electrons}$$

$$+ \text{charge} = 0 \text{ electrons}$$

$$\text{total} = 32 \text{ electrons}$$

Rule 3

There are 11 sigma bonds using 22 electrons.

Rule 4

There are 10 electrons left over for lone pairs and pi bonds. Place three lone pairs on the oxygen atom. Two lone pairs are left over. Put one lone pair each on C3 and C4 to maximize separation of the electrons.

Rule 5

If you add in the formal charges (more work vs. intuition), they will provide clues as to the best resonance structure(s). Borrowing from the O6 atom quenches the positive charge on C2. C3 and C4 both need two more bonds and can help each other by sharing their lone pairs. This is the best resonance structure because bonds are maximized and formal charge is minimized.

At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp, sp² or sp³.

This resonance structure minimizes the amount of formal charge and has full octets.

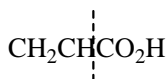
Lecture 4

h. This structure has a carboxylic acid (RCO_2H) and an alkene ($\text{C}=\text{C}$). As mentioned above in d and e, the oxygen atoms are attached to the central carbon atom. The hydrogen atom is attached to one of the oxygen atoms, not the carbon atom. (See Common Errors 2 on pages 3-4) There are atoms with fewer than the expected number of bonds, so pi bonds are present.

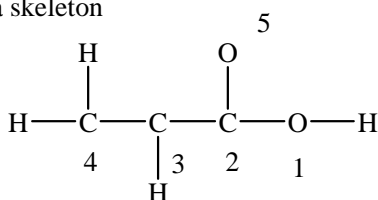
condensed bond-line formula



break into pieces

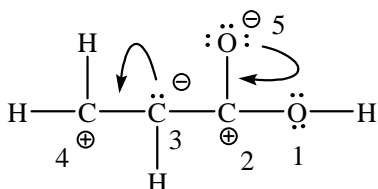


2D sigma skeleton

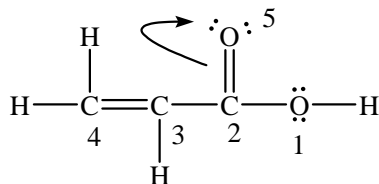


add in excess electrons

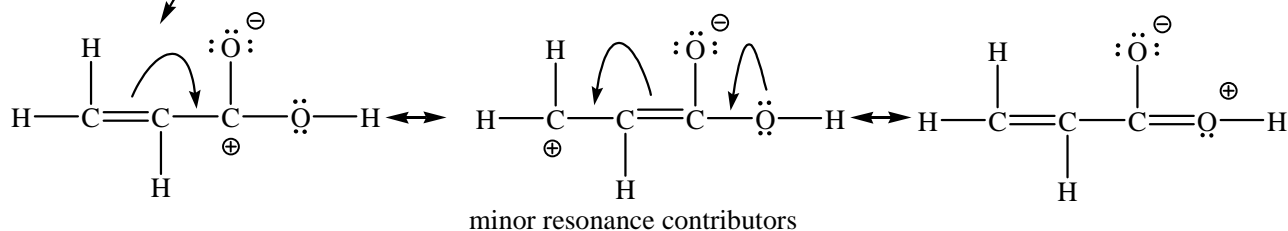
- to electronegative atoms ($2 \times \text{O}$)
- to alternate carbon atoms (1 pair)
- indicate formal charge



- share electrons to make pi bonds and complete any octets
- quench formal charge, if possible



major (best) resonance contributor



Rule 2

total available electrons

$$3 \times \text{C} = 12 \text{ electrons}$$

$$4 \times \text{H} = 4 \text{ electrons}$$

$$2 \times \text{O} = 12 \text{ electrons}$$

$$+/- \text{ charge} = \text{none}$$

$$\text{total} = 28 \text{ electrons}$$

Rule 3

There are 8 sigma bonds using 16 electrons.

Rule 4

There are 12 electrons left over for lone pairs and pi bonds. Place two lone pairs on one oxygen and three lone pairs on the other oxygen. There are two electrons left over and two adjacent carbon atoms without full octets. Place the two electrons on of these carbon atoms. The structure is not complete because there are missing bonds and incomplete octets.

Rule 5

If you add in the formal charges, they will provide clues as to the best resonance structure(s). Borrowing from atoms that have negative charge (O5 and C3) quenches the positive charge (C2 and C4). Other resonance structures are possible (C2 can borrow electrons from O1 or C3), but there is residual charge. The neutral resonance contributor is the best one because it maximizes the number of bonds and quenches all formal charge.

At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .

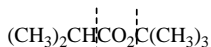
Lecture 4

i. This structure has an ester (RCO_2R). The oxygen atoms are connected in a manner similar to the carboxylic acid example in h, with the $-\text{C}(\text{CH}_3)_3$ attached to one of the oxygen atoms. There are atoms with fewer than the expected number of bonds, so a pi bond is likely present. C2 can borrow electrons from either O1 or O3. O3 will form the better resonance contributor since that will quench formal charge and supply an extra bond that both atoms need. Borrowing electrons from O1 produces the same number of bonds, but leaves residual charge.

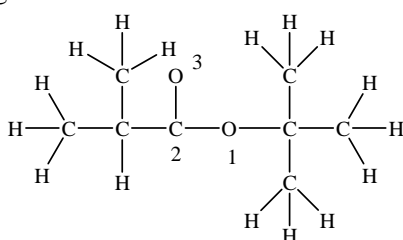
condensed bond-line formula



break into pieces

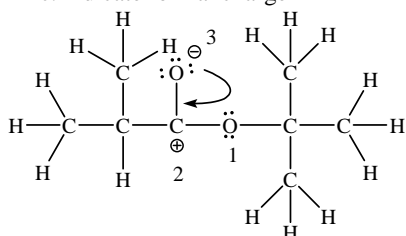


2D sigma skeleton

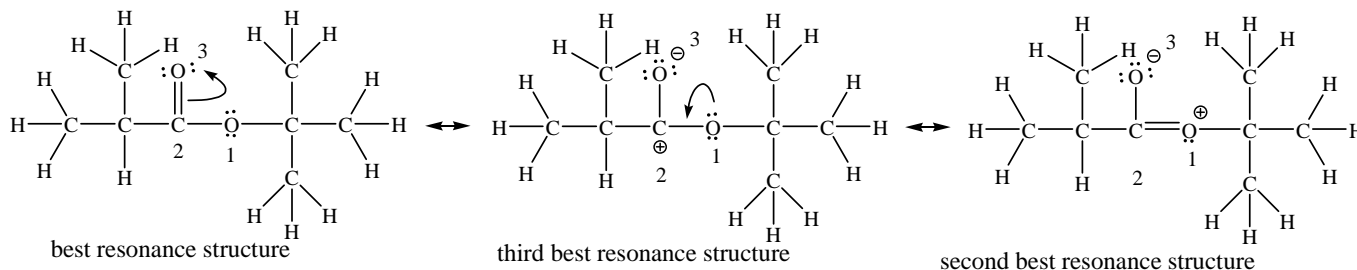


add in excess electrons

- to electronegative atoms ($2 \times \text{O}$)
- to alternate carbon atoms (none)
- indicate formal charge



- share electrons to make pi bonds and complete any octets
- quench formal charge, if possible



Rule 2

total available electrons

$$8 \times \text{C} = 32 \text{ electrons}$$

$$16 \times \text{H} = 16 \text{ electrons}$$

$$2 \times \text{O} = 12 \text{ electrons}$$

$$+/- \text{ charge} = \text{none}$$

$$\text{total} = 60 \text{ electrons}$$

Rule 3

There are 25 sigma bonds using 50 electrons.

Rule 4

There are 10 electrons left over for lone pairs and pi bonds. Place two lone pairs on O1 and three lone pairs on O3. There no electrons left over and one adjacent carbon atom without full octet. The structure is not complete because there is a missing bond and there is an incomplete octet.

Rule 5

If you add in the formal charges, they will provide clues as to the best resonance structure(s).

Borrowing from atoms that have negative charge (O3) quenches the positive charge (C2). Other resonance structures are possible (electrons borrowed from O1), but this leaves residual charge. The neutral resonance contributor is the best one because it maximizes the number of bonds and quenches all formal charge.

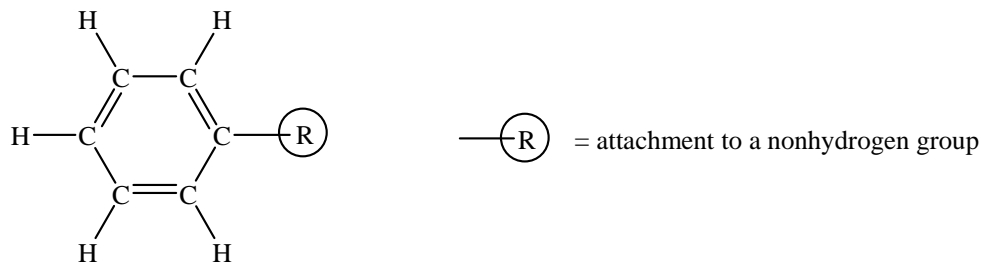
At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .

j. This structure has a nitrile ($\text{C}\equiv\text{N}$ triple bond), an alkyne ($\text{C}\equiv\text{C}$ triple bond), an alkene ($\text{C}=\text{C}$) and there is an aromatic ring present (RC_6H_5).

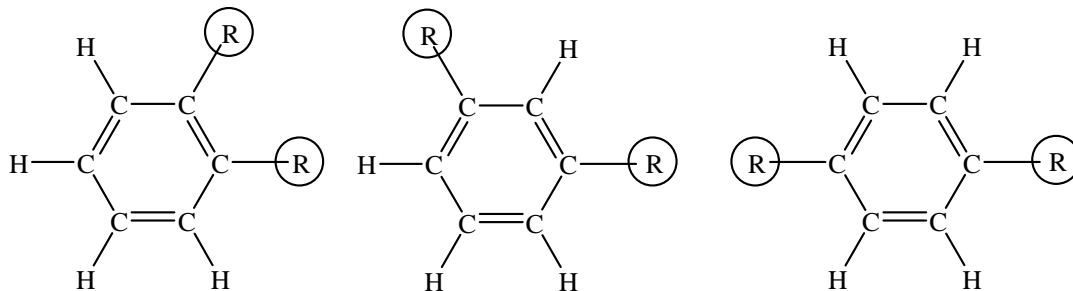
We need to pause for a moment, and briefly describe aromatic rings. Aromatic rings are common in organic chemistry and biochemistry. Organic texts typically devote two chapters to aromatic compounds. The structure of an aromatic ring cannot be shown in a condensed line formula, so if there is an aromatic ring, I will let you know by writing "six carbon ring present". There is only one bonding position available on each carbon of the aromatic ring, which limits the number of attachments to the ring. If the ring is attached as a branch off of the side of the parent chain or at the end of a chain, there will still

Lecture 4

be five hydrogen atoms present and its formula will be C_6H_5- . C_6H_5- has its own special name of “phenyl”. If an aromatic ring is internal to the parent chain, it will be attached at two points and only four hydrogen atoms will be present in its formula ($-C_6H_4-$). There are three patterns for attachment of two groups on an aromatic ring (ortho, meta and para), but I will assume that “para” is the pattern in problems of this nature. Para substitution allows a 2D structure to be drawn in a linear fashion, which is easier to place on the page. You can choose to draw any disubstituted aromatic rings however you like, if there is no designation.



monosubstituted
aromatic ring, (C_6H_5-R)



ortho disubstituted
aromatic ring, ($R-C_6H_4-R$)

meta disubstituted
aromatic ring, ($R-C_6H_4-R$)

para disubstituted
aromatic ring, ($R-C_6H_4-R$),
I'll assume this pattern,
because it's easier to draw
in a straight line.

Now, let's turn back to our 2D structure below. There are atoms with fewer than the expected number of bonds in the 2D sigma skeleton, so pi bonds are likely present. We know there will be lone pairs of electrons, because there is a heteroatom (one nitrogen atom). At rule 4 there will be many lone pairs of electrons to add in because of all of the pi bonds that need to be made. Three lone pairs are placed on the more electronegative nitrogen atom first. The additional electrons are placed on alternate carbon atoms to minimize electron-electron repulsion. Place lone pairs of electrons on C3, C5 and at alternate positions in the ring (it makes little difference where since they can shift either to the left or to the right). There are still two electrons that have to be added, so I put those electrons on C4 and bumped the electrons on C5 over to C6.

This problem is a great example of where good intuition can save a lot of time. We need one extra bond at each carbon of the aromatic ring. We can only do this with alternating double bonds (two equivalent ways). C5 and C6 each need one more bond, which can be solved with a pi bond between them. C3 and C4 each need two more bonds, which can be solved with two pi bonds between them. C2 and N1 each need two more bonds, which can, again, be solved with two pi bonds between them. Finally, nitrogen needs a lone pair of electrons.

Lecture 4

condensed bond-line formula



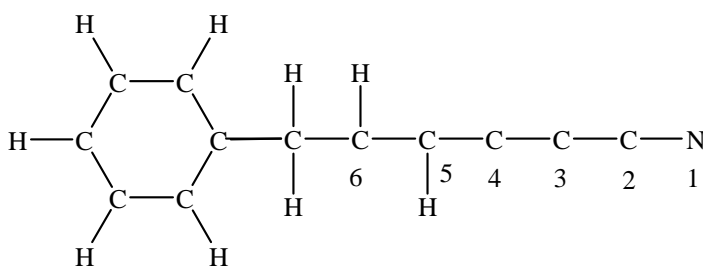
(six carbon ring present)

break into pieces



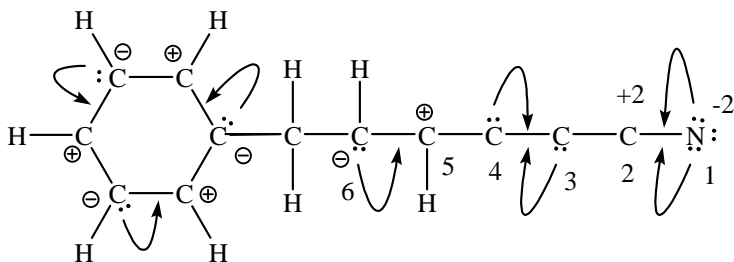
(six carbon ring present)

2D sigma skeleton

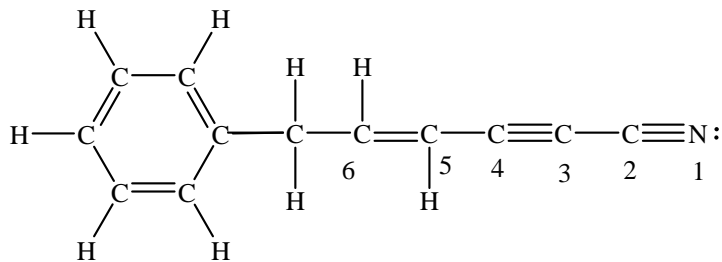


add in excess electrons

- to electronegative atoms (N)
- to alternate carbon atoms (6 pairs)
- indicate formal charge



- share electrons to make pi bonds and complete any octets
- quench formal charge, if possible, the electrons in the ring can move in either direction (resonance)



Rule 2

total available electrons

$$12 \times \text{C} = 48 \text{ electrons}$$

$$9 \times \text{H} = 9 \text{ electrons}$$

$$1 \times \text{N} = 5 \text{ electrons}$$

$$+/- \text{ charge} = \text{none}$$

$$\text{total} = 62 \text{ electrons}$$

Rule 3

There are 22 sigma bonds using 44 electrons.

Rule 4

There are 18 electrons left over for lone pairs and pi bonds. Place three lone pairs on nitrogen. There are 12 electrons left over and several carbon atoms without full octets. Place the two electrons on of these carbon atoms at alternate positions to minimize electron-electron repulsion. The structure is not complete because there are missing bonds an incomplete octets.

Rule 5

If you add in the formal charges, they will provide clues as to the best resonance structure(s). Borrowing from atoms that have negative charge quenches the positive charge. Other resonance structures are possible, but this is the best one because it maximizes the number of bonds and quenches all formal charge.

At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .

Lecture 4

k. This structure has an amide (RCONH_2), an amine (RNH_2) and an alkene ($\text{C}=\text{C}$). The oxygen atom and the nitrogen atom on the right side are attached to the carbon atom next to them (similar to examples i and h above). Both of the hydrogen atoms to the right of the "N" are attached to the nitrogen atom. There are atoms with fewer than the expected number of bonds, so pi bonds are likely present.

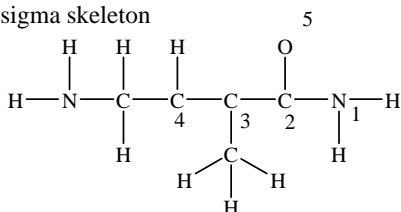
condensed bond-line formula



break into pieces

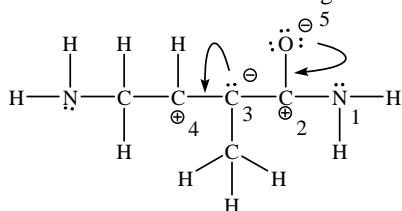


2D sigma skeleton

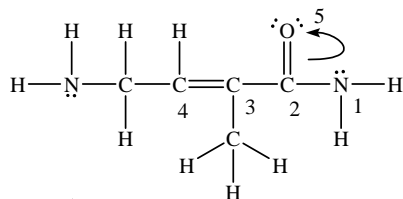


add in excess electrons

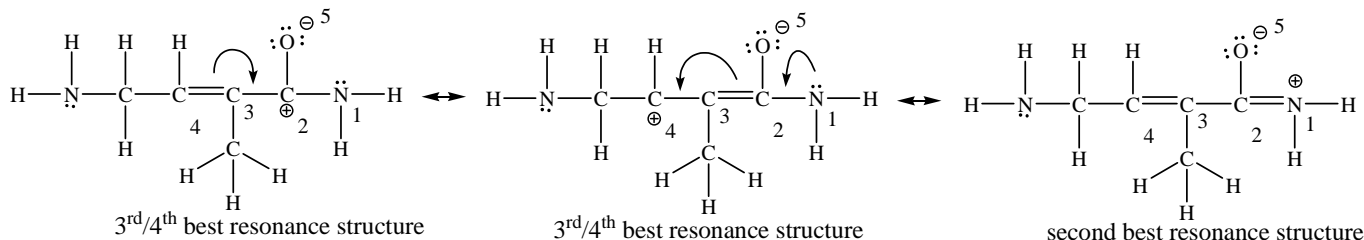
- to electronegative atoms ($1 \times \text{O}, 2 \times \text{N}$)
- to alternate carbon atoms (1 pair)
- indicate formal charge



- share electrons to make pi bonds and complete any octets
- quench formal charge, if possible



best resonance structure



Rule 2

total available electrons

$$5 \times \text{C} = 20 \text{ electrons}$$

$$10 \times \text{H} = 10 \text{ electrons}$$

$$1 \times \text{O} = 6 \text{ electrons}$$

$$2 \times \text{N} = 10 \text{ electrons}$$

$$+/- \text{ charge} = \text{none}$$

$$\text{total} = 46 \text{ electrons}$$

Rule 3

There are 17 sigma bonds using 34 electrons.

Rule 4

There are 12 electrons left over for lone pairs and pi bonds. Place three lone pairs on O5 and one lone pair on each of the nitrogen atoms. There are 2 electrons left over and two carbon atoms without full octets (C2 and C4). Place the two electrons on one of these carbon atoms. Use those electrons to make a pi bond with the other one. C2 can borrow a lone pair from O5, quench formal charge and supply a necessary bond to both of the atoms. C2 can also borrow a lone pair from N1 or C3, but both of possibilities would leave residual formal charge. Borrowing from N1 would form the same number of bonds as the neutral resonance contributor. Borrowing from C3 would form one fewer bond and leave C4 without an octet. Even though these are minor resonance contributors, they provide useful information about the structure and chemistry of this compound. We will use them when it serves our purpose.

Rule 5

If you add in the formal charges, they will provide clues as to the best resonance structure(s). Borrowing from atoms that have negative charge quenches the positive charge. Other resonance structures are possible, but this is the major contributor because it maximizes the number of bonds and quenches all formal charge.

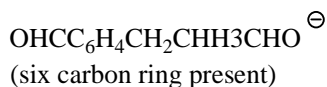
At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure.

There are only three choices for every atom: sp , sp^2 or sp^3 . The amide nitrogen, N1, is sp^2 hybridized because of resonance with the carbonyl pi bond ($\text{C}=\text{O}$). The amine nitrogen at the other end of the molecule is sp^3 hybridized since there is no opportunity for resonance.

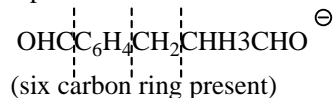
Lecture 4

1. This structure has an enolate (an anion), an aldehyde (OHCR) and a disubstituted aromatic ring ($-C_6H_4-$). The OHC- on the left and the $-CHO$ on the right can be very confusing. While they do share some similarities, the negative charge on the right $-CHO$ makes it different. The negative charge can be placed on either O1 or C3 (resonance structures). Both are reasonable, but having the negative charge on the oxygen atom is better. There are atoms with fewer than the expected number of bonds, so pi bonds are present. C2 can borrow electrons from either O1 or C3. Lone pairs placed at alternate positions in the aromatic ring can be shifted left or right to make three alternate pi bonds. Finally, C4 can get its needed electrons from O5 and satisfy each atom's bond requirement and quench formal charge. C4 can also borrow electrons from the aromatic ring, but we won't show this until aromatic chemistry is covered.

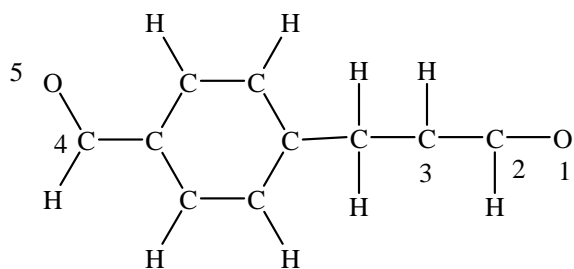
condensed bond-line formula



break into pieces

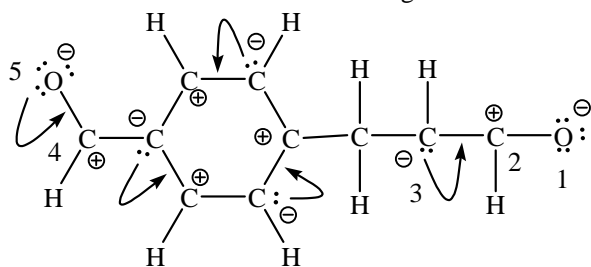


2D sigma skeleton

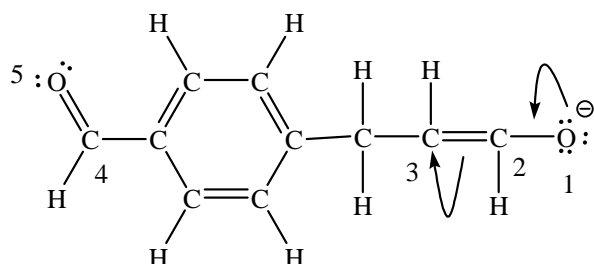


add in excess electrons

- to electronegative atoms ($2 \times \text{O}$)
- to alternate carbon atoms (4 pairs)
- indicate formal charge



- share electrons to make pi bonds and complete any octets
- quench formal charge, if possible



Rule 2

total available electrons

$$10 \times \text{C} = 40 \text{ electrons}$$

$$9 \times \text{H} = 9 \text{ electrons}$$

$$2 \times \text{O} = 12 \text{ electrons}$$

$$-1 \text{ charge} = 1 \text{ electron}$$

$$\text{total} = 62 \text{ electrons}$$

Rule 3

There are 21 sigma bonds using 42 electrons.

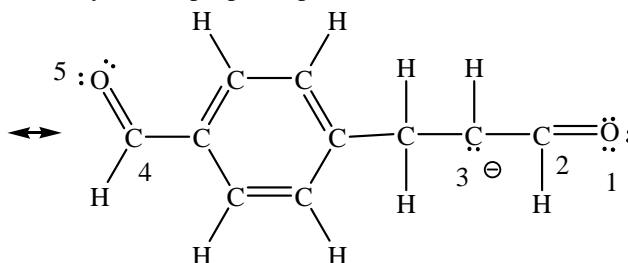
Rule 4

There are 20 electrons left over for lone pairs and pi bonds. Place three lone pairs on each of the oxygen atoms. There are 8 electrons left over and nine carbon atoms without full octets. Place electron pairs on carbon atoms at alternate positions in the ring to minimize electron-electron repulsion. Place two electrons on C3 to minimize electron repulsion with O1. The structure is not complete because there are missing bonds and incomplete octets.

Rule 5

If you add in the formal charges, they will provide clues as to the best resonance structure(s). Borrowing from atoms that have negative charge quenches the positive charge. Several reasonable resonance structures are possible because of the negative charge and the aromatic ring. The best resonance contributor maximizes the number of bonds, minimizes the amount of formal charge and it places the negative formal charge on the oxygen atom.

At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 .



Lecture 4

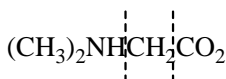
These last two resonance structures show the resonance of an enolate anion. Most of the negative charge is on O1, but most of the common reactions that we study occur with electron pair donation from C3. Can you see why C3 would be able to donate electrons? O1 is clearly shown to be sp^2 hybridized in the right resonance contributor above, while C3 is clearly shown to be sp^2 in the left structure. Be very careful to base your decision about an atom's hybridization on the resonance contributor where the atom has its greatest number of bonds. This would be difficult to determine using only the resonance contributor on the left, where O1 only shows a single bond. Overall, the molecule is neutral.

m. This structure is an unnatural amino acid. There is an atom with fewer than the expected number of bonds, so a pi bond is likely present. C2 can borrow electrons equally well from O1 and O3. Two equally good resonance contributors are possible, showing the negative formal charge is shared evenly between the two oxygen atoms. The positive formal charge is fully on the nitrogen atom.

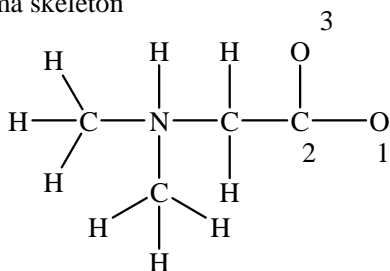
condensed bond-line formula



break into pieces

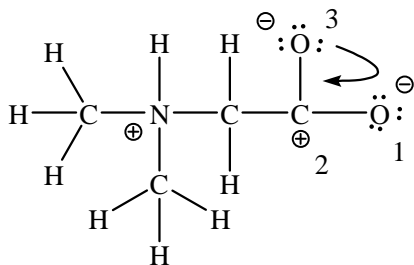


2D sigma skeleton



add in excess electrons

- to electronegative atoms ($2 \times \text{O}, 1 \times \text{N}$)
- to alternate carbon atoms (none)
- indicate formal charge



- share electrons to make pi bonds and complete any octets
- quench formal charge, if possible

Continued on the next page.

Rule 2

total available electrons
 $4 \times \text{C} = 16$ electrons
 $9 \times \text{H} = 9$ electrons
 $2 \times \text{O} = 12$ electrons
 $1 \times \text{N} = 5$ electrons
 \pm charge = none
 total = 42 electrons

Rule 3

There are 15 sigma bonds using 30 electrons.

Rule 4

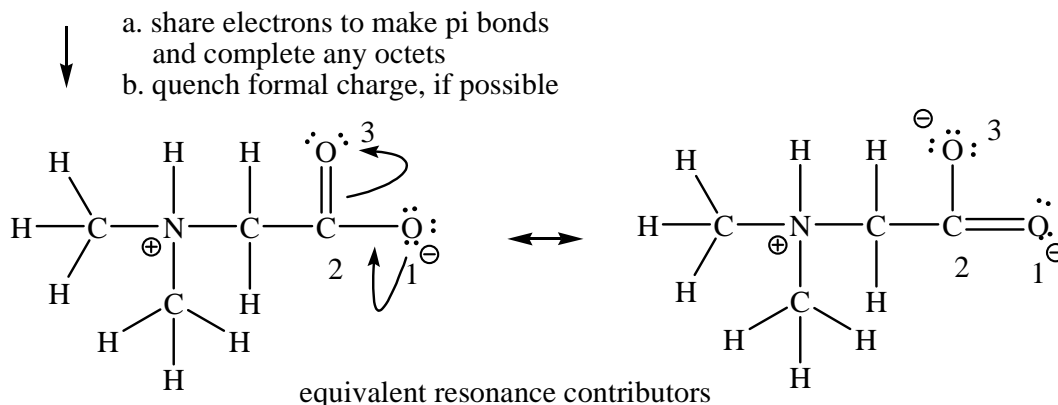
There are 12 electrons left over for lone pairs and pi bonds. Place three lone pairs on both of the oxygen atoms (O1 and O3). There are no electrons left over, C2 lacks a full octet.

Rule 5

If you add in the formal charges, they will provide clues as to the best resonance structure(s). Borrowing from atoms that have negative charge quenches the positive charge. C2 can borrow electrons equally well from either O1 or O3, quench formal charge and supply necessary bonds for both atoms. There are two very good resonance structures that maximize the number of bonds and leave the negative formal charge on oxygen. These will be the best resonance structures.

At this point we should be able to determine the hybridization, shape, bond angles, number of sigma and pi bonds, and the number of lone pairs of electrons for every single atom in the structure. There are only three choices for every atom: sp , sp^2 or sp^3 . Each oxygen shows a double bond in one of the resonance structures, so both are sp^2 hybridized.

Lecture 4

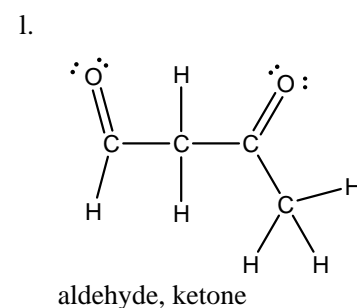
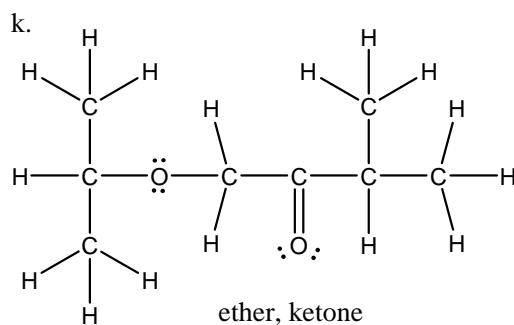
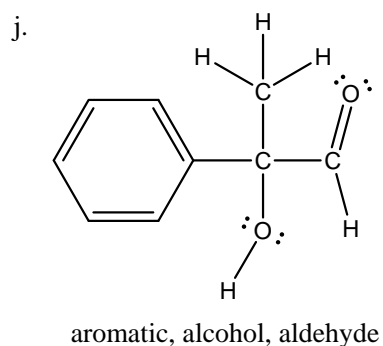
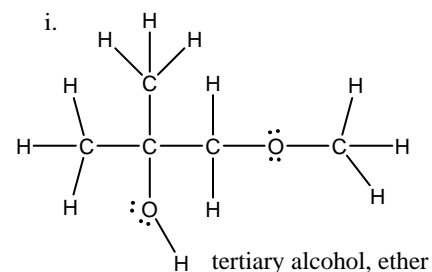
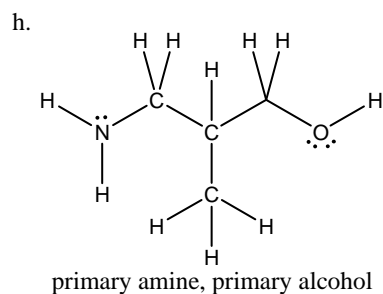
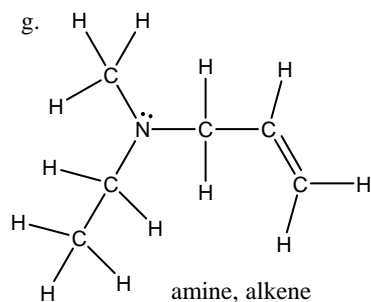
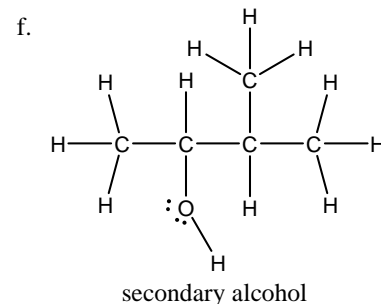
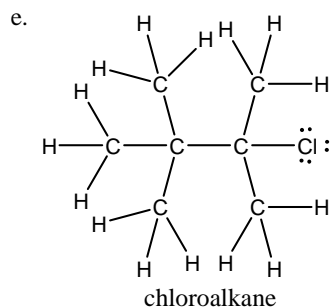
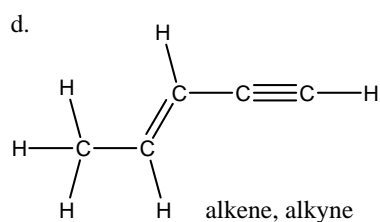
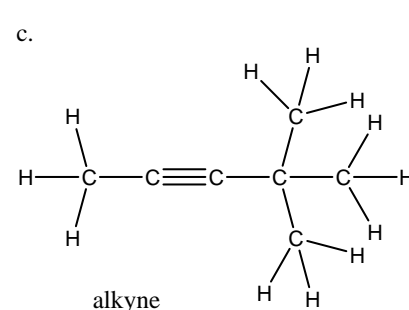
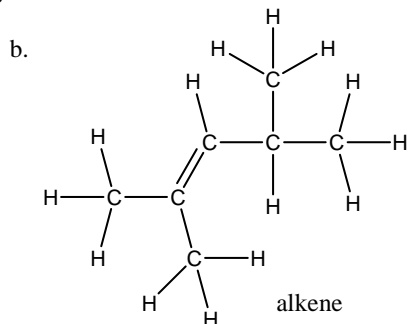
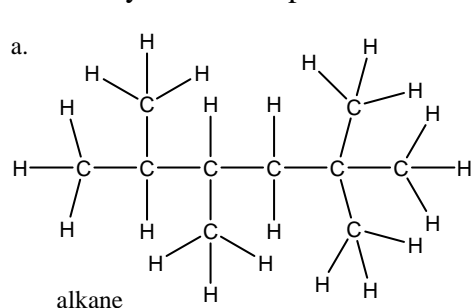


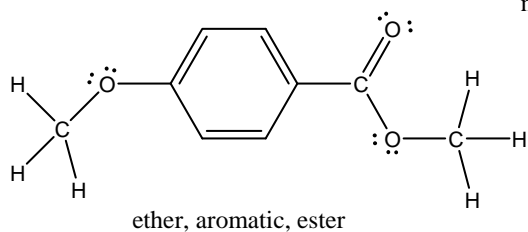
Problem 1 - Draw two dimensional Lewis structures for the following condensed line formulas of common functional groups and carbon skeletal patterns. Include two dots for any lone pair electrons. You should be able to predict the hybridization, shape, bond angles, number of sigma bonds, pi bonds and lone pairs of electrons on every nonhydrogen atom below. Even though we have not covered nomenclature and functional groups, the functional group names are included with the following formulas to increase your familiarity with these patterns. Soon, you will need to know these.

- a. $(\text{CH}_3)_2\text{CHCHCH}_3\text{CH}_2\text{C}(\text{CH}_3)_3$
alkane
- b. $(\text{CH}_3)_2\text{CCHCH}(\text{CH}_3)_2$
alkene
- c. $\text{CH}_3\text{CCC}(\text{CH}_3)_3$
alkyne
- d. $\text{CH}_3\text{CHCHCCH}$
alkene, alkyne
- e. $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{Cl}$
chloroalkane
- f. $\text{CH}_3\text{CHOHCH}(\text{CH}_3)_2$
secondary alcohol
- g. $\text{CH}_3\text{N}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CHCH}_2$
amine, alkene
- h. $\text{NH}_2\text{CH}_2\text{CHCH}_3\text{CH}_2\text{OH}$
primary amine, primary alcohol
- i. $(\text{CH}_3)_2\text{COHCH}_2\text{OCH}_3$
tertiary alcohol, ether
- j. $\text{C}_6\text{H}_5\text{COH}(\text{CH}_3)\text{CHO}$
aromatic, alcohol, aldehyde
- k. $(\text{CH}_3)_2\text{CHOCH}_2\text{COCH}(\text{CH}_3)_2$
ether, ketone
- l. $\text{OHCCH}_2\text{COCH}_3$
aldehyde, ketone
- m. $\text{CH}_3\text{OC}_6\text{H}_4\text{CO}_2\text{CH}_3$
ether, aromatic, ester
- n. $(\text{CH}_3)_2\text{CHO}_2\text{CCCC}(\text{CH}_3)_2\text{CO}_2\text{H}$
ester, alkyne, carboxylic acid
- o. NCCCCHCHCHO
nitrile, alkyne, alkene, aldehyde
- p. $\text{HOCH}(\text{CH}_3)\text{CH}_2\text{CONH}_2$
secondary alcohol, primary amide
- q. $(\text{CH}_3)_2\text{NOCCCC}(\text{CH}_3)_3$
tertiary amide, alkyne
- r. $\text{ClCH}_2\text{COCH}_2\text{COCl}$
chloro, ketone, acid chloride
- s. $\text{CH}_2\text{CHC}_6\text{H}_4\text{CCCH}(\text{CH}_3)_2$
alkene, aromatic, alkyne
- t. $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CCCH}_3$
ammonium ion, alkyne
- u. $\text{CH}_3\text{CH}_2\text{O}_2\text{CCCCO}_2^-$
ester, alkyne, carboxylate
- v. $\text{C}_6\text{H}_5\text{CH}_2\text{CH}(\text{CO}_2\text{H})\text{CH}(\text{CHO})\text{CH}(\text{CO}_2\text{CH}_3)\text{CH}(\text{CONH}_2)\text{CH}(\text{COCl})\text{CH}(\text{CN})\text{CH}(\text{COCH}_3)\text{CH}_3$
A variety of branches: aromatic ring, carboxylic acid, aldehyde, ester, amide, acid chloride, nitrile, ketone

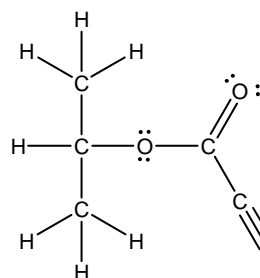
Lecture 4

Problem 1 answers - Draw two dimensional Lewis structures for the following condensed line formulas of common functional groups and carbon skeletal patterns. Include two dots for any lone pair electrons. You should be able to predict the hybridization, shape, bond angles, number of sigma bonds, pi bonds and lone pairs of electrons on every nonhydrogen atom below. Even though we have not covered nomenclature and functional groups, the functional group names are included with the following formulas to increase your familiarity with these patterns. Soon, you will need to know these.

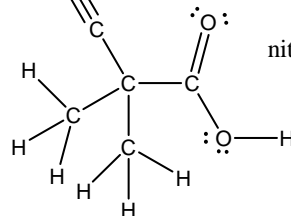
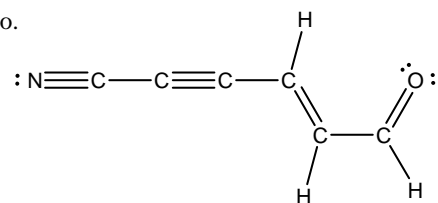


Lecture 4
m.

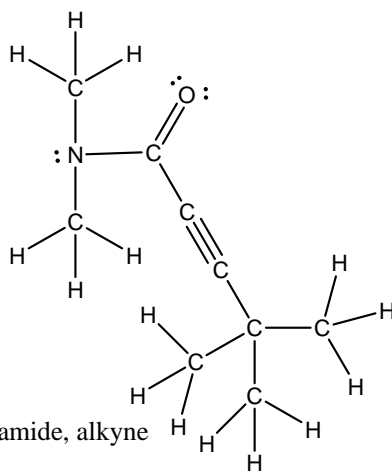
n.



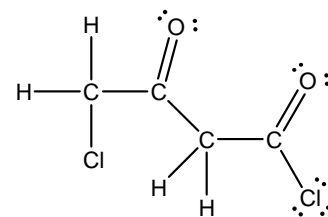
o.



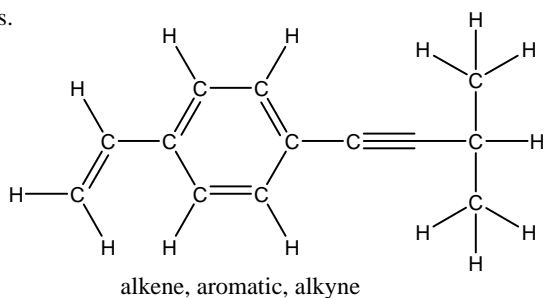
q.



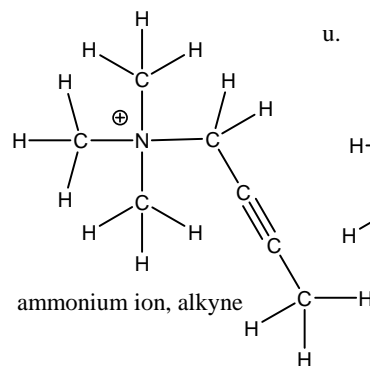
r.



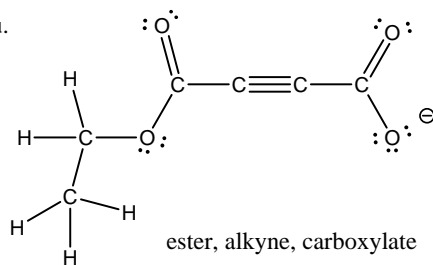
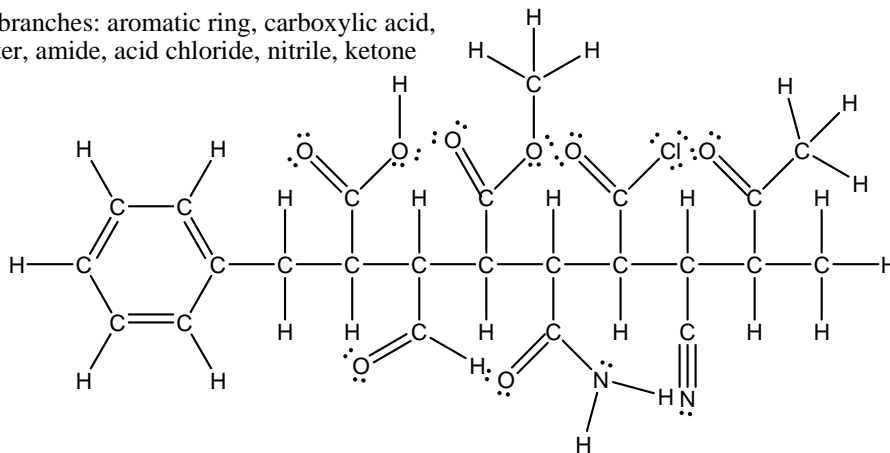
s.



t.



u.

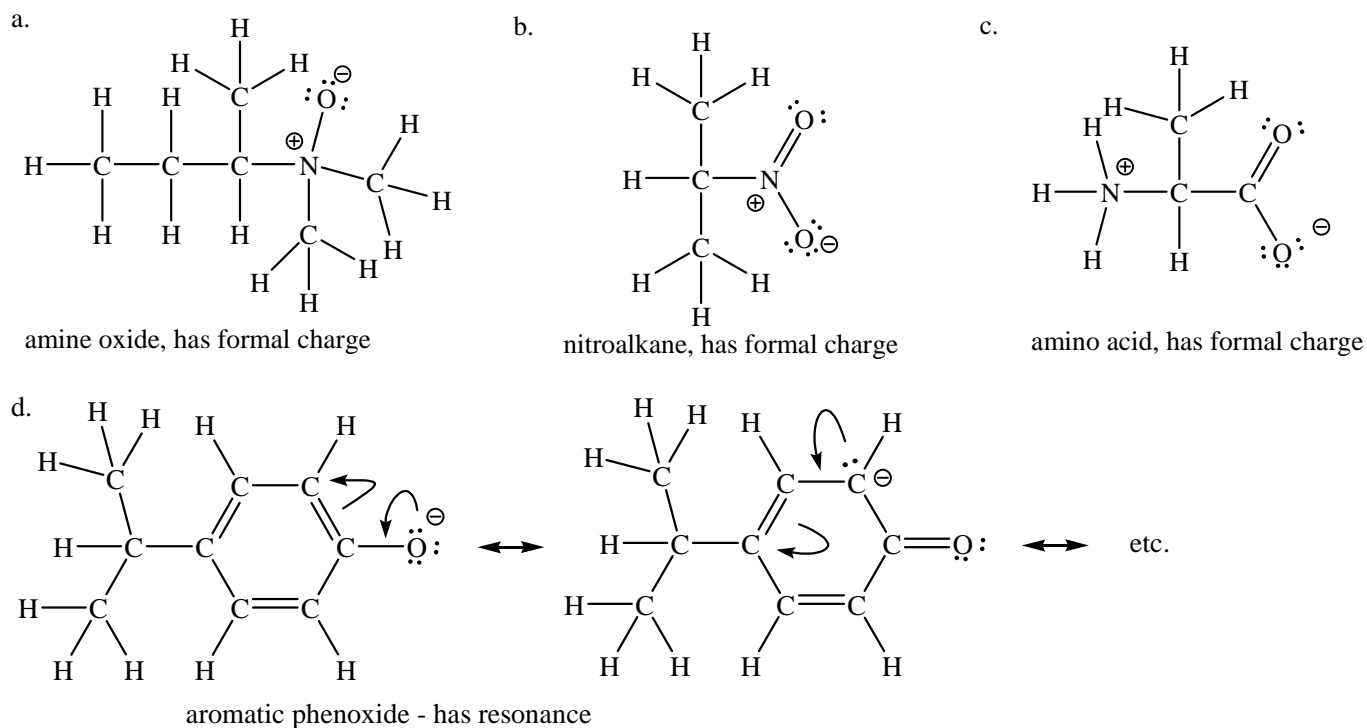
A variety of branches: aromatic ring, carboxylic acid,
aldehyde, ester, amide, acid chloride, nitrile, ketone

Lecture 4

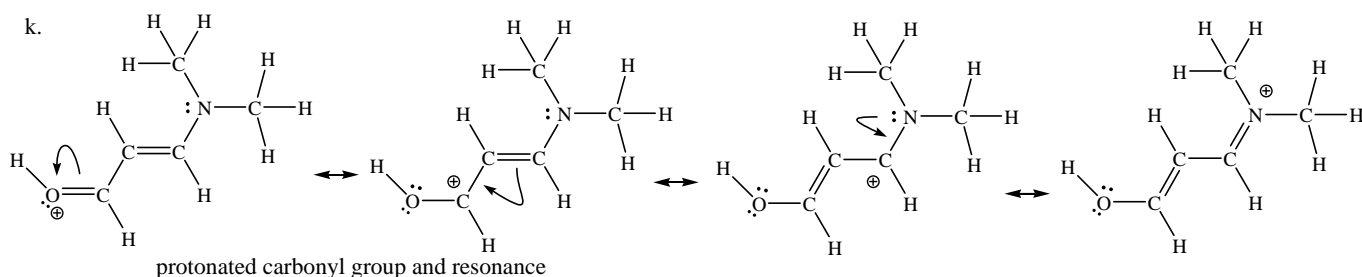
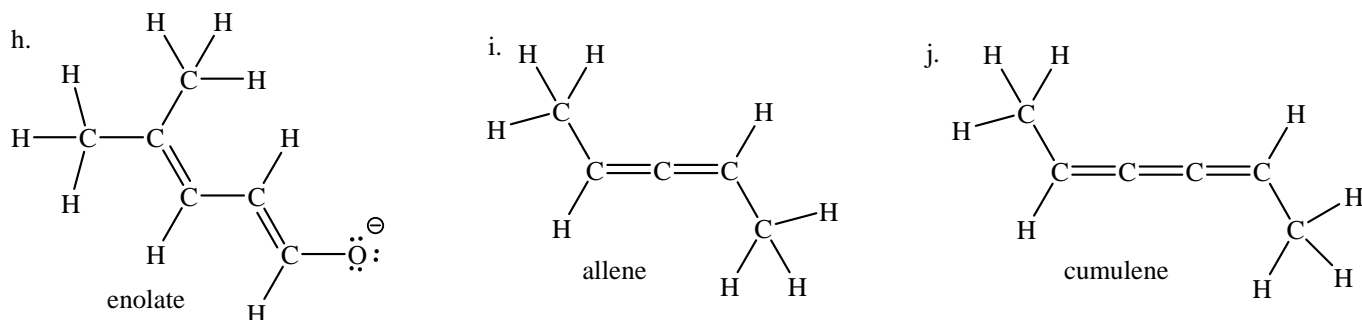
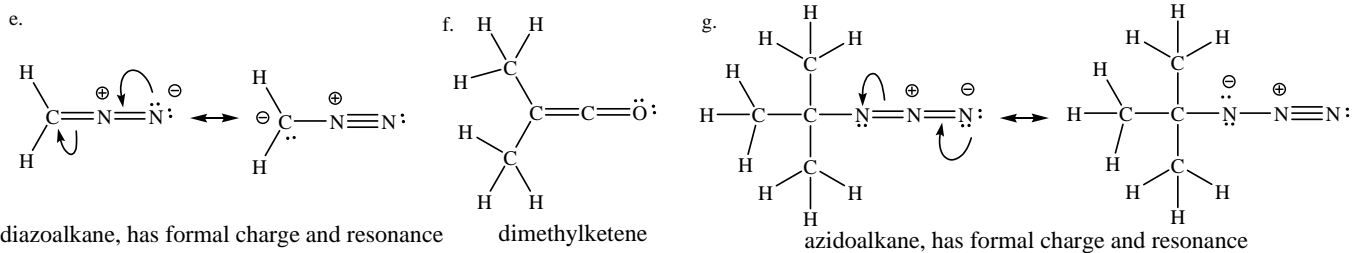
Problem 2 - Draw two dimensional Lewis structures for the following condensed line formulas of less common functional groups and some groups with formal charge. Include two dots for any lone pair electrons and show any formal charge on atoms. Occasionally, resonance structures are possible. You should be able to predict the hybridization, shape, bond angles, number of sigma bonds, pi bonds and lone pairs of electrons on every nonhydrogen atom below.

- a. $\text{CH}_3\text{CH}_2\text{CHCH}_3\text{N}(\text{CH}_3)_2\text{O}$ amine oxide, has formal charge
 b. $(\text{CH}_3)_2\text{CHNO}_2$ nitroalkane, has formal charge
 c. $\text{H}_3\text{NCHCH}_3\text{CO}_2$ amino acid, has formal charge
 d. $(\text{CH}_3)_2\text{CHC}_6\text{H}_4\text{O}^-$ aromatic phenoxide
 e. CH_3CHN_2 diazoalkane, has formal charge
 f. $(\text{CH}_3)_2\text{CCO}$ ketene
 g. $(\text{CH}_3)_3\text{CN}_3$ azidoalkane, has formal charge
 h. $(\text{CH}_3)_2\text{CCHCHCHO}^-$ enolate
 i. $\text{CH}_3\text{CHCCH}_3$ allene
 j. $\text{CH}_3\text{CHCCCH}_3$ cumulene
 k. $\text{HOHCCHCHN}(\text{CH}_3)_2^+$ protonated carbonyl group and tertiary amine

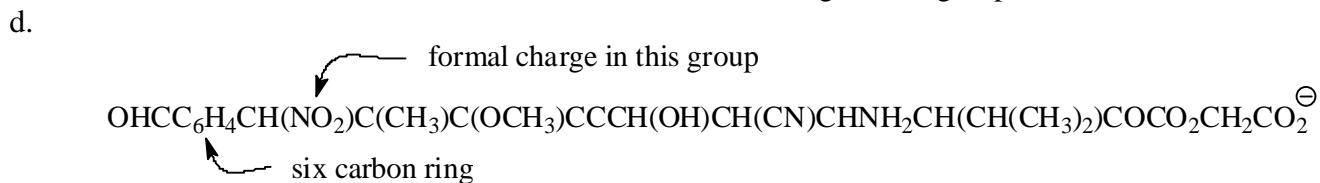
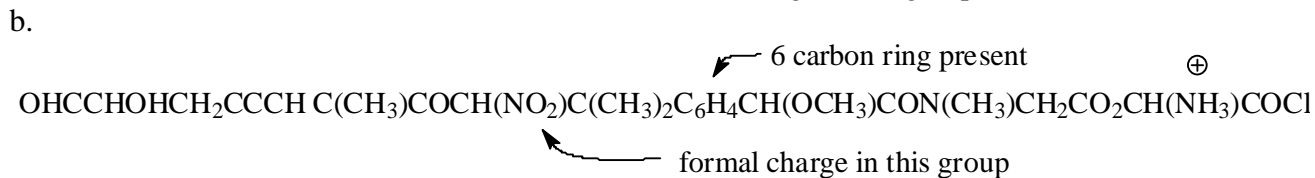
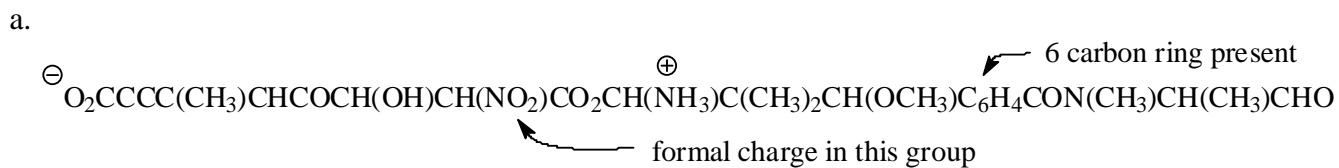
Problem 2 answers - Draw two dimensional Lewis structures for the following condensed line formulas of less common functional groups and some groups with formal charge. Include two dots for any lone pair electrons and show any formal charge on atoms. Occasionally, resonance structures are possible. You should be able to predict the hybridization, shape, bond angles, number of sigma bonds, pi bonds and lone pairs of electrons on every nonhydrogen atom below.



Lecture 4



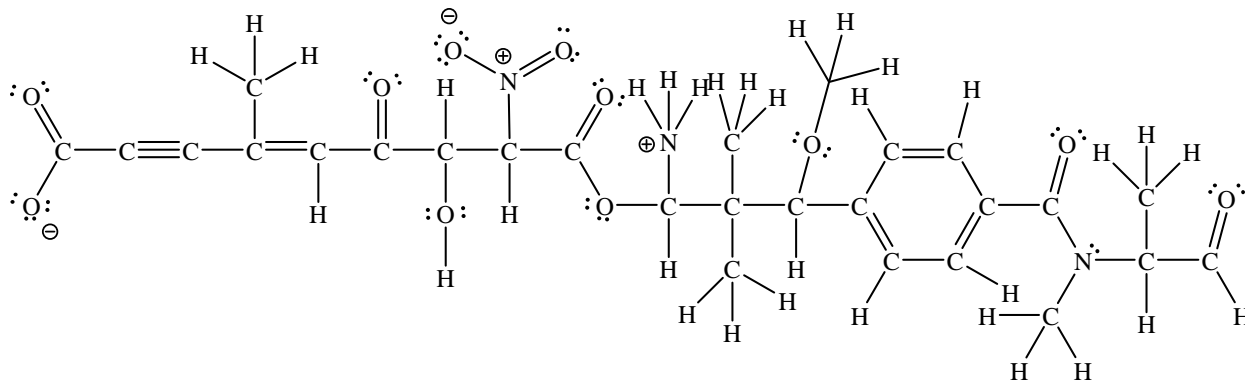
Problem 3 - Draw 2D Lewis structures for the following condensed line formulas. Include two dots for any lone pair electrons. These are more challenging than the previous structures, but they are doable, if you break them into simpler pieces as described earlier.



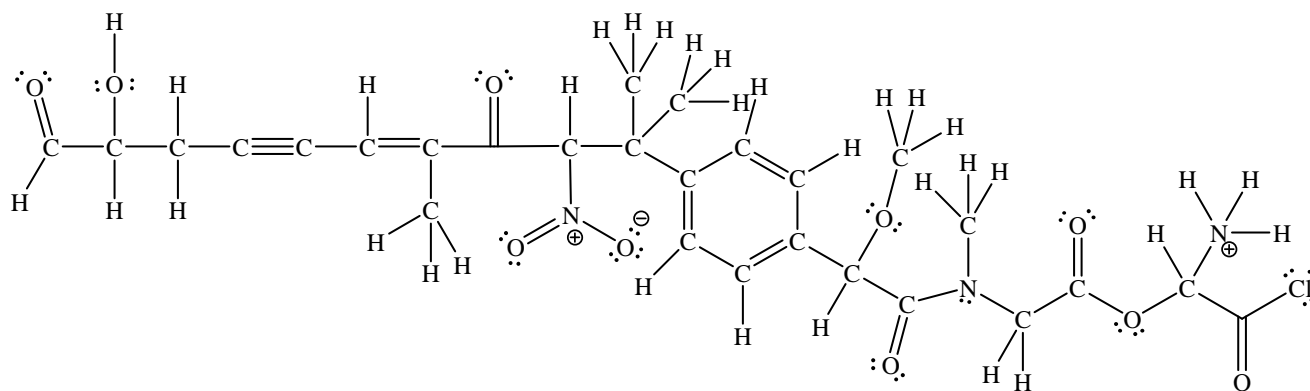
Lecture 4

Problem 3 answers - Draw 2D Lewis structures for the following condensed line formulas. Include two dots for any lone pair electrons. These are more challenging than the previous structures, but they are doable, if you break them into simpler pieces as described earlier.

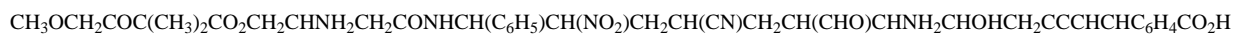
a.



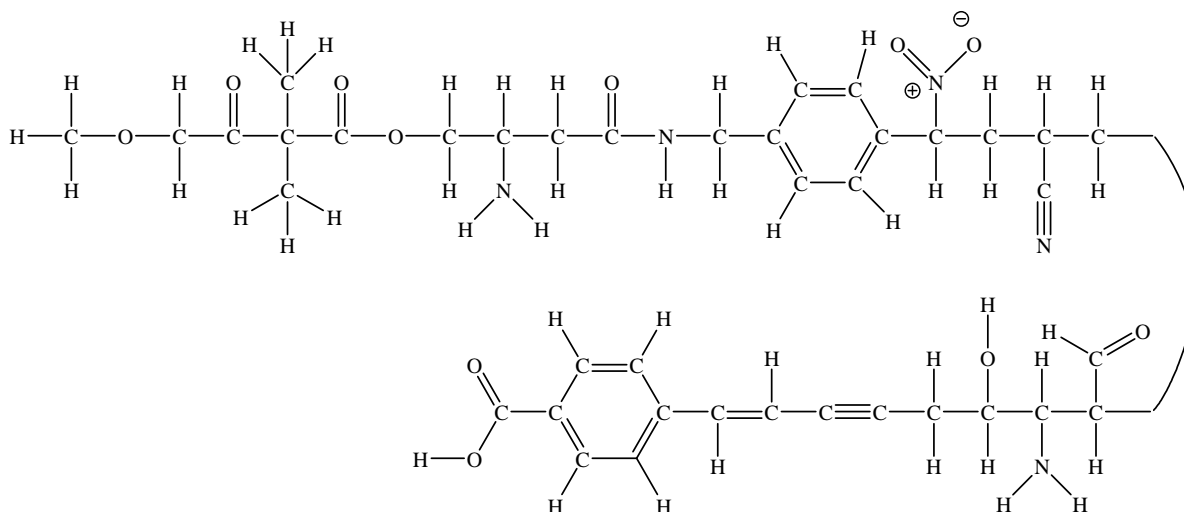
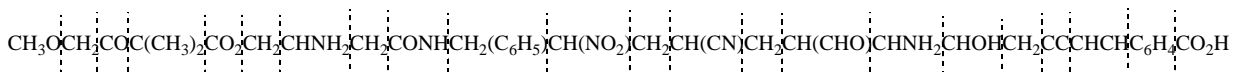
b.



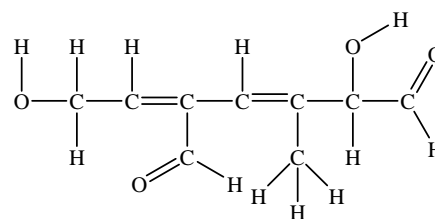
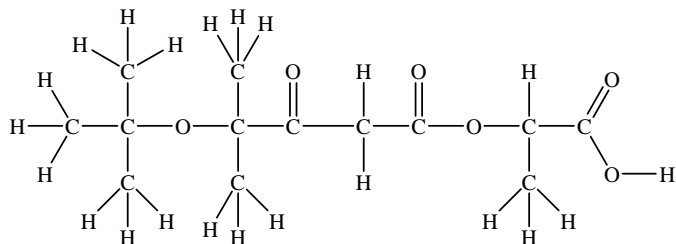
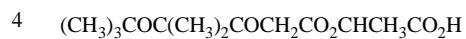
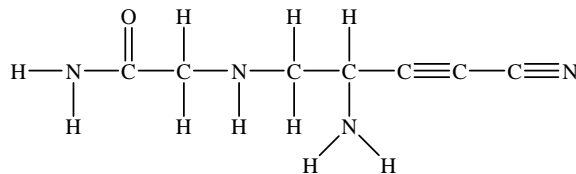
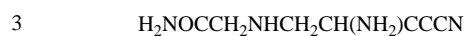
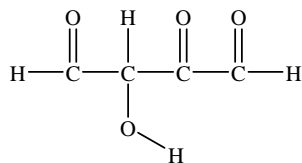
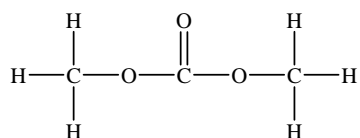
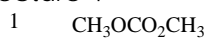
It's time to go back and take another look at that "hopelessly complex molecule" on page 2.



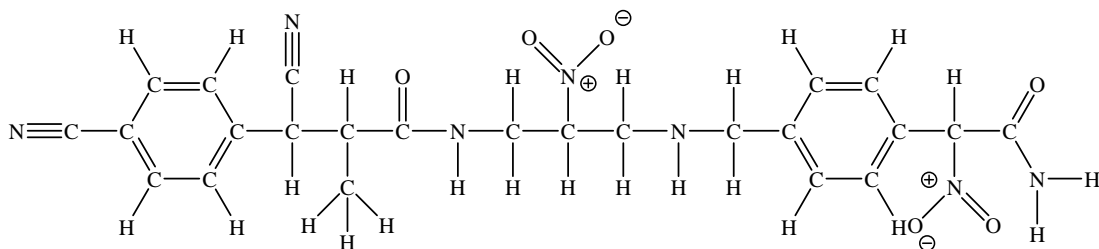
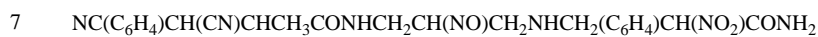
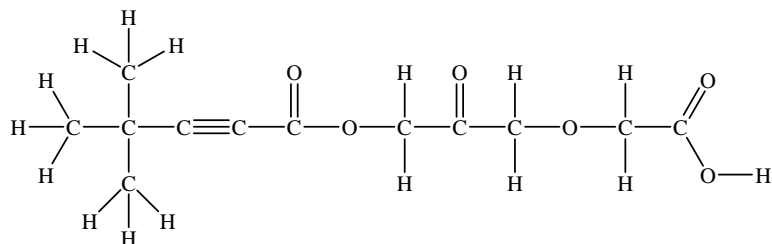
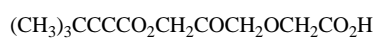
There are two six carbon rings present.



Lecture 4

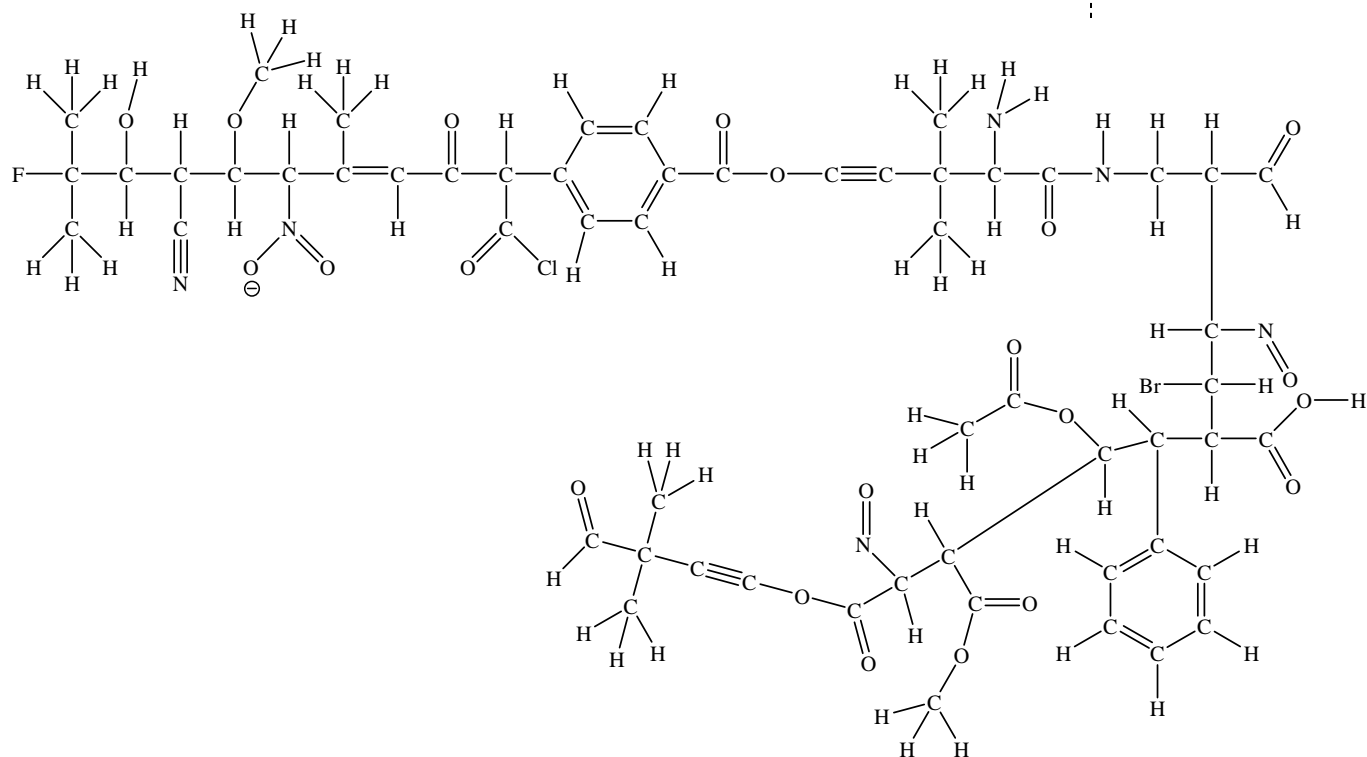
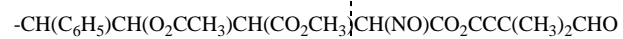
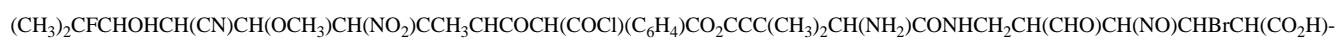


6



Lecture 4

8



Guidelines for Three Dimensional Lewis Structures – build molecular models to visualize the structures

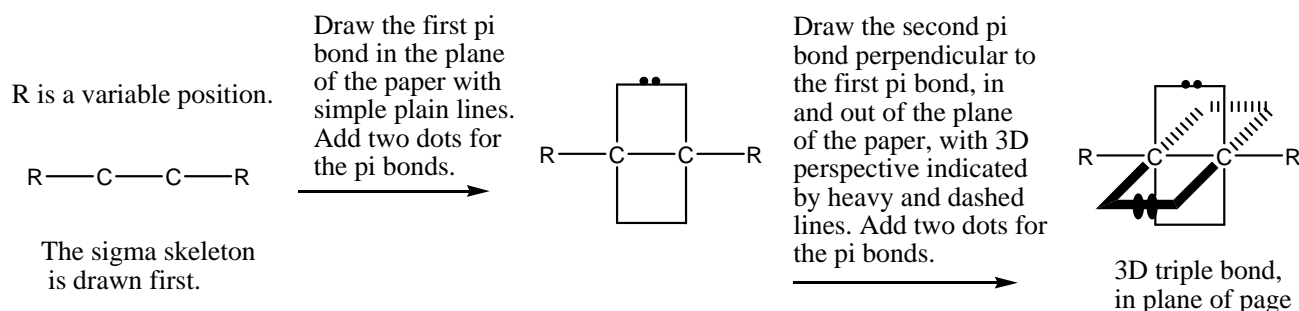
Rigid rules won't work for drawing 3D organic structures. There are too many ways that sigma bonds can rotate, and they rotate too fast to consider any 3D structure as the "real" structure. What we will try and do is to develop some guidelines that allow us to draw 3D structures that are reasonably accurate representations of a stable conformation (shape) of the molecule to train our minds to visualize molecules in three dimensions. As your hand draws these structures, it will be helping to create visual images in your mind's eye. Pay attention to the details because you want those images to be correct in your thinking. Another very important feature of 3D structures will be to show the parallel arrangement of p orbitals and pi bonds in resonance structures (when present). Being able to see the continuous overlap of 2p orbitals will provide us with genuine insight into how resonance works and why it is so important to your understanding of organic chemistry and biochemistry.

Guideline 1 – Draw a 2D Lewis structure as described above. This will allow you to determine the connections of the atoms, the hybridization, the shape, the bond angles, the number of sigma bonds, pi bonds and hydrogen atoms, and the nature of any lone pairs of electrons.

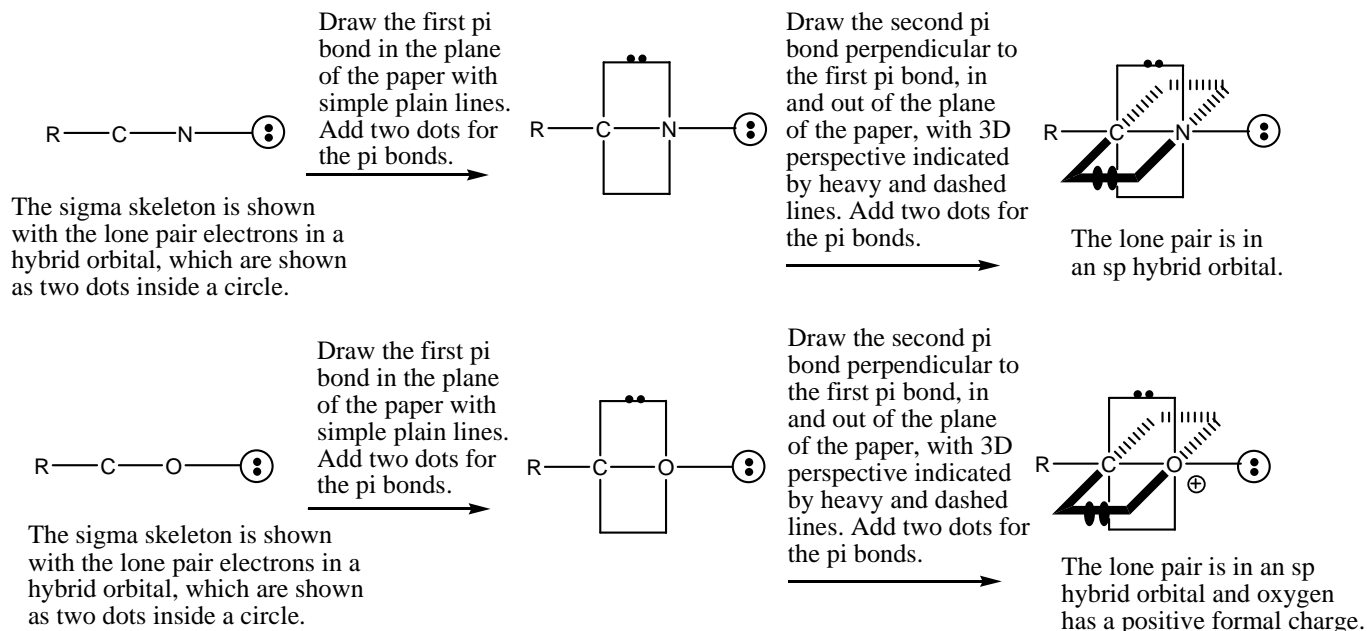
Guideline 2 – Draw all reasonable 2D resonance structures to allow a determination of each atom's hybridization. We mentioned this idea several times in the 2D examples above, but we will explicitly state it again. The hybridization of any atom is determined by the resonance structure in which that atom has its maximum number of bonds. This is a very important idea that you will probably overlook on occasion. If I make a big deal about it here, maybe you won't forget about it...but you probably will!

Guideline 3 – Place as many atoms as possible in the plane of the paper when you begin to draw your 3D structure. You only need to know how to draw three different shapes (sp , sp^2 and sp^3), but you really need to know how to draw them well.

a. If any triple bonds are present in your 2D Lewis structure, begin here. Because of the linear shape of sp hybridized atoms, you can place as many as four atoms in a straight line (or three atoms and a lone pair of electrons) in the plane of the paper. Sp hybridization is possible with neutral carbon and nitrogen and positively charged oxygen. One of the pi bonds will be parallel to the plane of the paper. Draw these 2p orbitals as simple straight lines. The other pi bond of the triple bond will be drawn perpendicular, in and out of the paper. Use a heavy line to show the 2p lobe in front of the paper and a dash to show the 2p lobe behind the paper. As much as possible, draw any additional pi bonds parallel to the plane of the paper and to the first drawn pi bond. Show the pi electrons as two dots between the 2p orbitals in your 3D structures. These will be the electrons you push in most of the mechanisms of alkene, alkyne and aromatic chemistry, to be studied later.



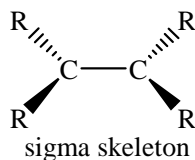
Lecture 4



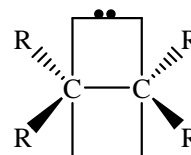
I suggest that you show lone pair electrons in hybrid orbitals as two dots inside a small circle. This clearly shows them to be a lone pair and identifies them in 3D structures in a manner similar to bonded atoms using hybrid orbitals. By now you should be getting the idea that lone pairs of electrons are very important in organic chemistry. Lone pair electrons and pi bond electrons reveal potential sites of future bonds and provide insights into the types of chemical reactions that are possible.

b. If only double bonds are present, begin by drawing one of the double bonds in the plane of the paper. The pi bond will be parallel to the paper. As much as possible, draw any additional pi bonds parallel to the plane of the paper and your original pi bond. sp^2 hybridization is possible with neutral carbon, nitrogen, oxygen and positively charged fluorine. Only certain perspectives are allowed for wedges and dashes. There are a number of parallel sigma bonds that, if recognized, make it easier to draw a 3D structure. Show the pi electrons as two dots between the 2p orbitals in your 3D structures. Show any lone pair electrons in hybrid orbitals in a circle at the end of the line showing the hybrid orbital (simple, wedged or dashed line). Examples of these are shown below. Additional pi bonds, not included below, are $-N=O$ and $-N=N-$.

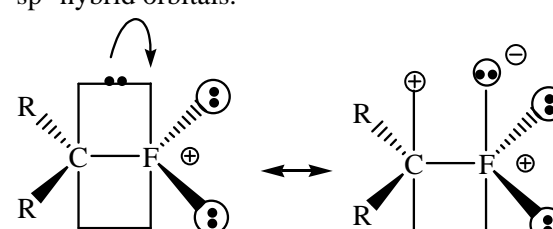
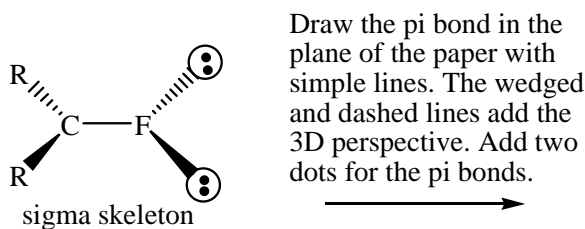
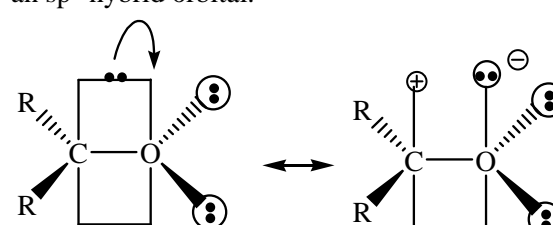
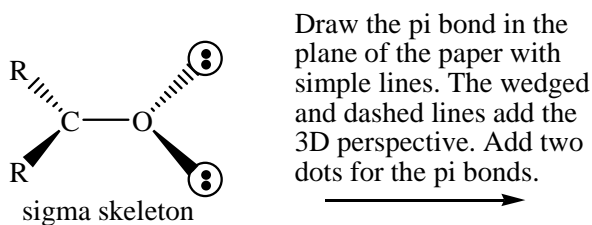
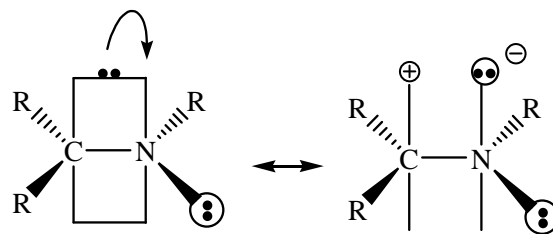
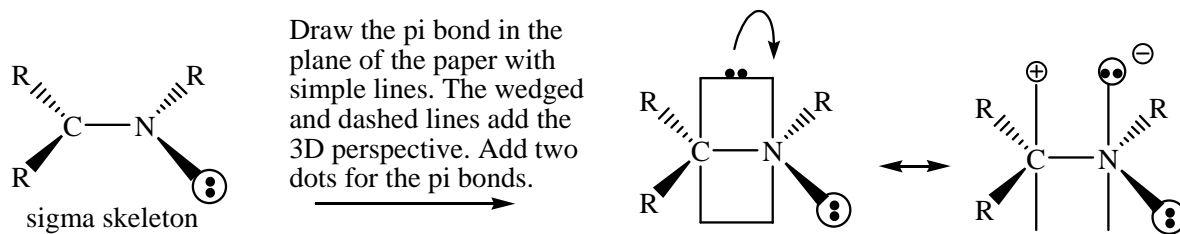
R is a variable position.



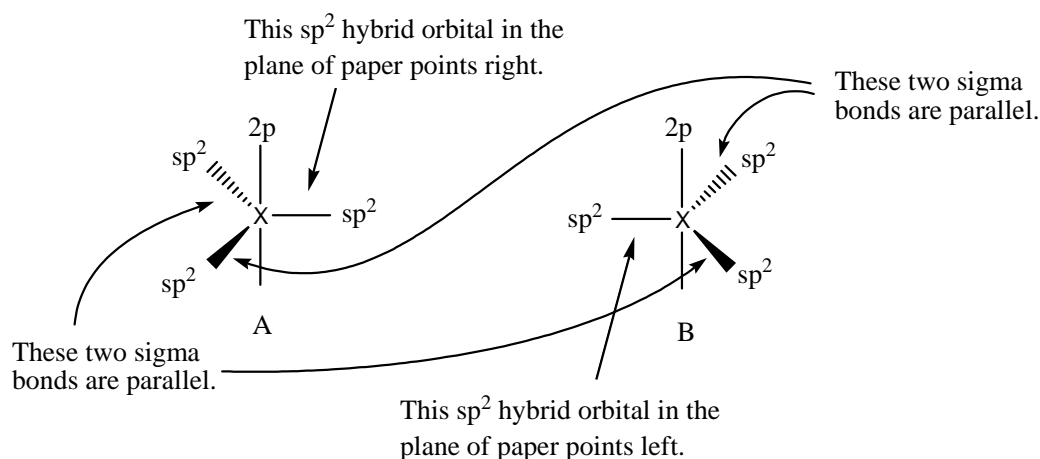
Draw the pi bond in the plane of the paper with simple lines. The wedged and dashed lines add the 3D perspective. Add two dots for the pi bonds.



2D pi bond, in plane of page

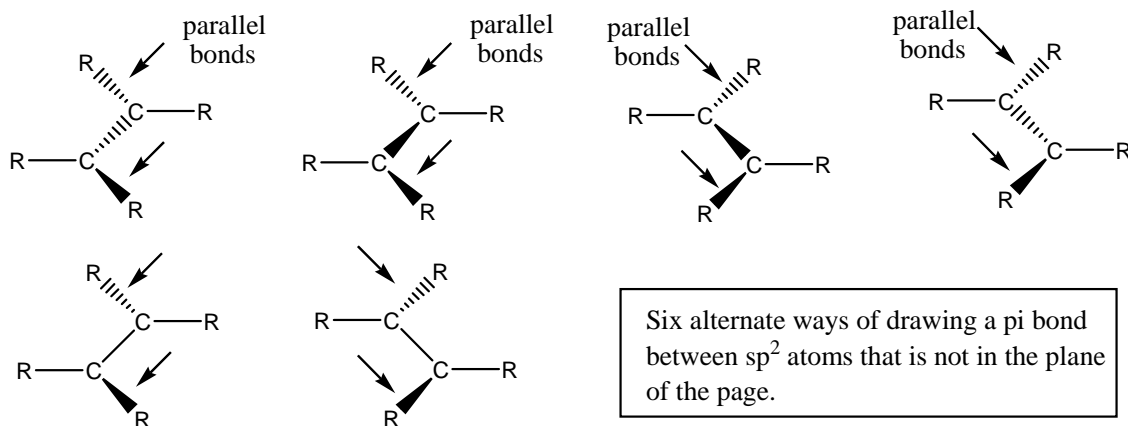


There are only two possible shapes for an sp^2 hybridized atom, if the pi bond is drawn in the plane of the paper. The sp^2 hybrid orbital in the plane of the paper either points to the left or to the right (drawn as a simple plain line). One of the other two sp^2 hybrid orbitals will be a wedged line and the other will be a dashed line. X (below) represents any sp^2 hybridized atom (C, N, O, F). The dashed line pointing left in A and the wedged line pointing right in B are parallel. Similarly, the wedged line pointing left in A and the dashed line pointing right in B are parallel. Recognizing the parallel nature of these bonds will allow you to more accurately draw sp^2 hybridized atoms when more than one pi bond is present.



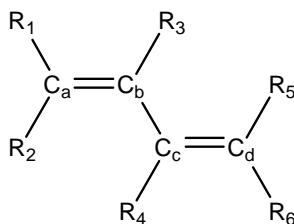
Lecture 4

There are additional ways that an sp^2 pi bond can be drawn when the pi bond is in or out of the plane of the paper. In each double bond there are two sp^2 hybrid orbitals parallel to one another in the plane of the paper (plain simple lines) and two sp^2 hybrid orbitals parallel to one another in and out of the paper (wedge and dash). The parallel bonds in and out of the paper have arrows drawn towards them in the structures, below. The bond between the two carbon atoms can either be shown with a wedge or with a dashed line. It really depends on what atom was written down first, because the perspective is relative. If you write the front carbon first, then you are likely to use a dashed line to the back carbon. If you write the rear carbon first, then you are likely to use a wedged line to the front carbon. To get around this ambiguity, you might consider using a plain simple line in this situation. You can let the other sigma bonds reveal the 3D perspective of the sp^2 atoms, since there is only one acceptable way of drawing the wedged and dashed lines for those sigma bonds. I allow any type of line between two carbon atoms like this, but you should draw such a double bond the way your instructor wants it drawn.



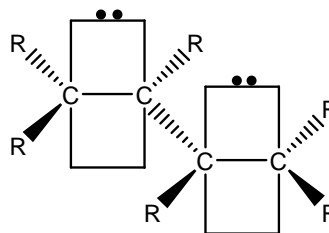
c. Pi bonds can be joined together in an almost endless number of possible ways. (two triples, triple plus a double, two doubles, cumulated, aromatic...etc.). Several examples are provided below. A nitrogen atom or an oxygen atom is occasionally switched in to illustrate the generality of the 3D structures. Atoms with formal charge will also easily fit into these same 3D patterns.

2D Lewis structure

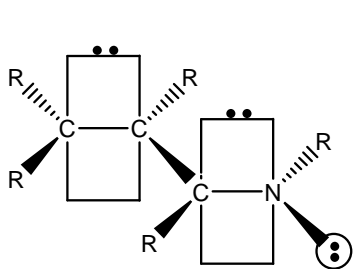


Notice that several bonds are parallel.
 R_1-C_a is parallel with C_b-C_c and C_d-R_6 .
 R_2-C_a is parallel with C_b-R_3 , C_c-R_4 and C_d-R_5 .
 C_a-C_b is parallel with C_c-C_d

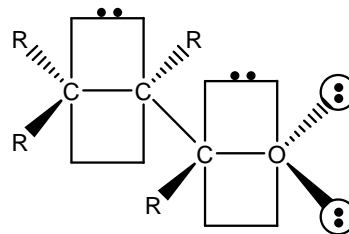
3D Lewis structure



The front pi bond was drawn first so the sigma bond between the two pi bonds is a dashed line. Use the parallel relationship of the sigma bonds to help you draw the correct perspective in these structures.

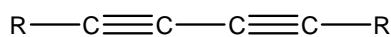


The back pi bond was drawn first so the sigma bond between the two pi bonds is a wedged line.

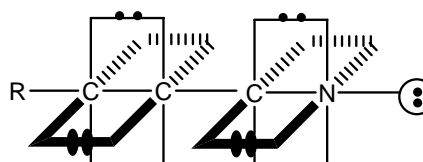
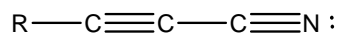
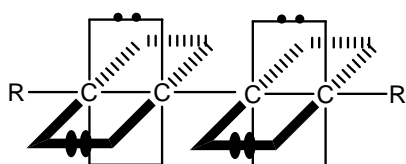


Since the middle bond can be drawn either way, no indication is made and the 3D features are determined by the other sigma bonds that show dashes and wedges.

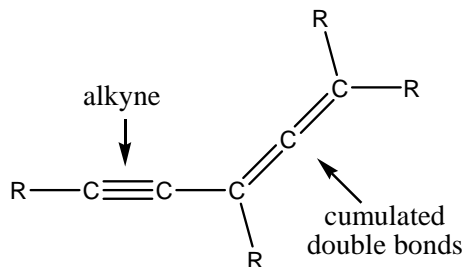
2D Lewis structure



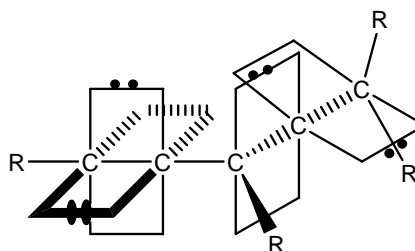
3D Lewis structures



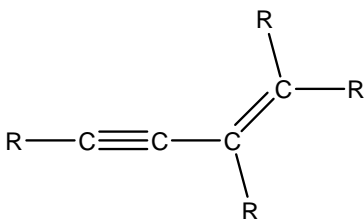
2D Lewis structure



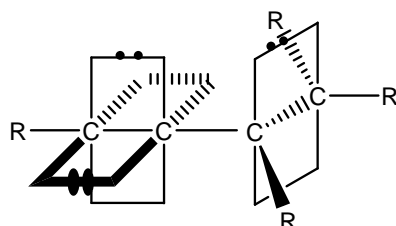
3D Lewis structure



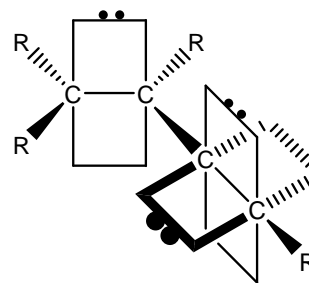
2D Lewis structure



3D Lewis structures



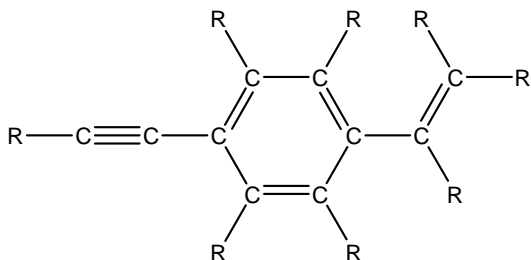
Triple bond in the plane, double bond in and out of the plane.



Double bond in the plane, triple bond in and out of the plane.

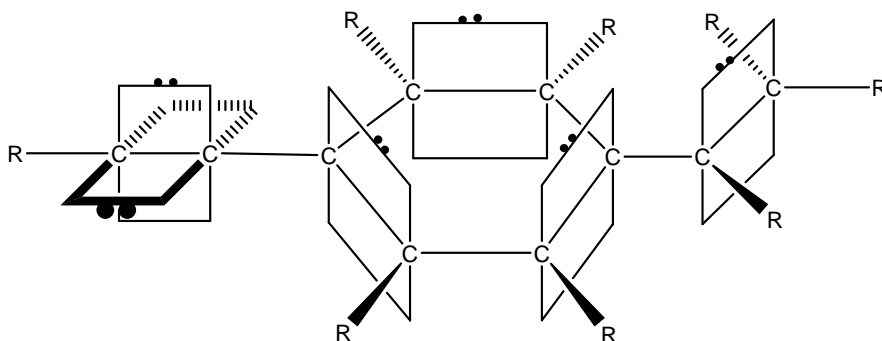
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2D Lewis structure

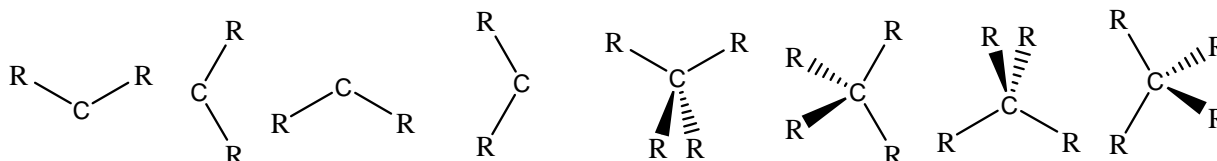


If you have to draw a 3D structure with an aromatic ring, draw the ring big so that the 2p orbitals in the front do not cover the 2p orbitals in the back. In this structure the sigma bonds of the substituents on the aromatic ring are supplying the 3D perspective. If you want to get more fancy, you can add that perspective to the sigma bonds in the ring. We can see clearly that all of the 2p orbitals of the pi bonds are parallel, except for the second pi bond of the alkyne which is perpendicular to the other pi bonds. There is resonance among the parallel pi bonds. There are a number of places where we could switch in a heteroatom and some lone pairs of electrons.

3D Lewis structures



d. sp^3 hybridization may be the most difficult to represent in three dimensions. Simple single bonds allow unlimited rotations. To simplify our 3D drawing problems as much as possible, we will assume that tetrahedral atoms are in a zig-zag conformation (shape) in the plane of the paper. Only certain perspectives will be allowed for wedges and dashes. Usually, we will draw two simple lines, in the plane of the paper and one wedged line and one dashed line. The two simple lines will have to be drawn close to one another, as will the dashed and wedged lines. These can be difficult to draw accurately and we will allow shapes to be drawn that are “pretty close”. Examples of these are shown below, along with some of the common problems.

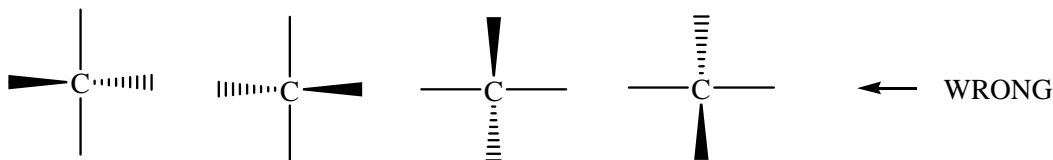


Simple lines can be drawn close together four different ways, pointing up, pointing right, pointing down and pointing left.

Wedged and dashed lines can be drawn close together four different ways, pointing up, pointing right, pointing down and pointing left.

These lines are drawn correctly.

These lines are drawn **incorrectly**.

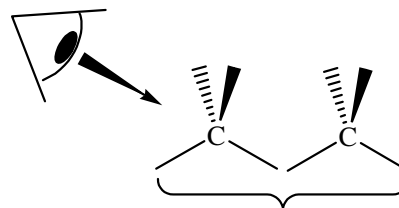
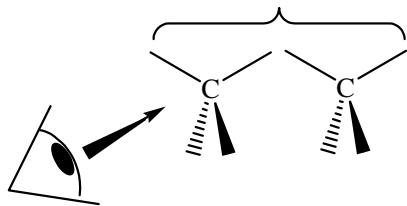


Drawing the simple lines or the wedged and dashed lines opposite one another implies that there are 180° bond angles...but we know that sp^3 atoms have approximately 109° bond angles.

Lecture 4

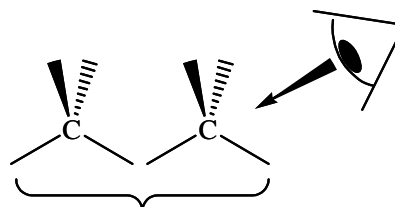
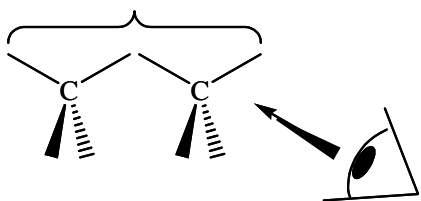
Point of view provides yet another complication in drawing tetrahedral 3D atoms. Are you viewing a structure from the left or from the right? Whichever it is, you will want stay consistent in your drawing for all of the sp^3 atoms.

The perspective of these two atoms is consistent when viewed from the left. The dashes are parallel and the wedges are parallel.

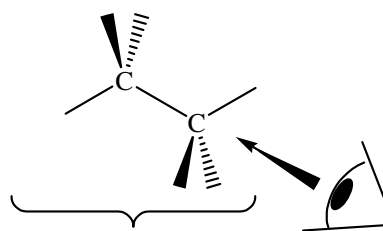
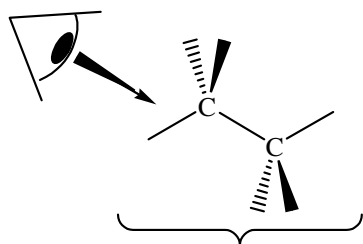


The perspective of these two atoms is consistent when viewed from the left. The dashes are parallel and the wedges are parallel.

The perspective of these two atoms is consistent when viewed from the right. The dashes are parallel and the wedges are parallel.



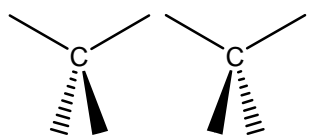
The perspective of these two atoms is consistent when viewed from the right. The dashes are parallel and the wedges are parallel.



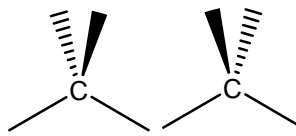
The perspective of these two atoms is consistent when viewed from the left. The wedges pointing up are parallel to the dashes pointing down, and vice versa.

The perspective of these two atoms is consistent when viewed from the right. The wedges pointing up are parallel to the dashes pointing down, and vice versa.

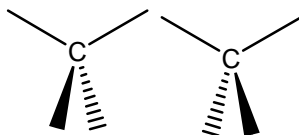
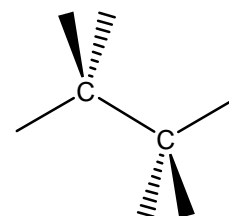
None of the perspectives of these pairs of atoms is consistent when viewed from the either side. All of these are drawn incorrectly.



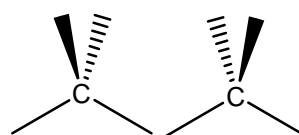
WRONG



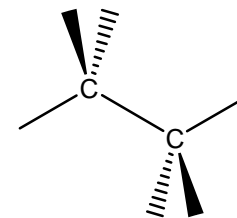
WRONG



WRONG



WRONG



As much as possible, draw a 3D sequence of sp^3 atoms in a zig-zag shape. Besides there being a logical “energetic” reason for drawing a structure this way, it is easier to draw and see on a piece of paper. The zig-zag bonds in the plane of the paper all use simple lines and there will be a wedged and

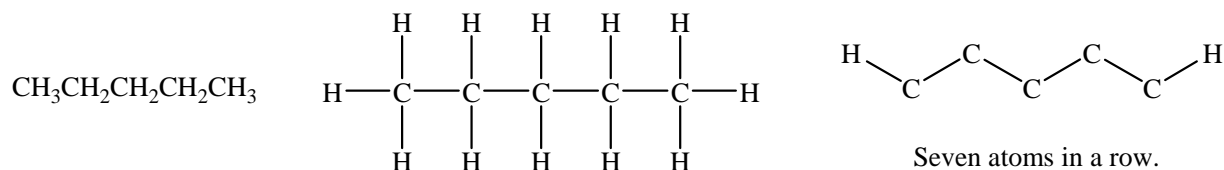
Lecture 4

dashed line coming off each sp^3 atom. At alternate positions they will be pointing up, when the chain is up, and then down, when the chain is down. Keep in mind the point of view restrictions shown above.

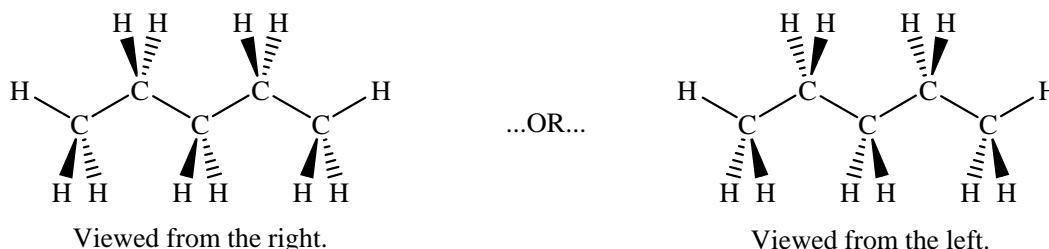
2D condensed formula

2D Lewis structure

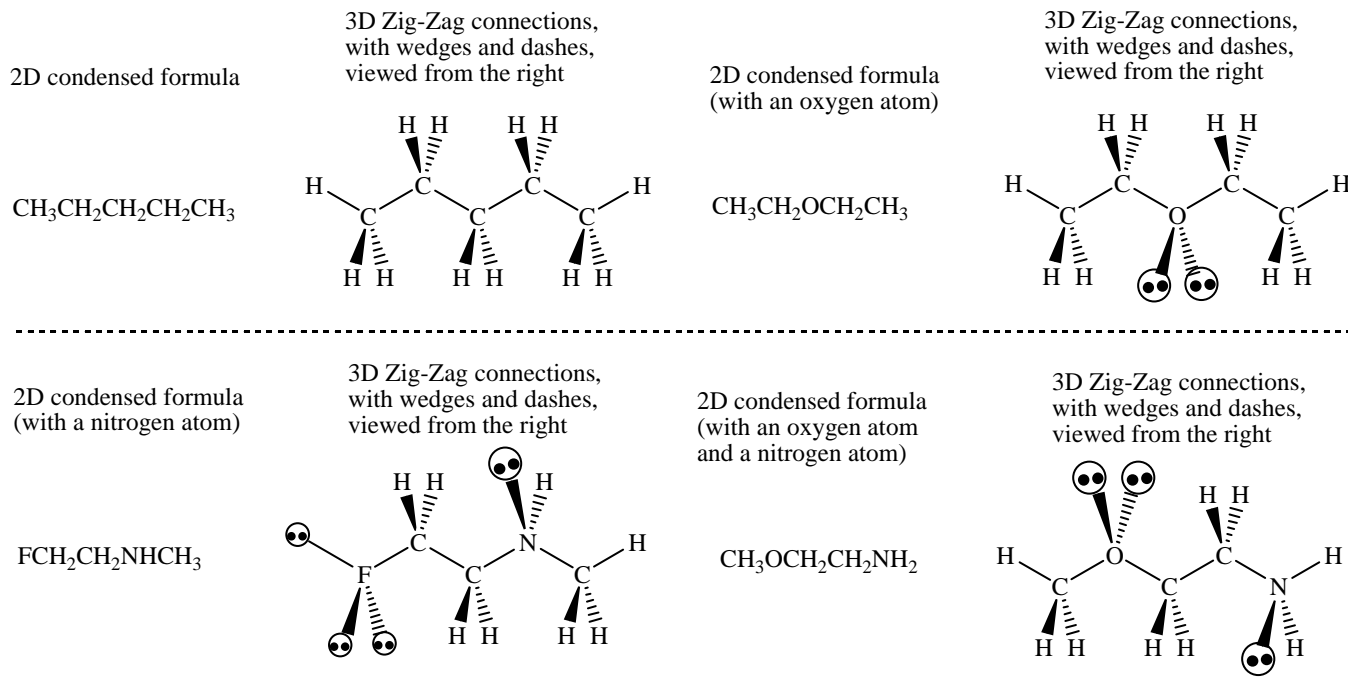
Zig-Zag connections



Zig-Zag connections, with wedges and dashes



It's easy to switch in an sp^3 heteroatom in place of an sp^3 carbon atom. All we need to do is place a lone pair at the end of one of the hybrid orbitals in place of an atom (all hydrogen atoms here).



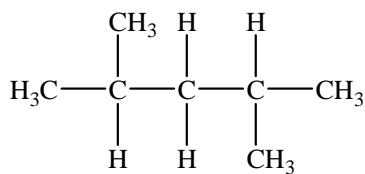
Branches off of the zig-zag chain are generally difficult to draw. Anything that moves off the plane of the paper makes the 3D drawing more difficult. We will try to minimize drawing 3D structures with these features. Our main goal is to develop strong visual images so that we can think in three dimensions using the three shapes of organic chemistry and biochemistry. These visualization skills will only grow in importance as we progress through the book. I'll give a shot at drawing a branch in front and a branch in back, so you have an idea of what it might look like, but it's a challenge for me too.

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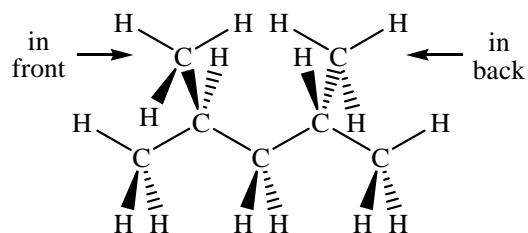
2D condensed formula



2D Lewis structure



3D Zig-Zag connections, with wedges and dashes, viewed from the right in a structure with branches. Can you "visualize" this in 3D?

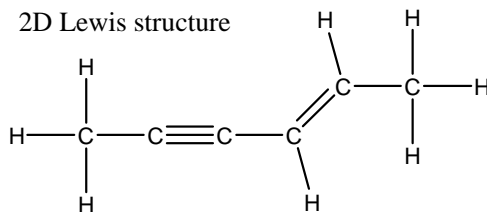


Here are two examples, showing all three possible hybridization states in one molecule, and some heteroatoms thrown in to boot.

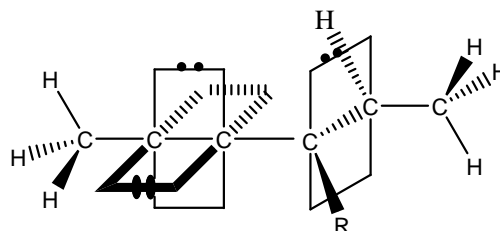
Condensed line formula



2D Lewis structure



3D Lewis structures

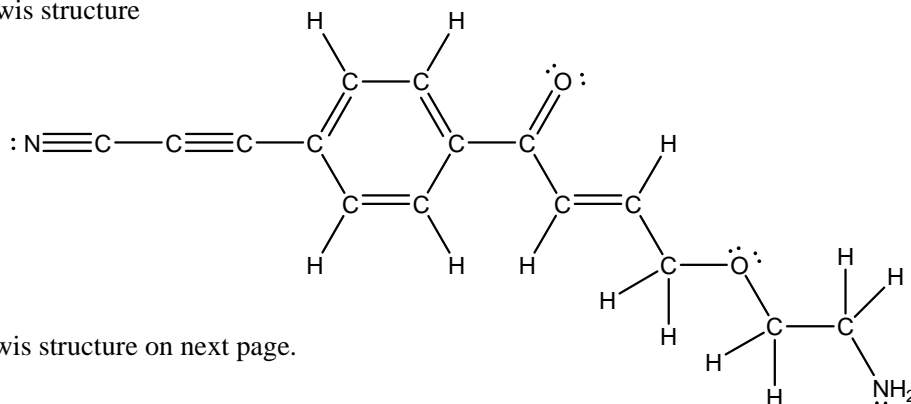


Triple bond in the plane, double bond in and out of the plane, viewed from the left.

Condensed line formula



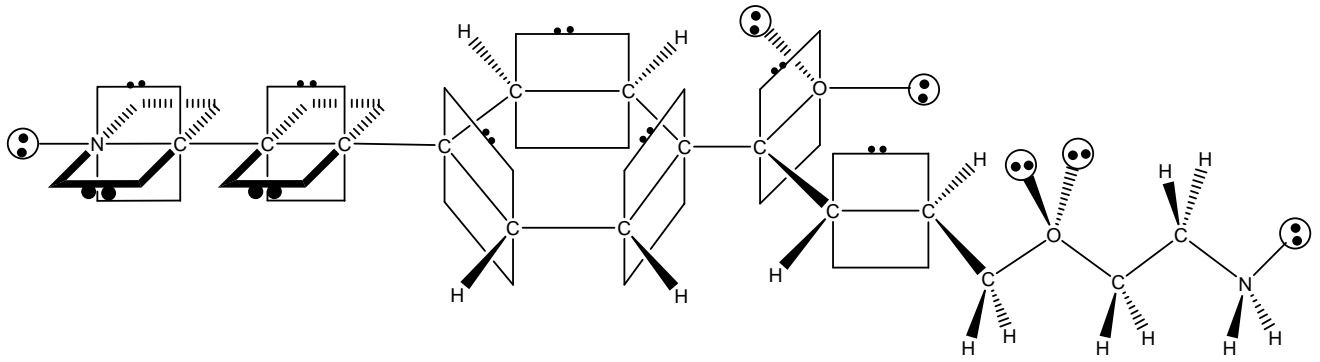
2D Lewis structure



3D Lewis structure on next page.

This is one humongous 3D Lewis structure, and a challenge to draw. I doubt that you will ever have to draw a 3D structure this complex, but hopefully you can visualize in your mind's eye the 3D perspective implied in the drawing. Of course, you can always build a model. Whatever you draw on the paper is a good approximation of what is in your head. Errors on the page imply errors in your mind. Be careful and precise in what you write down.

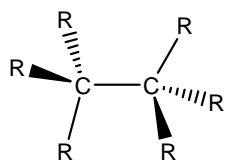
Lecture 4



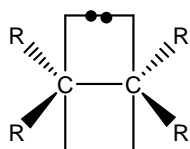
Lecture 4

Summary of 3D shapes for carbon, nitrogen, oxygen and fluorine

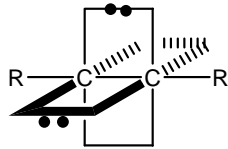
Carbon: Four ways to draw carbon in organic chemistry.



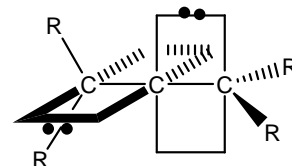
hybridization: sp^3
 bond angles: 109°
 number of sigma bonds: 4
 number of pi bonds: 0
 number of lone pairs: 0



hybridization: sp^2
 bond angles: 120°
 number of sigma bonds: 3
 number of pi bonds: 1
 number of lone pairs: 0

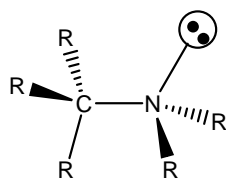


hybridization: sp
 bond angles: 180°
 number of sigma bonds: 2
 number of pi bonds: 2
 number of lone pairs: 0

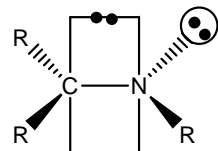


hybridization: sp
 bond angles: 180°
 number of sigma bonds: 2
 number of pi bonds: 2
 number of lone pairs: 0

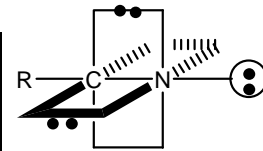
Nitrogen: Four ways to draw nitrogen in organic chemistry.



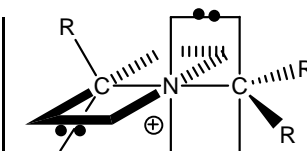
hybridization: sp^3
 bond angles: 109°
 number of sigma bonds: 3
 number of pi bonds: 0
 number of lone pairs: 1



hybridization: sp^2
 bond angles: 120°
 number of sigma bonds: 2
 number of pi bonds: 1
 number of lone pairs: 1

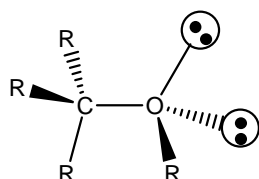


hybridization: sp
 bond angles: 180°
 number of sigma bonds: 1
 number of pi bonds: 2
 number of lone pairs: 1

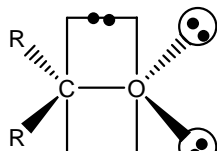


hybridization: sp
 bond angles: 180°
 number of sigma bonds: 2
 number of pi bonds: 2
 number of lone pairs: 0
 positive formal charge

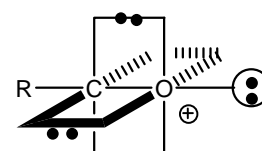
Oxygen: Three ways to draw oxygen in organic chemistry.



hybridization: sp^3
 bond angles: 109°
 number of sigma bonds: 2
 number of pi bonds: 0
 number of lone pairs: 2

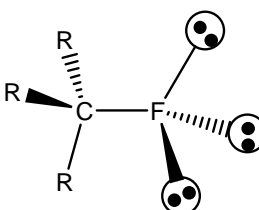


hybridization: sp^2
 bond angles: 120°
 number of sigma bonds: 1
 number of pi bonds: 1
 number of lone pairs: 2

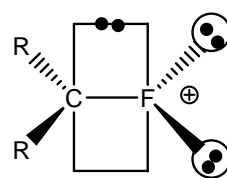


hybridization: sp
 bond angles: 180°
 number of sigma bonds: 1
 number of pi bonds: 2
 number of lone pairs: 1
 positive formal charge

Fluorine: Two ways to draw fluorine in organic chemistry.



hybridization: sp^3
 bond angles: 109°
 number of sigma bonds: 1
 number of pi bonds: 0
 number of lone pairs: 3



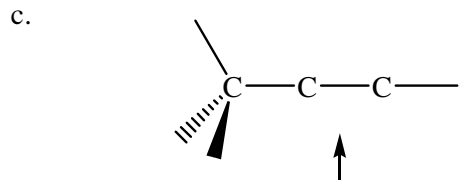
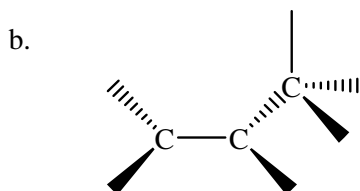
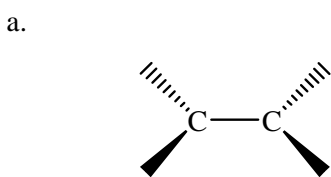
hybridization: sp^2
 bond angles: 120°
 number of sigma bonds: 1
 number of pi bonds: 1
 number of lone pairs: 2
 positive formal charge

Lecture 4

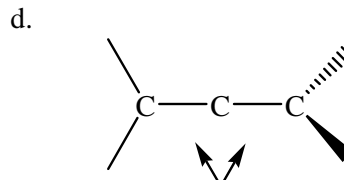
Problem 4 – First, convert the condensed line formulas of the following hydrocarbons into 2D Lewis structures. This will let you know the hybridization, shape, bond angles, etc. of all the atoms in the structure. You will need this information before you can decide how to draw the shape to structure. Next, draw 3D structures for each of the 2D structures. You should show the bonds in front of the page as wedges and bonds in back of the page with dashed lines and bonds in the plane of the page as simple lines. Show the 2p orbitals for π bonds using similar conventions (simple lines, heavy lines and dashed lines). Also show two dots for any pi electrons. Building a molecular model of the structure will help. Partial 3D sigma bond skeletons have been drawn below in case you cannot visualize the structures. Use these as a last resort. There are a variety of ways to draw these structures. I have drawn them according to the guidelines above.

Condensed line formulas

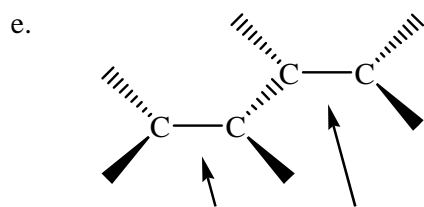
- a. H_2CCH_2 b. CH_2CHCH_3 c. H_3CCCH d. CH_2CCH_2 e. $\text{CH}_2\text{CHCHCH}_2$
 f. $\text{H}_2\text{CCCHCH}_3$ g. $\text{CH}_3\text{CCCH}_2\text{CH}_2\text{CH}_3$ h. H_2CCCCH_2 i. $\text{C}_6\text{H}_5\text{CCCHCH}_2$ j. $\text{CH}_3\text{CCCCCH}_3$



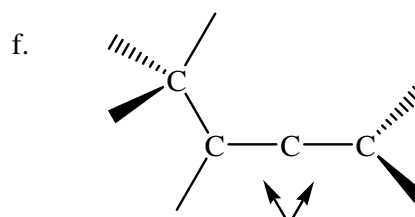
What is the angle of the pi bonds relative to one another?



What is the angle of the pi bonds relative to one another?



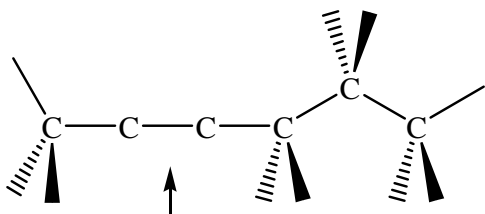
What is the angle of the pi bonds relative to one another?



What is the angle of the pi bonds relative to one another?

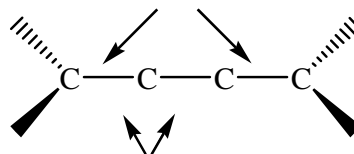
Lecture 4

g.



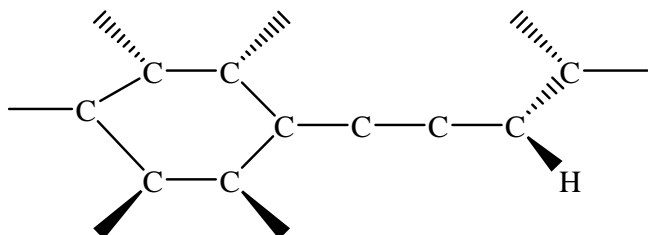
What is the angle of the pi bonds relative to one another?

h.



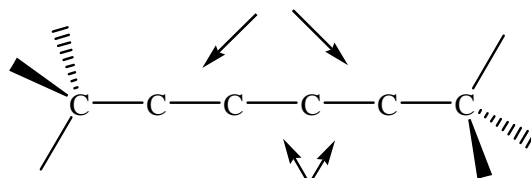
What is the angle of the pi bonds relative to one another?

i.



What is the angle of the pi bonds relative to one another throughout?

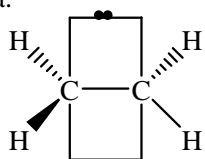
j.



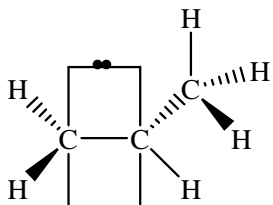
What is the angle of the pi bonds relative to one another?

Problem 4 – Possible answers.

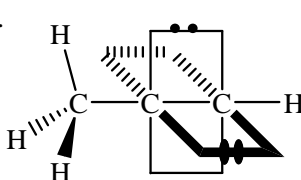
a.



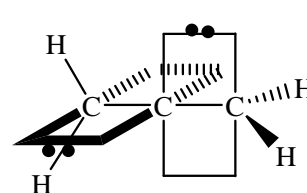
b.



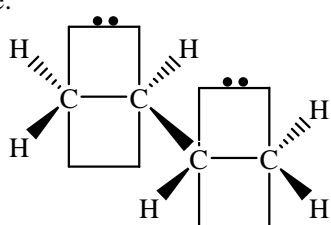
c.



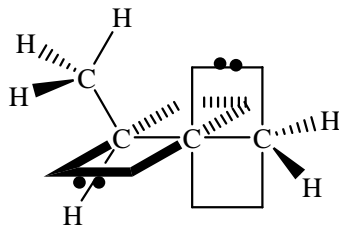
d.



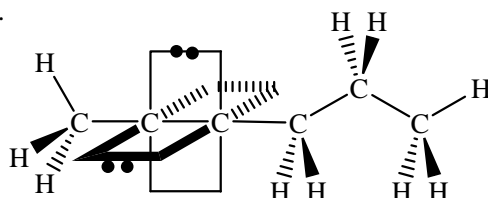
e.



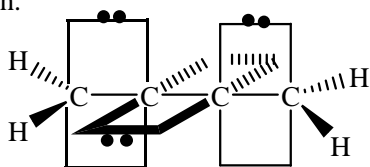
f.



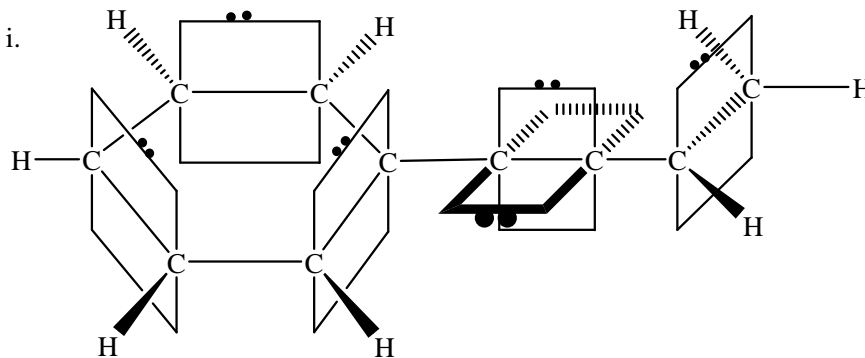
g.



h.

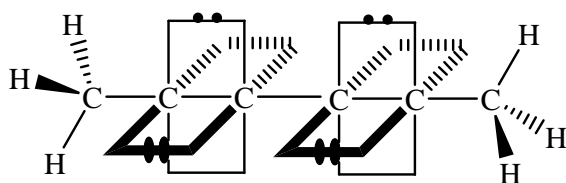


i.



Lecture 4

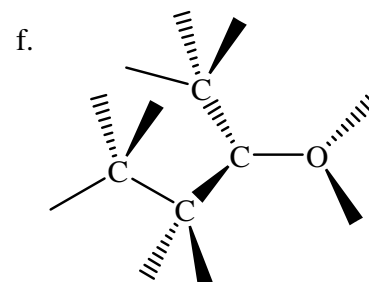
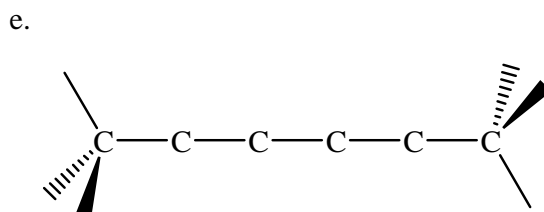
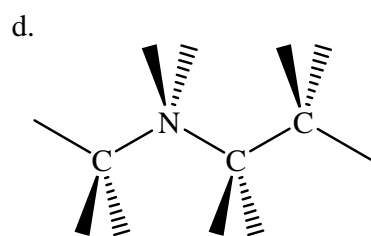
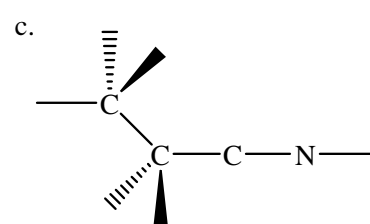
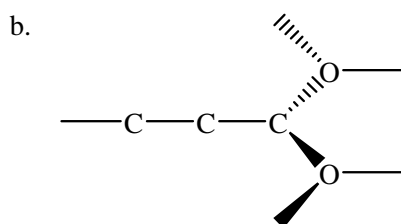
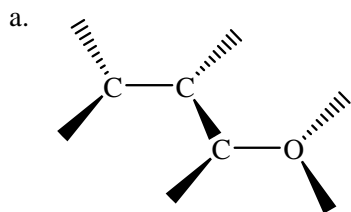
j.



Problem 5 – This problem is very similar to the above problem, except heteroatoms (N, O and F) are substituted in for some of the carbon atoms and some structures have formal charge. As above, first convert the condensed line formulas into 2D Lewis structures; you need this to draw the 3D structure. Next, draw 3D structures for each of the 2D structures. You should show the bonds and lone pairs of electrons in hybrid orbitals (use two dots in a circle) in front of the page as wedges and bonds in back of the page with dashed lines and bonds in the plane of the page as simple lines. Show the 2p orbitals for π bonds using similar conventions (simple lines, heavy lines and dashed lines). Also show two dots for any pi electrons. Building a molecular model of the structure will help. Partial 3D sigma bond skeletons have been drawn below in case you cannot visualize the structures. Use these as a last resort. There are a variety of ways to draw these. I have drawn them according to the guidelines above.

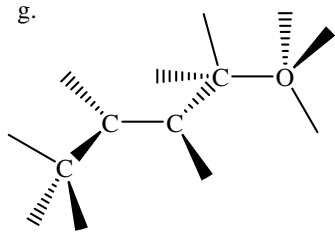
Condensed line formulas

- a. CH₂CHCHO b. HCCCO₂H c. H₃CCH₂CN d. CH₃NHCH₂CH₃ e. CH₃CCCCCH₃
- f. CH₃CH₂COCH₃ g. CH₃CHCHCH₂OH h. CH₂CHN₃ i. OHCC₆H₄CN j. CH₃CHN₂
- k. CH₂CHC₆H₄CCCO₂CH₃ l. ClCH₂CH₂CONHCH₃ m. O₂NCHCHCCCH₃ n. CH₃C₅NH₄
 six atom ring six atom heterocyclic ring

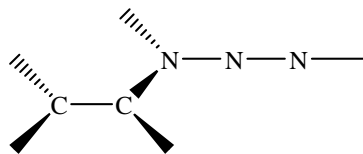


Lecture 4

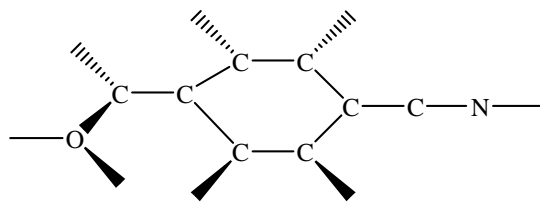
g.



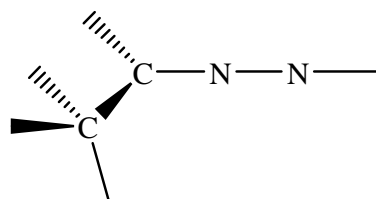
h.



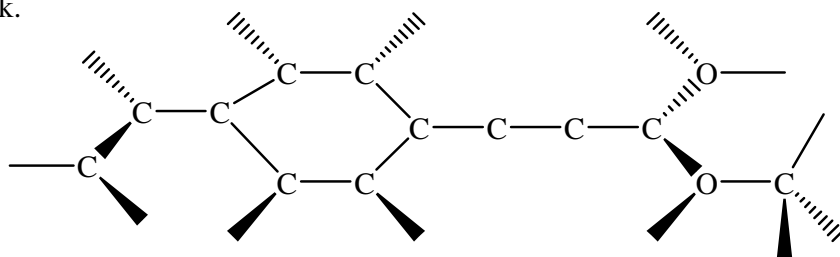
i.



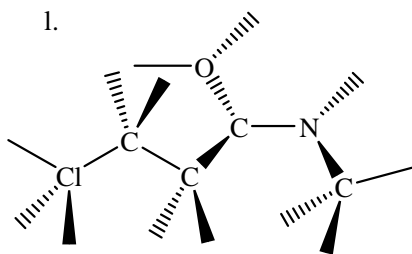
j.



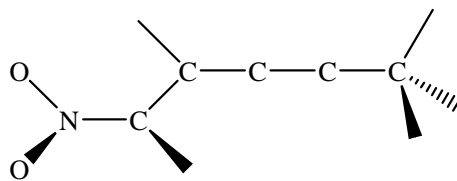
k.



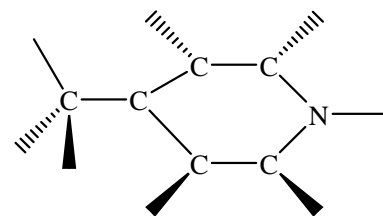
l.



m.

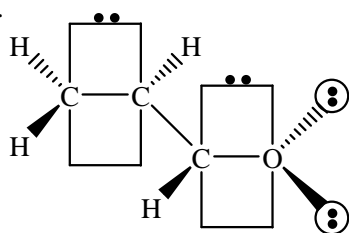


n.

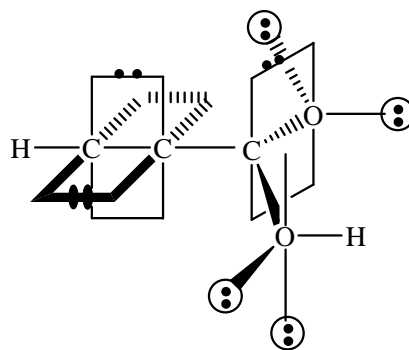


Problem 5 – Possible answers.

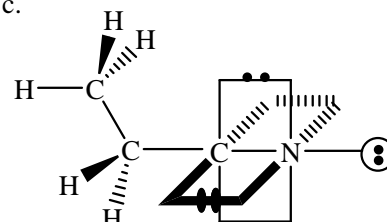
a.



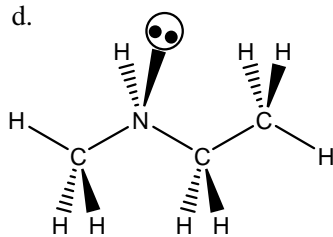
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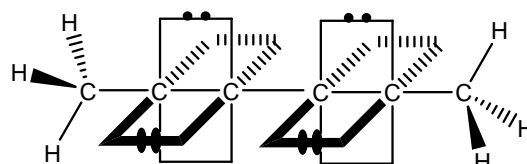
c.



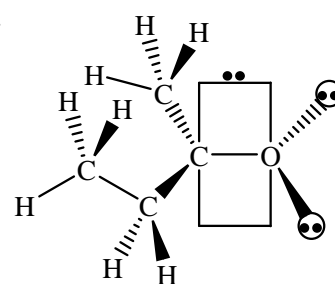
d.



e.



f.



Lecture 4

