

Chapter 1

Working with Models and Molecules

In This Chapter

- ▶ Diagramming Lewis structures
- ▶ Predicting bond dipoles and dipole moments of molecules
- ▶ Seeing atom hybridizations and geometries
- ▶ Discovering orbital diagrams

Organic chemists use models to describe molecules because atoms are tiny creatures with some very unusual behaviors, and models are a convenient way to describe on paper how the atoms in a molecule are bonded to each other. Models are also useful for helping you understand how reactions occur.

In this chapter, you use the Lewis structure, the most commonly used model for representing molecules in organic chemistry. You also practice applying the concept of atom hybridizations to construct orbital diagrams of molecules, explaining where electrons are distributed in simple organic structures. Along the way, you see how to determine dipoles for bonds and for molecules — an extremely useful tool for predicting solubility and reactivity of organic molecules.

Constructing Lewis Structures

The *Lewis structure* is the basic word of the organic chemist; these structures show which atoms in a molecule are bonded to each other and also show how many electrons are shared in each bond. You need to become a whiz at working with these structures so you can begin speaking the language of organic chemistry.

To draw a Lewis structure, follow four basic steps:

1. Determine the connectivity of the atoms in the molecule.

Figure out how the atoms are attached to each other. Here are some guidelines:

- In general, the central atom in the molecule is the least electronegative element. (Electronegativity decreases as you go down and to the left on the periodic table.)
- Hydrogen atoms and halide atoms (such as F, Cl, Br, and I) are almost always peripheral atoms (not the central atom) because these atoms usually form only one bond.



2. Determine the total number of valence electrons (electrons in the outermost shell).

Add the valence electrons for each of the individual atoms in the molecule to obtain the total number of valence electrons in the molecule. If the molecule is charged, add one electron to this total for each negative charge or subtract one electron for each positive charge.

3. Add the valence electrons to the molecule.

Follow these guidelines:

- Start adding the electrons by making a bond between the central atom and each peripheral atom; subtract two valence electrons from your total for each bond you form.
- Assign the remaining electrons by giving lone pairs of electrons to the peripheral atoms until each peripheral atom has a filled octet of electrons.
- If electrons are left over after filling the octets of all peripheral atoms, then assign them to the central atom.

4. Attempt to fill each atom's octet.

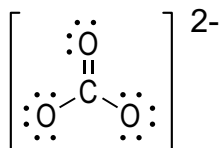
If you've completed Step 3 and the central atom doesn't have a full octet of electrons, you can share the electrons from one or more of the peripheral atoms with the central atom by forming double or triple bonds.

You can't break the octet rule for second-row atoms; in other words, the sum of the bonds plus lone pairs around an atom can't exceed four.

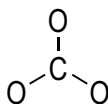


Q. Draw the Lewis structure of CO_3^{2-} .

A.



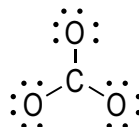
Most often, the *least* electronegative atom is the central atom. In this case, carbon is less electronegative than oxygen, so carbon is the central atom and the connectivity is the following:



Carbon has four valence electrons because it's an atom in the fourth column of the

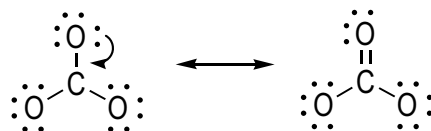
periodic table, and oxygen has six valence electrons because it's in the sixth column. Therefore, the total number of valence electrons in the molecule is $4 + 6(3) + 2 = 24$ valence electrons. You add the additional two electrons because the molecule has a charge of -2 (if the molecule were to have a charge of -3 , you'd add three electrons; if -4 , you'd add four; and so forth).

Start by forming a bond between the central carbon atom and each of the three peripheral oxygen atoms. This accounts for six of the electrons (two per bond). Then assign the remaining 18 electrons to the oxygens as lone pairs until their octets are filled. This gives you the following configuration:



The result of the preceding step leaves all the oxygen atoms happy because they each have a full octet of electrons, but the central carbon atom remains unsatisfied because this atom is still two electrons short of completing its octet. To remedy this situation, you move a lone pair from one of the oxygens toward the carbon to form a carbon-oxygen double bond. Because the oxygens are identical, which

oxygen you take the lone pair from doesn't matter. In the final structure, the charge is also shown:



1. Draw the Lewis structure of BF_4^- .

Solve It

2. Draw the Lewis structure of H_2CO .

Solve It

3. Draw the Lewis structure of NO_2^- .

Solve It

Predicting Bond Types

Bonds can form between a number of different atoms in organic molecules, but chemists like to broadly classify these bonds so they can get a rough feel for the reactivity of that bond. These bond types represent the extremes in bonding.

In chemistry, a bond is typically classified as one of three types:

- ✓ **Purely covalent:** The bonding electrons are shared equally between the two bonding atoms.
- ✓ **Polar covalent:** The electrons are shared between the two bonding atoms, but unequally, with the electrons spending more time around the more electronegative atom.
- ✓ **Ionic:** The electrons aren't shared. Instead, the more electronegative atom of the two bonding atoms selfishly grabs the two electrons for itself, giving this more electronegative atom a formally negative charge and leaving the other atom with a formal positive charge. The bond in an ionic bond is an attraction of opposite charges.



You can often determine whether a bond is ionic or covalent by looking at the difference in electronegativity between the two atoms. The general rules are as follows:

- ✓ If the electronegativity difference between the two atoms is 0.0, the bond is purely covalent.
- ✓ If the electronegativity difference is between 0.0 and 2.0, the bond is considered polar covalent.
- ✓ If the electronegativity difference is greater than 2.0, the bond is considered ionic.

Figure 1-2 shows the electronegativity values.

Figure 1-2:
Electronegativity values
for common
atoms.

H 2.1	
Li 1.0	Be 1.5
Na 0.9	Mg 1.2
K 0.8	Ca 1.0

B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
				Br 2.8
				I 2.5

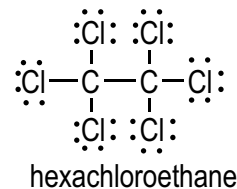
4. You classify the N-H bonds as polar covalent and the N-K bond as ionic.

Therefore, the N-H bonds are classified as polar covalent.

4. Classify the bond in NaF as purely covalent, polar covalent, or ionic.

Solve It

5. Using the following figure, classify the bonds in hexachloroethane as purely covalent, polar covalent, or ionic.



Solve It

Determining Bond Dipoles

Most bonds in organic molecules are of the polar covalent variety. Consequently, although the electrons in a polar covalent bond are shared, on average they spend more time around the more electronegative atom of the two bonding atoms. This unequal sharing of the bonding electrons creates a separation of charge in the bond called a *bond dipole*.

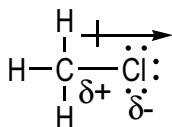


Bond dipoles are used all the time to predict and explain the reactivity of organic molecules, so you need to understand what they mean and how to show them on paper. You represent this separation of charge on paper with a funny-looking arrow called the *dipole vector*. The head of the dipole vector points in the direction of the partially negatively charged atom (the more electronegative atom) and the tail (which looks like a + sign) points toward the partially positive atom of the bond (the less electronegative atom).



- Q. Show the bond dipole of the C-Cl bond in CH_3Cl using the dipole vector.

A.

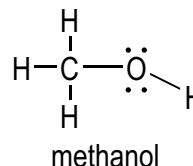


Chlorine is more electronegative than carbon, so in this bond, the bonding electrons spend more time around chlorine than around carbon. Therefore, the chlorine holds a partial negative charge (the symbol δ indicates a partial charge), and the carbon holds a partial positive charge. To draw the dipole vector, the head of the vector points to the atom that has the partial negative charge (the more electronegative atom) — in this case, chlorine — while the tail points to the atom that has a partial positive charge (the less electronegative atom) — in this case, carbon.

6. Show the bond dipoles of the C-O bonds in CO_2 by using the dipole vector. (**Hint:** Draw the Lewis structure of CO_2 first.)

Solve It

7. Using the following figure, show the bond dipole of the C-O bond and the O-H bond in methanol by using the dipole vector.



methanol

Solve It

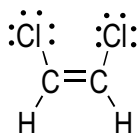
Determining Dipole Moments for Molecules

The sum of all the bond dipoles on a molecule is referred to as the molecule's *dipole moment*. Molecule dipole moments are useful in predicting the solubility of organic molecules. For example, by using dipole moments, you can predict that oil and water won't mix and will be insoluble in each other, whereas water and alcohol will mix. Solubilities are important for practical organic chemistry because it's hard to get a reaction between two molecules that don't dissolve in the same solvent.

To determine the dipole moment of a molecule, follow these steps:

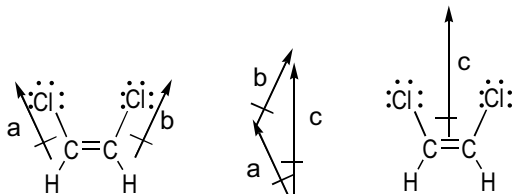
1. Draw the bond dipole vector for each of the bonds in the molecule.

8. Using the following figure, determine the dipole moment of *cis*-1,2-dichloroethene.



cis-1,2-dichloroethene

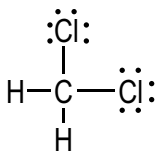
A.



individual bond dipoles vector addition molecular dipole

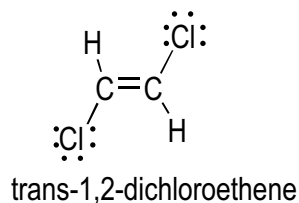
First draw the bond dipoles for each of C-Cl bonds. You can ignore the bond dipoles from the other bonds in the molecule because C-H bonds have such small bond dipoles that you can ignore them because C-C bonds have no bond dipole. After you draw the two C-Cl bond dipoles (labeled *a* and *b*), you add the vectors to give a third vector (labeled *c*). This new vector (*c*) is the molecule's overall dipole moment vector.

8. Determine the dipole moment of dichloromethane, CH_2Cl_2 , shown here. For this problem, you can assume that the molecule is flat as drawn.



Solve It

9. Determine the dipole moment of *trans*-1,2-dichloroethene shown here.



Solve It

Predicting Atom Hybridizations and Geometries

Organic molecules often have atoms stretched out into three-dimensional space. Organic chemists care about how a molecule arranges itself in 3-D space because the geometry of a molecule often influences the molecule's physical properties (such as melting point, boiling point, and so on) and its reactivity. The 3-D shape of molecules also plays a large role in a molecule's biological activity, which is important if you want to make a drug, for example. To predict the geometry around an atom, you first need to determine the hybridization of that atom.

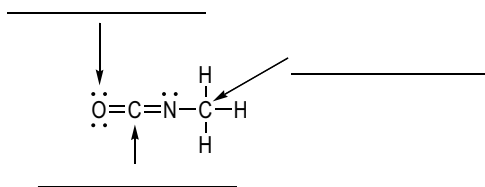


You can often predict the *hybridization* of an atom simply by counting the number of atoms to which that atom is bonded (plus the number of lone pairs on that atom). Table 1-1 breaks down this information for you.

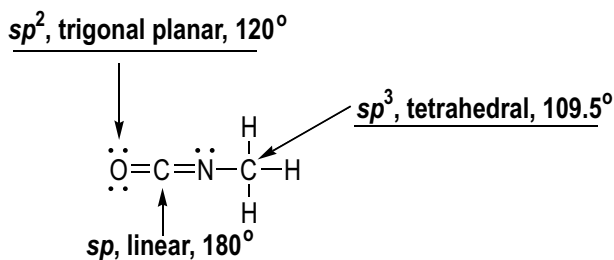
Table 1-1 The Hybridization of an Atom			
Number of Attached Atoms Plus Lone Pairs	Hybridization	Geometry	Approximate Bond Angle
2	sp	Linear	180°
3	sp^2	Trigonal planar	120°
4	sp^3	Tetrahedral	109.5°



- Q. Predict the hybridizations, geometries, and bond angles for each of the atoms where indicated in the shown molecule.

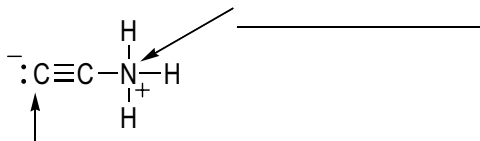


A.



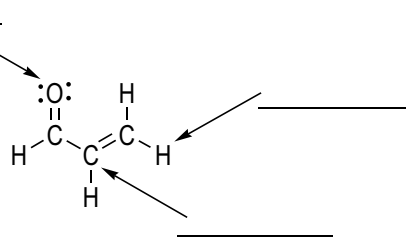
The oxygen has three attachments from the adjacent carbon plus the two lone pairs, making this atom sp^2 hybridized. Atoms that are sp^2 -hybridized have a trigonal planar geometry and bond angles of 120° separating the three attachments. **Note:** Don't take the oxygen's double bond into account; rather, simply count the number of attached atoms plus lone pairs. The carbon has two attachments and so is sp hybridized with a linear geometry and 180° bond angles between the attachments. And the right-most carbon, with four attachments, is sp^3 hybridized with a tetrahedral arrangement between the four attachments and bond angles of 109.5° .

- 10.** Predict the hybridizations, geometries, and bond angles for each of the atoms where indicated in the shown molecule.



Solve It

- 11.** Predict the hybridizations, geometries, and bond angles for each of the atoms where indicated in the shown molecule.



Solve It

Making Orbital Diagrams

An *orbital diagram* expands on a Lewis structure (check out the “Constructing Lewis Structures” section earlier in this chapter) by explicitly showing which orbitals on atoms overlap to form the bonds in a molecule. Organic chemists use such orbital diagrams extensively to explain the reactivity of certain bonds in a molecule, and the diagrams also do a better job than Lewis structures of showing exactly where electrons are distributed in a molecule. Follow these three steps to draw an orbital diagram:

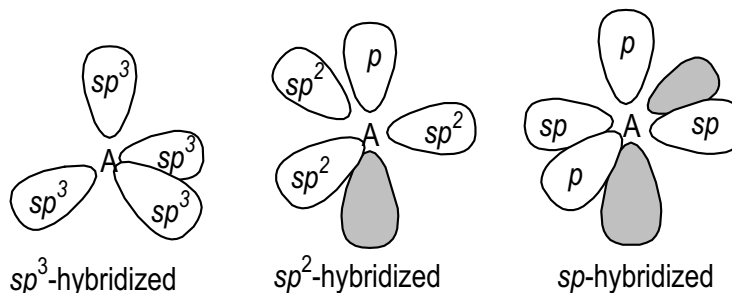
- 1. Determine the hybridization for each atom in the molecule.**

Check out the preceding section for help on this step.

- 2. Draw all the valence orbitals for each atom.**

sp^3 -hybridized atoms have four valence sp^3 orbitals; sp^2 -hybridized atoms have three sp^2 -hybridized orbitals and one p orbital; and sp -hybridized atoms have two

sp -hybridized orbitals and two p orbitals. You may find the following templates helpful for constructing your orbital diagrams (where A represents the hybridized atom):



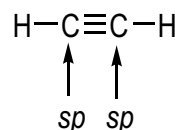
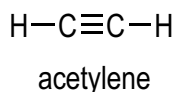
3. Determine which orbitals overlap to form bonds.



Single bonds are always *sigma bonds* — bonds that form from the overlapping of orbitals between the two nuclei of the bonding atoms. A double bond, on the other hand, consists of one sigma bond and one pi bond. A *pi bond* is formed from the side-by-side overlapping of two p orbitals above and below the nuclei of the two bonding atoms. A triple bond consists of two pi bonds and one sigma bond.

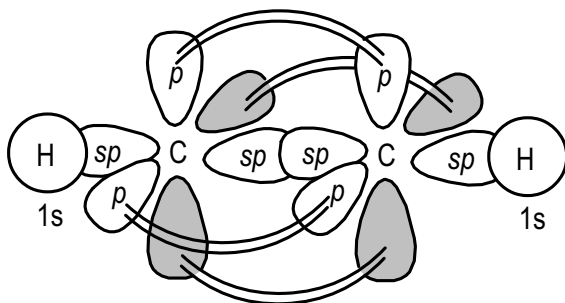


- Q. Referring to the following figure, draw the orbital diagram of acetylene.

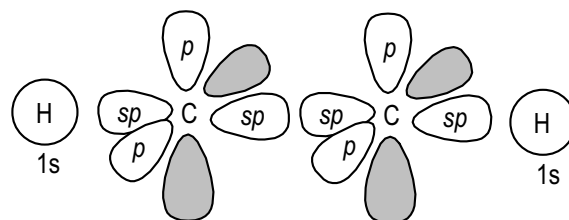


Next, draw the valence orbitals as shown here. Hydrogen has only the $1s$ orbital, and you can use the earlier template for sp -hybridized atoms for each of the carbons.

A.



This problem is daunting, but you can tackle it step by step. The first thing to do is determine the hybridizations for all the atoms. The two carbons are sp hybridized. The hydrogens, having only one electron, remain unhybridized (hydrogen is the only atom that doesn't rehybridize in organic molecules):



Next, you need to figure out which orbitals overlap to give rise to the bonds in acetylene. The C-H bonds form from overlap of the hydrogen $1s$ orbitals with the sp orbitals on carbon. Triple bonds consist of two pi bonds and one sigma bond. The one sigma bond comes from overlap of the two carbon sp orbitals. The two pi bonds come from overlap of the two p orbitals on each carbon, giving you the final answer shown earlier.

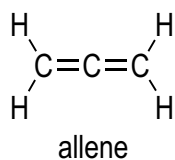
12. Draw the orbital diagram for methane, CH_4 .

Solve It

13. Draw the orbital diagram of formaldehyde, H_2CO . (*Hint:* Draw the full Lewis structure first.)

Solve It

14. Use the following figure to draw the orbital diagram for allene (very challenging).

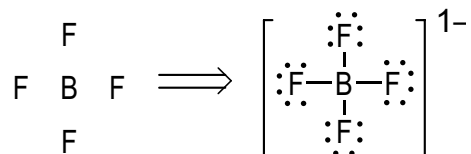


Solve It

Answer Key

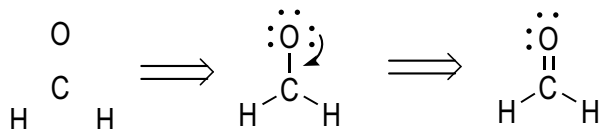
The following are the answers to the practice questions presented in this chapter.

1



Boron is the central atom because it's less electronegative than fluorine (and in any case, halogens such as F almost never form more than one single bond). Boron has three valence electrons, fluorine has seven, and the charge on the molecule is -1 , so the total number of valence electrons in this molecule is $3 + 7(4) + 1 = 32$. Adding single bonds from boron to each of the four fluorines (for a total of eight electrons, two per bond) and adding the remaining 24 electrons to the fluorines as lone pairs gives the Lewis structure shown. Each atom is happy because it has a full octet of electrons, so there's no need to make multiple bonds.

2

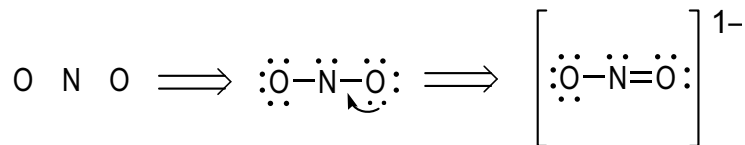


Carbon is the central atom because it's less electronegative than oxygen. A hydrogen can never be the central atom because hydrogens don't form more than one bond.

Hydrogen has one valence electron, carbon has four valence electrons, and oxygen has six valence electrons, so the total number of valence electrons is $2(1) + 4 + 6 = 12$ valence electrons.

Adding a single bond from carbon to each of the two hydrogens and a single bond to the oxygen and peppering the remaining lone pairs onto the oxygen gives you the structure in the middle. Although oxygen is happy because it has a full octet of electrons, carbon isn't faring as well because it's two electrons short of its octet. Therefore, you push down one of the lone pairs from oxygen to form a double bond from oxygen to carbon. After that move is complete, all the atoms are happy because each atom has a full octet of electrons. **Note:** You can't give any lone pairs to hydrogen because with one bond already, hydrogen has satisfied its valence shell with two electrons (recall that the first shell holds only two electrons, and then it's eight in the second shell).

3



Nitrogen is the central atom in NO_2^- because nitrogen is less electronegative than oxygen.

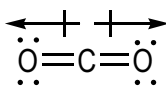
Nitrogen has five valence electrons, oxygen has six, and the charge on the molecule is -1 , so the molecule has $5 + 2(6) + 1 = 18$ valence electrons.

Making single bonds from N to both oxygens (for a total of four electrons, two per bond) leaves 14 electrons. Adding these electrons onto the oxygens until both oxygens have completed their octet still leaves two electrons left over. Place these two electrons on the central nitrogen. Examining this structure reveals that both oxygens have a complete octet, but nitrogen is still shy two electrons. So a lone pair on one of the oxygens is pushed onto the nitrogen to form a nitrogen-oxygen double bond. Last, add the charge to complete the final structure.

4 Ionic. Fluorine has an electronegativity of 4.0, and sodium has an electronegativity of 0.9, so the electronegativity difference is 3.1, making this bond an ionic bond.

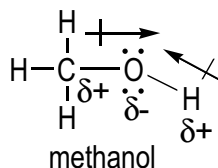
5 The C-C bonds are purely covalent; the C-Cl bonds are polar covalent. The C-C bond in hexachloroethane is purely covalent because there's 0.0 electronegativity difference between the two atoms (because they're the same). The C-Cl bonds are all polar covalent because the electronegativity difference between chlorine (3.0) and carbon (2.5) is 0.5.

6



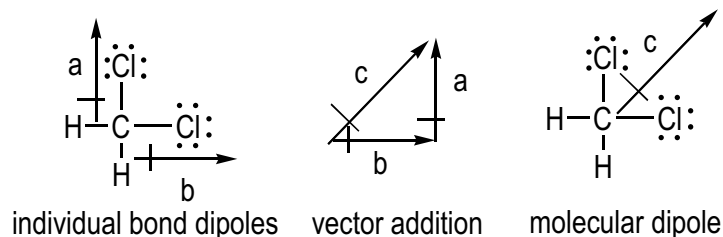
Oxygen is more electronegative than carbon, so oxygen is partially negatively charged and carbon is partially positively charged. Therefore, the bond dipole vectors point toward the oxygens.

7



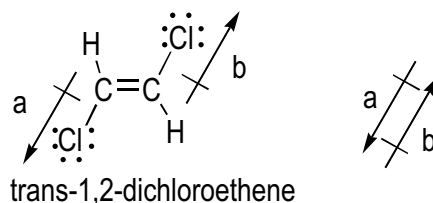
In methanol, the oxygen is more electronegative than either carbon or hydrogen. Therefore, the oxygen is partially negative charged and the carbon and hydrogen are partially positively charged. As a result, both bond dipole vectors point toward the oxygen.

8



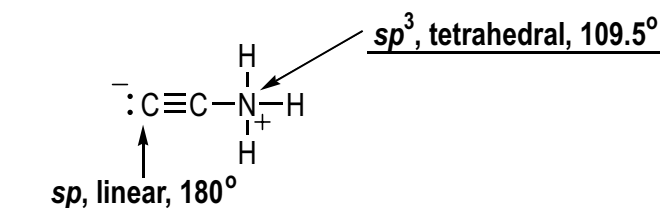
The two C-Cl bonds have dipole vectors pointing toward the chlorine (because chlorine is more electronegative than carbon). Summing these two vectors gives the dipole moment vector (vector c) for the molecule, which points between the two carbon-chlorine bonds.

9



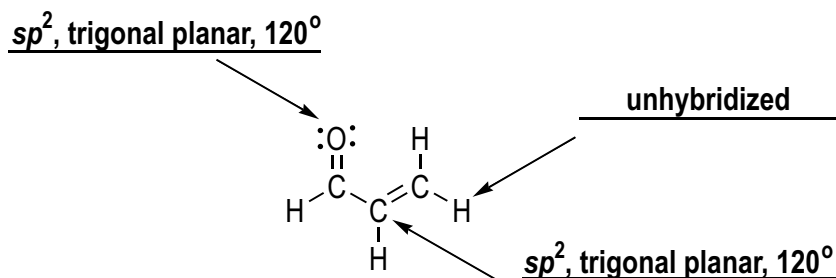
Both C-Cl bond vectors point toward the chlorine because chlorine is more electronegative than carbon. However, summing up the two vectors gives a net dipole moment of 0.0 — the two individual bond dipole vectors cancel each other out. Therefore, although the individual C-Cl bonds do have bond dipoles, the molecule has no net dipole moment.

10



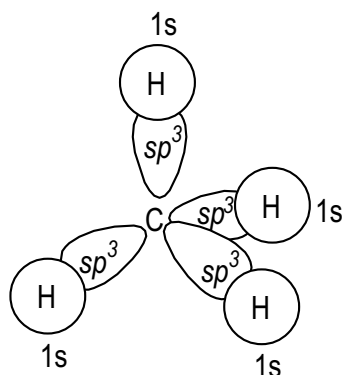
The carbon has two attachments (one being the lone pair), making this atom sp hybridized. The nitrogen has four attachments, making this atom sp^3 hybridized. Sp -hybridized atoms have a linear geometry with a 180° bond angle between the two attachments. Sp^3 -hybridized atoms have a tetrahedral geometry with a 109.5° bond angle between the four attachments.

11



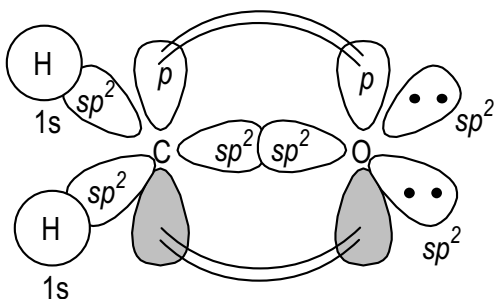
Both the carbon and oxygen in this molecule have three attachments, so both atoms are sp^2 hybridized. Sp^2 -hybridized atoms are trigonal planar and have bond angles of 120° between the three attachments. Hydrogen is the one atom type that remains unhybridized.

12

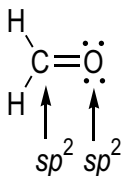


The carbon has four attachments, so this atom is sp^3 -hybridized, with four sp^3 orbitals to bond with the four hydrogen 1s orbitals.

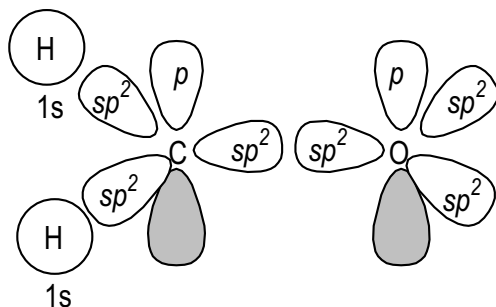
13



First drawing the Lewis structure of formaldehyde and then assigning the hybridizations shows that both the carbon and the oxygen are sp^2 hybridized.

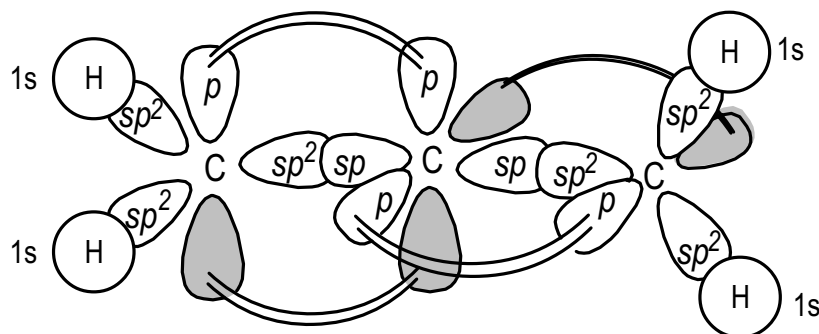


Next, drawing out all the valence orbitals for the atoms gives the following (using the templates here may help to speed up this process).

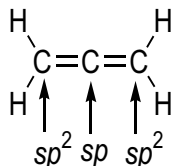


Finally, show the orbital overlap. The C-H bonds are formed from overlap of two carbon sp^2 orbitals with the two hydrogen $1s$ orbitals. This leaves one carbon sp^2 orbital and one carbon p orbital for forming the double bond. The carbon sp^2 orbital and one of the oxygen sp^2 orbitals overlap to form a sigma bond. The pi bond is formed from overlap of the carbon p orbital and the oxygen p orbital. Last, place the two oxygen lone pairs into the remaining unoccupied sp^2 hybridized orbitals on oxygen as shown earlier.

14



This problem is admittedly pretty difficult. The first step is assigning the hybridizations of each of the atoms. The outer carbons are sp^2 hybridized, and the inner carbon is sp hybridized.



Next, show all the valence orbitals on each of the atoms. The tricky part is lining up the orbitals from the middle carbon to the outer carbons so the orbitals can overlap to form one double bond each. Each double bond consists of a sigma bond and a pi bond. Therefore, each of the carbon-carbon sigma bonds must consist of an sp^2 - sp orbital overlap. Pi bonds are formed from the p orbital overlaps. Therefore, you have to line up the p orbitals so it's possible for the orbitals to overlap with the central carbon.

Finally, show the orbital overlap. First, the C-H bonds are formed from the overlap between the outer carbon sp^2 orbitals and the hydrogen $1s$ orbitals. The sigma bonds in the two double bonds are formed in both cases from the overlap between the central carbon sp orbital and the two outer carbon sp^2 orbitals. The pi bonds are then formed from the overlap of the two p orbitals on the central carbon and the lone p orbitals on the outer carbons.

An interesting outcome of this orbital diagram is that the orbital diagram predicts that the two hydrogens on the left will be coming into and out of the plane of the paper, while the two hydrogens on the right will be going up and down in the plane of the paper. As a matter of fact, this turns out to be the geometry found experimentally. Chalk one up to orbital diagrams!