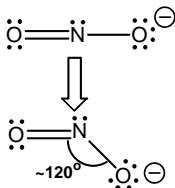


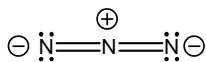
# Chapter 6

## Molecular Structure

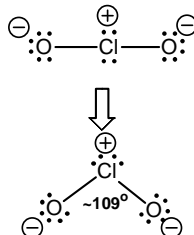
1. Draw the Lewis structure of each of the following ions, showing all nonzero formal charges. Indicate whether each ion is linear or bent. If the ion is bent, what is the bond angle?



A lone pair on the N results in three electron groups and a bent structure with  $\sim 120^\circ$  bond angle.

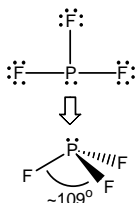


No lone pair on the central N result in two electron groups and a linear structure with a  $180^\circ$  bond angle.

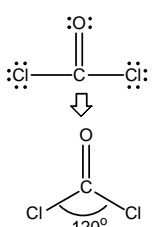


Two bonding and two lone pairs results in four electron groups and a  $\sim 109^\circ$  bond angle

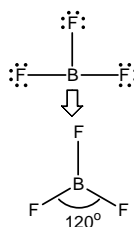
3. Draw Lewis structures for the following molecules. Indicate nonzero formal charges and whether each is trigonal planar or trigonal pyramidal.



One lone pair on P results in four electron groups and trigonal pyramidal structure with  $\sim 109^\circ$  bond angles.



No lone pairs on central atom, so it has only three electron groups. The molecules are trigonal planar with  $120^\circ$  bond angles.

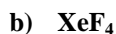
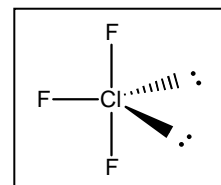


Note that  $\text{BF}_3$  does not have a double bond because a double bond to a halogen puts positive formal charge on the halogen. Instead, the boron is electron deficient having only six electrons.

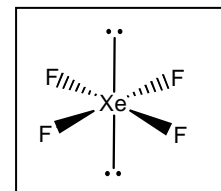
5. Describe the shapes of the following:



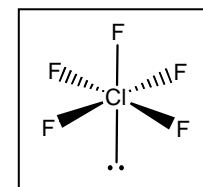
$\text{SP} = \frac{1}{2}(32-28) = 2$  shared pair, which is not sufficient for three Cl-F bonds. Cl uses an expanded valence shell, so use Eq. 6.1 to get lone pairs. Cl is in Group 7 and is in the +3 oxidation state, so  $\text{LP} = \frac{1}{2}(7-3) = 2$ . There are three bonds and two lone pairs, so the five electron regions are situated in a trigonal bipyramid arrangement about Cl. The lone pairs go into the equatorial positions, so  $\text{ClF}_3$  is T-shaped.



$\text{SP} = \frac{1}{2}(40-36) = 2$  shared pair, which is insufficient for four Xe-F bonds. Xe is in Group 8 and has a +4 oxidation state, so Eq 6.1 yields  $\text{LP} = \frac{1}{2}(8-4) = 2$  lone pairs. Six electron regions assume octahedral geometry with the lone pairs opposite one another.  $\text{XeF}_4$  is square planar.



$\text{SP} = \frac{1}{2}(48-42) = 3$  shared pair, which is insufficient for five Cl-F bonds. Cl is in Group 7 and has a +5 oxidation state, so Eq 6.1 yields  $\text{LP} = \frac{1}{2}(7-5) = 1$  lone pair. Six electron regions assume octahedral geometry with the lone pair in any position.  $\text{ClF}_5$  is a square pyramid.



7. What is the hybridization on the central atom in each of the ions in Exercise 1?

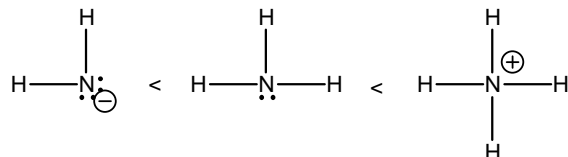
	Central atom electron regions	hybridization
a) $\text{NO}_2^{1-}$	2 bonding + 1 lone pairs = 3	$\text{sp}^2$
b) $\text{N}_3^{1-}$	2 bonding + 0 lone pairs = 2	$\text{sp}$
c) $\text{ClO}_2^{1-}$	2 bonding + 2 lone pairs = 4	$\text{sp}^3$

# Molecular Structure

## 9. What is the hybridization on the central atom in each of the molecules in Exercise 3?

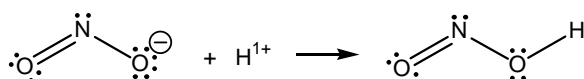
	Central atom electron regions	hybridization
a) $\text{PF}_3$	3 bonding + 1 lone pairs = 4	$\text{sp}^3$
b) $\text{COCl}_2$	3 bonding + 0 lone pairs = 3	$\text{sp}^2$
c) $\text{BF}_3$	3 bonding + 0 lone pairs = 3	$\text{sp}^2$

## 11. Rank the following in order of increasing H-N-H bond angles: $\text{NH}_2^-$ , $\text{NH}_3$ , and $\text{NH}_4^+$ .



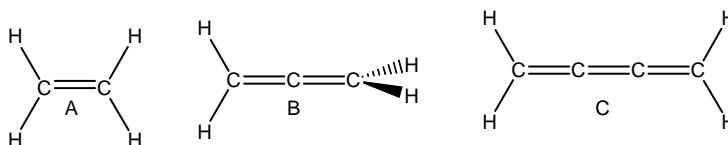
two lone pairs on N < one lone pair on N < no lone pairs on N

## 13. The nitrite ion ( $\text{NO}_2^-$ ) can add an $\text{H}^{1+}$ ion (proton) to become nitrous acid. Based on the formal charges in the Lewis structure of the anion (Exercise 1a), draw the Lewis structure of nitrous acid, $\text{HNO}_2$ .



The positively charged proton attacks the site of negative formal charge. The H is written first in the formula because  $\text{HNO}_2$  is an acid. We will discuss acids in detail in Chapter 11.

## 15. Explain why molecules A and C are planar while molecule B is not. Hint: which p orbitals are used to make each of the $\pi$ bonds?



The p orbitals that combine to form a  $\pi$  bond must both be either  $p_x$  or they must both be  $p_y$  orbitals if the bonding axis is the z axis.

- If the two p orbitals forming the  $\pi$  bond are the  $p_y$  orbitals, then the two sets of  $\text{sp}^2$  orbitals must use the  $p_x$  and  $p_z$  orbitals and lie in the xz plane. Since the two sets of  $\text{sp}^2$  orbitals are in the same plane, molecule A is planar.
- The central carbon atom must use different p orbitals to form two different  $\pi$  bonds. We arbitrarily assume that the carbon on the left uses its  $p_y$  orbital to form the  $\pi$  bond. In this case, the  $\text{sp}^2$  orbitals on the carbon on the left lie in the xz plane. If the central carbon uses its  $p_y$  orbital to  $\pi$  bond with the carbon on the left, then it must use its  $p_x$  orbital to  $\pi$  bond with the carbon on the right. The carbon on the right must then use its  $p_x$  orbital to  $\pi$  bond to the central carbon. Since the  $p_x$  is used to form a  $\pi$  bond, the  $\text{sp}^2$  orbitals on the carbon on the right must lie in the yz plane and are, therefore, perpendicular to those on the carbon to the left.
- If the  $\pi$  bond to the left most carbon results from the  $p_y$  orbitals then the central  $\pi$  bond must use the  $p_x$  orbitals and the one on the right must use the  $p_y$  orbitals. Since both terminal carbon atoms use the  $p_y$  orbitals to construct their  $\pi$  bonds, their  $\text{sp}^2$  hybrid orbitals must both be constructed from the  $p_x$  and  $p_z$  orbitals and lie in the xz plane. Thus, molecule C is planar.

## 17. Aspartame is the active ingredient in the sweetener Nutrasweet. What are the approximate bond angles $\alpha$ , $\beta$ , $\gamma$ , $\delta$ and $\epsilon$ in the aspartame structure?

There must be one lone pair on the N at  $\alpha$  and two on the O at  $\epsilon$

$$\alpha = \sim 109^\circ \quad \beta = \sim 109^\circ \quad \gamma = \sim 120^\circ \quad \delta = \sim 120^\circ \quad \epsilon = \sim 109^\circ$$

**19. Consider the structure of the explosive TNT and explain the following:**

- a) **Bond v is longer than bond w.**

Bond v is a C-C single bond while the bond order of w is 1.5 (resonance in benzene ring).

- b) **Bonds w and x are of equal length.**

The bonds in the benzene ring have identical bond orders of 1.5.

- c) **Bonds y and z are of equal length**

The two N-O bonds have identical bond lengths because they each have bond orders of 1.5 due to two identical resonance forms.

**21. How many  $\sigma$  bonds and how many  $\pi$  bonds are in each of the structures shown below? Note that lone pairs have been omitted for simplicity.**

Each bond contains one and only one  $\sigma$  bond. Multiple bonds contain one  $\sigma$  and 1 or 2  $\pi$  bonds.

	$C_3O_2$	HCN	$C_4H_4ONCl$
$\sigma$ bonds	4	2	10
$\pi$ bonds	4	2	3

**23. Indicate whether the following orbital interactions between s, p and d orbitals would result in  $\sigma$  bonds or  $\pi$  bonds.**

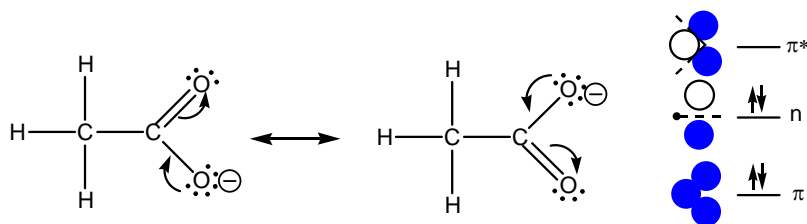
$s + p = \sigma$

$p + p = \sigma$

$p + d = \pi$

**25. Draw two resonance structures for the acetate ion,  $CH_3COO^{1-}$ . Draw an mo diagram for the  $\pi$  system.**

$ER = 4(8) + 3(2) = 38$ ;  $VE = 2(4) + 2(6) + 3(1) + 1 = 24$ ;  $SP = \frac{1}{2}(38 - 24) = 7$



The  $\pi$  system extends over the two oxygen atoms and the carbon to which they are bound. The MO diagram is analogous to that of  $SO_2$ . There are two pairs of electrons in the  $\pi$  system. One pair enters the lowest energy MO (delocalized  $\pi$  bond) and one pair enters the nonbonding orbital, which is a delocalized lone pair.

**27. How many  $\sigma$  bonds and  $\pi$  bonds are found in a single bond, a double bond, and a triple bond?**

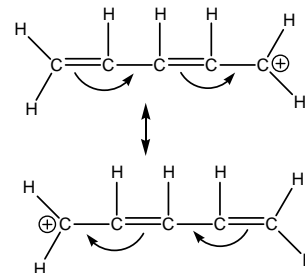
A single bond consists of one  $\sigma$  and no  $\pi$  bonds. A double bond is one  $\sigma$  and one  $\pi$  bond. A triple bond is the combination of one  $\sigma$  and two  $\pi$  bonds.

**29. Indicate the hybridization of a central atom with the following electron groups:**

- |  |        |
|--|--------|
| a) two $\sigma$ bonds, one $\pi$ bond and one lone pair    | $sp^2$ |
| b) three $\sigma$ bonds, no $\pi$ bonds, and one lone pair | $sp^3$ |
| c) two $\sigma$ bonds, two $\pi$ bonds, and no lone pairs  | $sp$   |
| d) two $\sigma$ bonds, no $\pi$ bonds, and two lone pairs  | $sp^3$ |

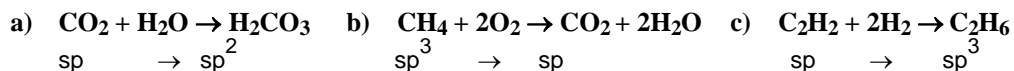
**31. Indicate whether the  $\pi$  bonds in the following are localized or delocalized. If the bonds are delocalized, draw the other resonance form(s).**

- a) Multiple bonds cannot be drawn to F, so the  $\pi$  bond in ONF is localized in the NO bond.
- b) The  $\pi$  bond in  $SO_2$  can reside in either S-O bond, so it is delocalized over both.
- c) As shown in the figure, systems with alternating single and double bonds are delocalized.

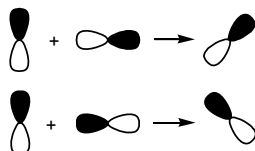


# Molecular Structure

33. What change in hybridization (if any) occurs on the carbon in each of the following reactions?

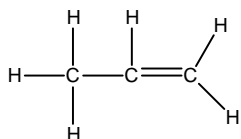


35. Draw the result of mixing a  $p_x$  and a  $p_y$  orbital.

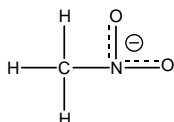


Mixing two p orbitals rotates them by  $45^\circ$ .

37. Add multiple bonds, lone pairs, and hydrogen atoms to the following:

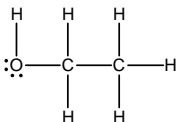


The bond lengths indicate one single and one double bond. Carbon must have four bonds in order to have no formal charge, so C-H bonds are added to bring the number of  $\sigma$  and  $\pi$  bonds to four.

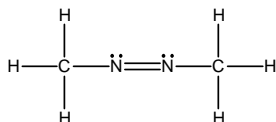


$1.5 \text{ \AA}$  indicates a C-N single bond while the  $1.3 \text{ \AA}$  bond length is intermediate between the N-O single and double bonds, so the bonds have bond orders of 1.5 (indicated by dotted lines). The carbon requires three C-H bonds in order to have zero formal charge.

39. Add multiple bonds, lone pairs, and hydrogen atoms to the following:



The C-C and C-O bond lengths are those of single bonds. To maintain zero formal charge, the oxygen has two bonds and each carbon has four. Lone pairs are added to the oxygen to give it an octet.



The bond lengths indicate that the C-N bonds are each single bonds, but the N-N bond is a double bond. Nitrogen has no formal charge when it is involved in three bonds, so there are no N-H bonds. Lone pairs are required on the nitrogens to obey the octet rule. C-H bonds are added to give each carbon atom four bonds (no formal charge).

41. An amide is a compound that has a nitrogen next to a  $\text{C}=\text{O}$  group.

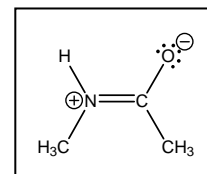
a) What are the predicted values of  $\alpha$  and  $\beta$  and what is the predicted hybridization on the nitrogen atom?

$\alpha \sim 109^\circ$  (Four regions around N, so it is  $sp^3$ )                       $\beta \sim 120^\circ$  (Three electron regions around C, so it is  $sp^2$ )

b) The experimentally C-N-C bond angle is  $120^\circ$  and the amide skeleton is planar. What is the hybridization on the nitrogen atom in this structure?

$120^\circ$  implies three electron groups and  $sp^2$  hybridization.

c) Draw another Lewis structure that is important in the bonding description as determined from the structural data. Indicate all nonzero formal charge in the structure.



**43. Classify each of the following  $\pi$  MO's as bonding, nonbonding, or antibonding.**

- a) one nonbonding interaction makes the MO a nonbonding MO
- b) two antibonding plus one bonding interaction makes this MO antibonding
- c) two nonbonding interactions makes this MO nonbonding
- d) two bonding and one antibonding interaction makes this MO bonding.

**45. Which of the above molecules are not predicted to form?**

Bonds with zero bond order are predicted not to form. Thus, the Be-Be and Ne-Ne bonds do not form, so  $\text{Be}_2$  and  $\text{Ne}_2$  would not form.

**47. Which has the strongest bond.  $\text{O}_2^{1-}$ ,  $\text{O}_2$ , or  $\text{O}_2^{1+}$ ?**

See Figure 6.23 for the MO diagram of  $\text{O}_2$ . An additional electron in  $\text{O}_2$  would enter a  $\pi^*(2p)$ . Since the added electron is antibonding, the O-O bond in the  $\text{O}_2^{1-}$  ion would be weaker than the O-O bond in  $\text{O}_2$ . A removed electron would come from a  $\pi^*(2p)$  orbital. Since the removed electron is antibonding,  $\text{O}_2^{1+}$  would have a stronger bond than  $\text{O}_2$ . Thus,  $\text{O}_2^{1+}$  has the strongest bond.

**49. Assume that the MO diagram for NO is the same as for  $\text{O}_2$ . Is NO more likely to gain or to lose an electron?**

NO has  $5 + 6 = 11$  valence electrons. Placing 11 electrons into the  $\text{O}_2$  diagram puts two electrons into the  $\sigma(2p)$ , four electrons into the  $\pi(2p)$ , and one in the  $\pi^*(2p)$  orbital. The NO bond order is then  $\frac{1}{2}(6-1) = 2.5$ . The additional electron in  $\text{NO}^{1-}$  would also go into the  $\pi^*(2p)$  orbital, so it is less stable than NO with a bond order of  $\frac{1}{2}(6-2) = 2$ . The highest energy electron in NO is antibonding, so removing it makes  $\text{NO}^{1+}$  more stable than NO ( $\text{BO} = \frac{1}{2}(6-0) = 3$ ), so NO is more likely to lose an electron.