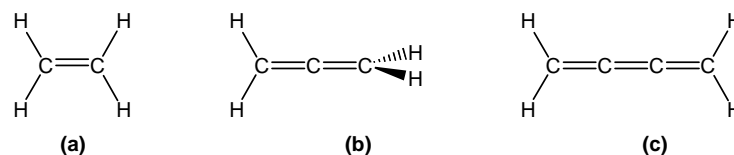


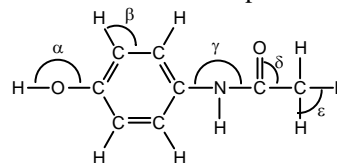
Chapter 6 Exercises

- 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?
 - NO_2^{1-}
 - N_3^{1-}
 - ClO_2^{1-}
- Draw the Lewis structure of each of the following molecules, showing all nonzero formal charges. Indicate whether each molecule is linear or bent. If the molecule is bent, what is the bond angle?
 - N_2O
 - HCN
 - OF_2
- Draw Lewis structures for the following molecules. Indicate nonzero formal charges and whether each is trigonal planar or trigonal pyramidal.
 - PF_3
 - COCl_2
 - BF_3
- Draw Lewis structures for the following ions. Indicate nonzero formal charge and whether each is planar or trigonal pyramidal.
 - ClO_3^{1-}
 - CO_3^{2-}
 - PO_3^{3-}
- Describe the shapes of the following:
 - ClF_3
 - XeF_4
 - ClF_5
- The Lewis structures of the sulfate and phosphate ions that obey the octet rule contain large, positive formal charges on the central atoms and an excess of negative formal charges on the oxygen atoms. Assume that S and P use expanded valence shells and draw Lewis structures for the ions that contain no formal charge on the central atoms.
- What is the hybridization on the central atoms in Exercise 1?
- What is the hybridization on the central atoms in Exercise 2?
- What is the hybridization on the central atoms in Exercise 3?
- What is the hybridization on the central atoms in Exercise 4?
- We use the approximate bond angles of 120° and 109° around central atoms with three and four electron groups, respectively. However, lone pairs affect bond angles differently than do bonding pairs. With this in mind, rank the following species in order of increasing H-N-H bond angles: NH_2^{1-} , NH_3 , and NH_4^{1+} .

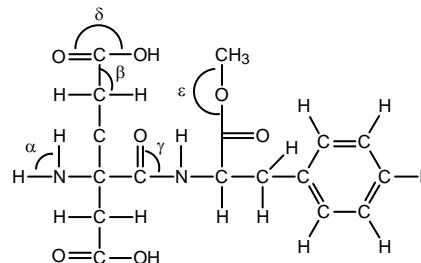
- List the following in order of increasing bond angles: SO_2 , CO_2 and H_2O .
- The nitrite ion (NO_2^{1-}) can add an H^{1+} ion (proton) to become nitrous acid. Based on the formal charges in the Lewis structure of the anion (Exercise 1a), draw the Lewis structure of nitrous acid, HNO_2 .
- The carbonate ion (CO_3^{2-}) can add two H^{1+} ions to become carbonic acid. Based on the formal charges in the Lewis structure of the anion (Exercise 4b), draw the Lewis structure of carbonic acid, H_2CO_3 .
- Explain why molecules A and C are planar while molecule B is not.



- Acetaminophen is an analgesic (pain killer) that is often purchased under the name Tylenol[®]. What are the approximate bond angles labeled α , β , γ , δ and ϵ in the acetaminophen structure shown below?

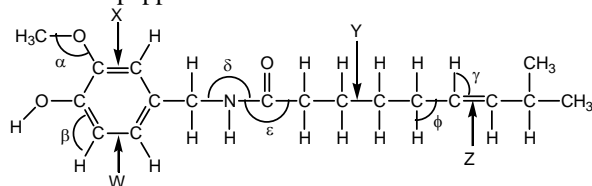


- Aspartame is the active ingredient in the sweetener NutraSweet[®]. What are the approximate bond angles α , β , γ , δ and ϵ in the aspartame structure shown below?

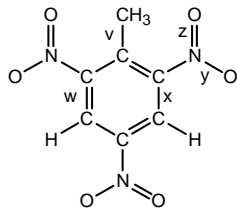


Chapter 6 Exercises

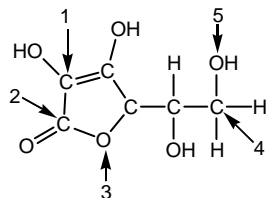
18. Consider the structure of capsaicin, the molecule responsible for the "heat" of chili peppers that is shown below.



- a) What are the approximate bond angles labeled α , β , δ , ϵ , ϕ , and γ ?
 b) Explain the following statements.
 i) Bonds W and X are the same length.
 ii) Bond Z is shorter than bond X .
 iii) Bond Y is longer than bond W .
19. Consider the structure of the explosive TNT shown below to explain the following:

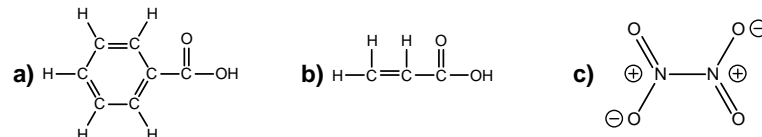


- a) Bond v is longer than bond w .
 b) Bonds w and x are of equal length.
 c) Bonds y and z are of equal length.
20. What are the hybridizations of the numbered atoms in the following structure of vitamin C?

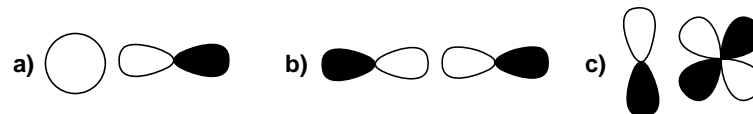


21. How many σ bonds and how many π bonds are in each of the structures shown below? Note that lone pairs have been omitted for simplicity.
- a) $O=C=C=C=O$
 b) $H-C\equiv N$
 c)

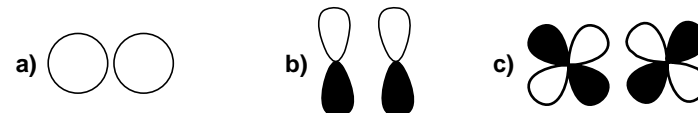
22. What are the numbers of σ and π bonds in each of the following? Note that lone pairs have been omitted for simplicity.



23. Indicate whether the following orbital interactions between s, p and d orbitals would result in σ bonds or in π bonds.



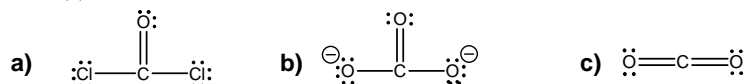
24. Indicate whether the following orbital interactions between p and d orbitals would result in σ bonds or in π bonds.



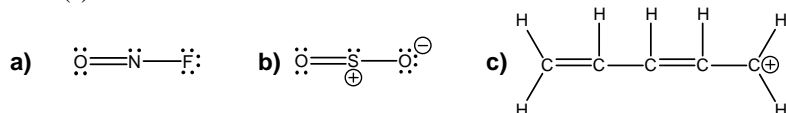
25. Draw two resonance structures for the acetate ion (CH_3COO^{1-}). Draw an MO diagram for the π system.
26. What is meant by a delocalized π system? Give an example of a molecule with a delocalized π bond and one with a localized π bond.
27. How many σ bonds and π bonds are found in a single bond, a double bond, and a triple bond?
28. How is the number of π bonds to a central atom related to its hybridization?
29. Indicate the hybridization of a central atom with the following electron groups:
- a) two σ bonds, one π bond and one lone pair
 b) three σ bonds, no π bonds, and one lone pair
 c) two σ bonds, two π bonds, and no lone pairs
 d) two σ bonds, no π bonds, and two lone pairs

Chapter 6 Exercises

30. Indicate whether the π bonds in the following are localized or delocalized. If the bonds are delocalized, draw the other resonance form(s).

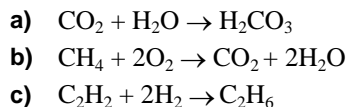


31. Indicate whether the π bonds in the following are localized or delocalized. If the bonds are delocalized, draw the other resonance form(s).

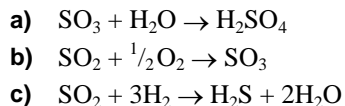


32. All of the elements of the second period form fluorides. What is the hybridization on the central atom in each of the following: BeF_2 , BF_3 , CF_4 , NF_3 , and OF_2 ? Arrange the fluorides in order of increasing bond angles. Hint: recall that lone pairs affect bond angles differently than bonding pairs.

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



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



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

36. Use circles to represent the contributions of the AOs to represent the MOs of the following bonds:

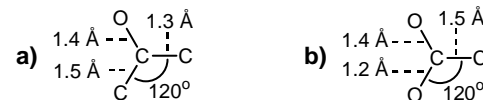


Instructions for 37 - 40 The relative positions of the atoms in a molecule can be obtained by a method known as x-ray diffraction. Lone pairs are not observed and hydrogen atoms are so small that their positions are often unknown, but we can construct the Lewis structure of the molecule, including placement of the lone pairs and hydrogen atoms from the bond lengths, the bond angles, and a knowledge of the relationships between bonding and structure given in Chapters 5 and 6. Assume that all atoms in Exercises 37-40 obey the octet rule and have minimum formal charge to add hydrogen atoms, lone pairs, and/or multiple bonds as required to complete each skeletal structure. Draw all resonance forms in cases where more than one resonance form is important. Refer to the table of bond lengths on the back cover to determine bond orders, Table 5.4 (page 94) to determine the number of bonds to an atom with zero formal charge, and the bond angles to determine hybridizations. Carbon has zero formal charge in all cases.

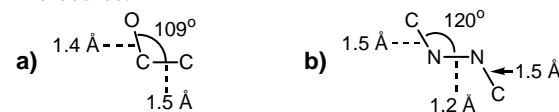
37. Add multiple bonds, lone pairs, and hydrogen atoms to the following molecules:



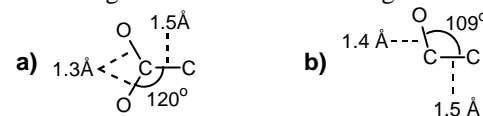
38. Add multiple bonds, lone pairs, and hydrogen atoms to the following molecules:



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

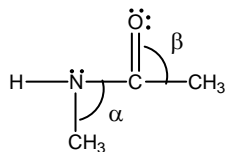


40. Add multiple bonds, lone pairs, and hydrogen atoms to each of the following *anions* that have -1 charges:

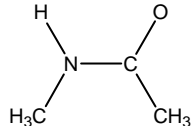


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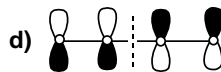
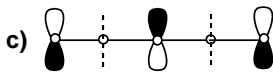
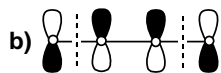
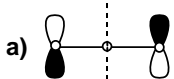
41. An *amide* is a compound that has a nitrogen next to a C=O group.
- a) Consider the Lewis structure of the amide $\text{CH}_3\text{NHCOCH}_3$ that contains no formal charge and is shown below. What are predicted values for angles α and β and what is the hybridization on the N atom?



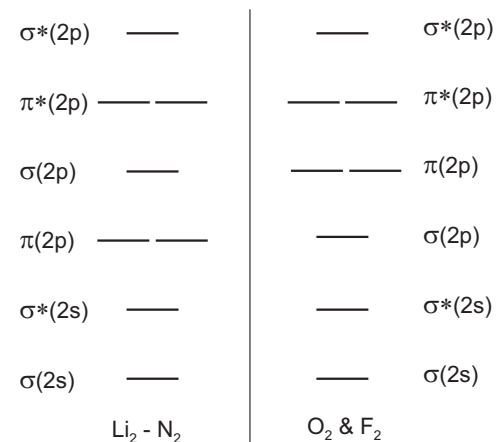
- b) The C-N-C bond angle is actually $\sim 120^\circ$ and the structure shown below is planar (except for the hydrogen atoms in the CH_3 groups). What is the hybridization of the N atom?



- c) Draw another Lewis structure that is important in the bonding description as determined from the structural information given in Part b. Indicate all nonzero formal charge in the structure. Are the π electrons localized or delocalized?
42. Use the rules for MO construction to draw an MO diagram for the pi system of linear A_5 . Label each MO as bonding, nonbonding, or antibonding. See Exercise 43c for one of the five orbitals.
43. Classify each of the following π MOs as bonding, nonbonding, or antibonding.



Use the appropriate MO diagram for the valence orbitals of the diatomic molecules of the elements of the second period shown below for Exercises 44-49. Note that the order of the $\pi(2p)$ and $\sigma(2p)$ orbitals for Li_2 through N_2 is reversed from that for O_2 and F_2 . To answer the questions, determine the number of valence electrons for each diatomic molecule and place them in the diagram.



44. What are the bond orders of the following bonds in the following diatomic molecules?
- | | | | |
|------------------|------------------|-----------------|------------------|
| a) Li_2 | b) Be_2 | c) B_2 | d) C_2 |
| e) N_2 | d) O_2 | e) F_2 | f) Ne_2 |
45. Which of the diatomic molecules in Exercise 44 should not form?
46. Which of the diatomic molecules in Exercise 44 have unpaired electrons?
47. Which has the strongest bond: O_2^{1-} , O_2 , or O_2^{1+} ? What is the bond order of the strongest bond?
48. The peroxide ion is O_2^{2-} . What is the O-O bond order in the peroxide ion?
49. Assume that the energy level order is the same for the bonding between nitrogen and oxygen in NO as it is between two O atoms in O_2 and construct an MO diagram for NO . NO has one unpaired electron. Is it more likely to gain an electron to form NO^{1-} or to lose an electron to form NO^{1+} ?