Assignment 12 – Solutions

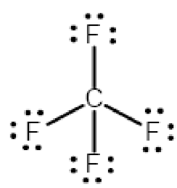
Assigned Problems: Chapter 14: 18, 19, 20, 22, 24, 26, 56, 1, 4, 34 part a
Challenge Problem: Chapter 14: 64

The Localized Electron Model and Hybrid Orbitals

18. For the molecules in Exercise 13.79, all have central atoms with dsp^3 hybridization because all are based on the trigonal bipyramid arrangement of electron pairs. See Exercise 13.79 for the Lewis structures.

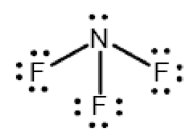
For the molecules in Exercise 13.80, all have central atoms with d^2sp^3 hybridization because all are based on the octahedral arrangement of electron pairs. See Exercise 13.80 for the Lewis structures.

19. a.



tetrahedral sp^3
109.5° nonpolar

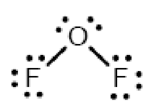
b.



trigonal pyramid sp^3
< 109.5° polar

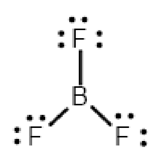
The angles in NF_3 should be slightly less than 109.5° because the lone pair requires more space than the bonding pairs.

c.



V-shaped sp^3
< 109°.5 polar

d.

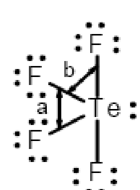


trigonal planar sp^2
120° nonpolar

e.

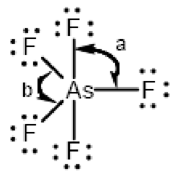
linear sp
180° nonpolar

f.



see-saw dsp^3
a) ≈120°, b) ≈90° polar

g.



trigonal bipyramid dsp^3

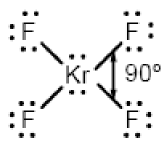
a) 90°, b) 120° nonpolar

h.

linear dsp^3

180° nonpolar

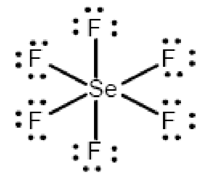
i.



square planar d^2sp^3

90° nonpolar

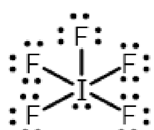
j.



octahedral d^2sp^3

90° nonpolar

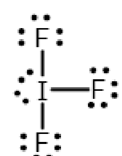
k.



square pyramid d^2sp^3

≈90° polar

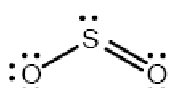
l.



T-shaped dsp^3

≈90° polar

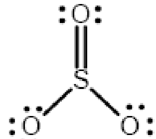
20. a.



V-shaped, sp^2, 120°

Only one resonance form is shown. Resonance does not change the position of the atoms. We can predict the geometry and hybridization from any one of the resonance structures.

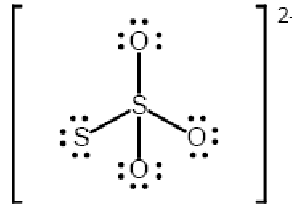
b.



trigonal planar, 120°, sp^2

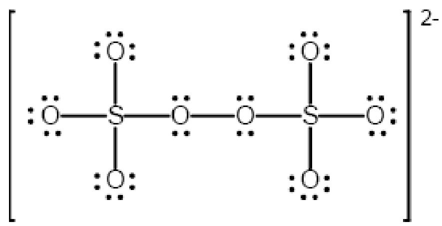
(plus two other resonance structures)

c.



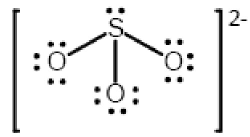
tetrahedral, 109.5°, sp^3

d.



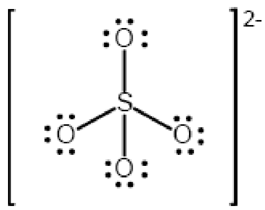
tetrahedral geometry about each S, 109.5°, sp^3 hybrids; V-shaped arrangement about peroxide O's, ≈109.5°, sp^3 hybrids

e.



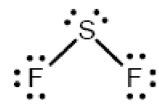
trigonal pyramid, < 109.5°, sp^3

f.



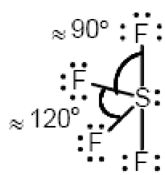
tetrahedral, 109.5°, sp^3

g.



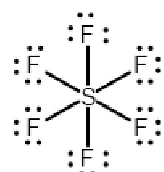
V-shaped, < 109.5°, sp^3

h.



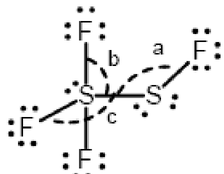
see-saw, ≈90° and ≈120°, dsp^3

i.



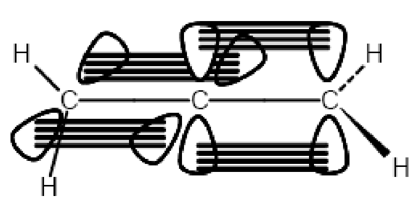
octahedral, 90°, d^2sp^3

j.



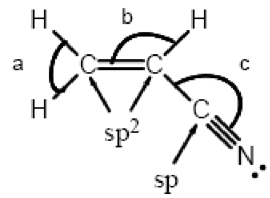
a) ≈109.5° b) ≈90° c) ≈120°
see-saw about S atom with one lone pair (dsp^3);
bent about S atom with two lone pairs (sp^3)

22. No, the CH_2 planes are mutually perpendicular to each other. The center C atom is sp hybridized and is involved in two π bonds. The p orbitals used to form each π bond must be perpendicular to each other. This forces the two CH_2 planes to be perpendicular.



24. Acrylonitrile: C_3H_3N has 3(4) + 3(1) + 5 = 20 valence electrons.

a) 120°
b) 120°
c) 180°

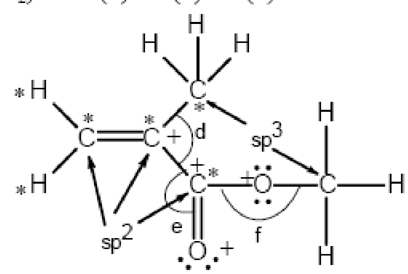


6 σ and 3 π bonds

All atoms of acrylonitrile must lie in the same plane. The π bond in the double bond dictates that the C and H atoms are all in the same plane and the triple bond dictates that N is in the same plane with the other atoms.

Methyl methacrylate ($C_5H_8O_2$) has 5(4) + 8(1) + 2(6) = 40 valence electrons.

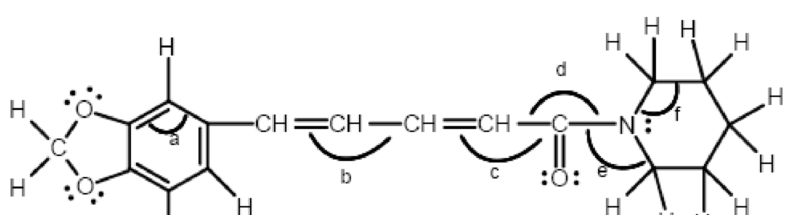
d) 120°
e) 120°
f) ≈109.5°



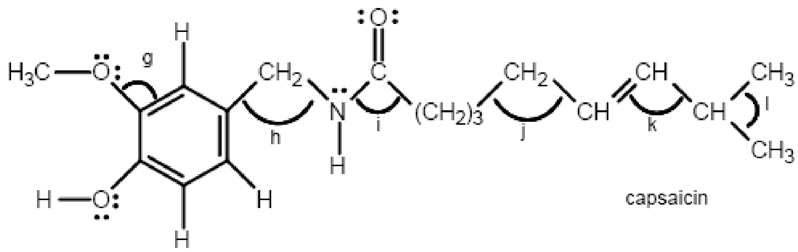
14 σ and 2 π bonds

The atoms marked with an asterisk must be coplanar with each other, as well as the atoms marked with a plus. The two planes, however, do not have to coincide with each other due to the rotations about sigma (single) bonds.

26. a. Piperine and capsaicin are molecules classified as organic compounds, i.e., compounds based on carbon. The majority of Lewis structures for organic compounds have all atoms with zero formal charge. Therefore, carbon atoms in organic compounds will usually form four bonds, nitrogen atoms will form three bonds and complete the octet with one lone pair of electrons, and oxygen atoms will form two bonds and complete the octet with two lone pairs of electrons. Using these guidelines, the Lewis structures are:



piperine



Note: The ring structures are all shorthand notation for rings of carbon atoms. In piperine the first ring contains six carbon atoms and the second ring contains five carbon atoms (plus nitrogen). Also notice that CH_3, CH_2, and CH are shorthand for a carbon atoms singly bonded to hydrogen atoms.

b. piperine: 0 sp, 11 sp^2, and 6 sp^3 carbons; capsaicin: 0 sp, 9 sp^2, and 9 sp^3 carbons

c. The nitrogens are sp^3 hybridized in each molecule.

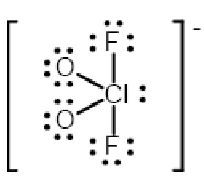
d.

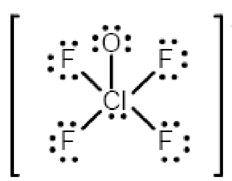
a) 120°	e) ≈109.5°	i) 120°
b) 120°	f) 109.5°	j) 109.5°
c) 120°	g) 120°	k) 120°
d) 120°	h) 109.5°	l) 109.5°

Additional Exercises

56. $FClO_2 + F^- \rightarrow F_2ClO_2^-$ $F_3ClO + F^- \rightarrow F_4ClO^-$

$F_2ClO_2^-$, $2(7) + 7 + 2(6) + 1 = 34\ e^-$ F_4ClO^-, $4(7) + 7 + 6 + 1 = 42\ e^-$



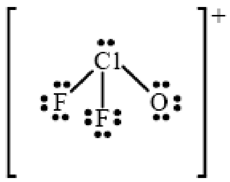


dsp^3 hybridization d^2sp^3 hybridization

Note: Similar to Exercise 14.55c, d, and e, $F_2ClO_2^-$ has two additional Lewis structures that are possible, and F_4ClO^- has one additional Lewis structure that is possible, depending on the relative placement of the O and F atoms. The predicted hybridization is unaffected.

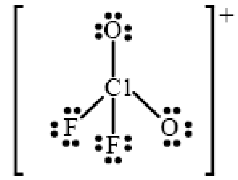
$F_3ClO \rightarrow F^- + F_2ClO^+$ $F_3ClO_2 \rightarrow F^- + F_2ClO_2^+$

F_2ClO^+, $2(7) + 7 + 6 - 1 = 26\ e^-$



sp^3 hybridization

$F_2ClO_2^+$, $2(7) + 7 + 2(6) - 1 = 32\ e^-$



sp^3 hybridization

The Molecular Orbital (MO) Model

34. If we calculate a nonzero bond order for a molecule, then we predict that it can exist (is stable).

a. H_2^+: $(\sigma_{1s})^1$ — B.O. = (1−0)/2 = 1/2, stable

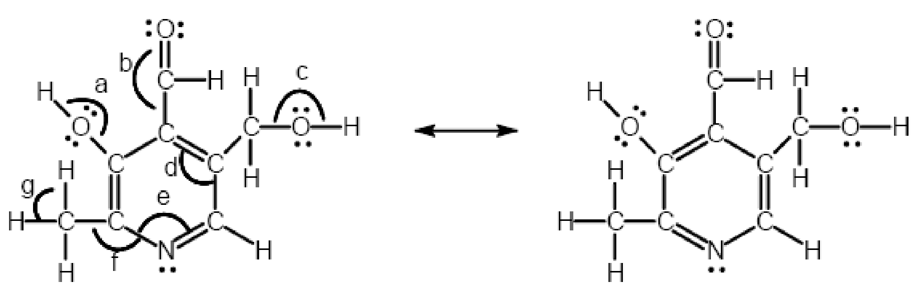
H_2: $(\sigma_{1s})^2$ — B.O. = (2−0)/2 = 1, stable

H_2^-: $(\sigma_{1s})^2(\sigma_{1s}{*})^1$ — B.O. = (2−1)/2 = 1/2, stable

H_2^{2-}: $(\sigma_{1s})^2(\sigma_{1s}{*})^2$ — B.O. = (2−2)/2 = 0, not stable

CHALLENGE PROBLEM:

64. For carbon, nitrogen, and oxygen atoms to have formal charge values of zero, each C atom will form four bonds to other atoms and have no lone pairs of electrons, each N atom will form three bonds to other atoms and have one lone pair of electrons, and each O atom will form two bonds to other atoms and have two lone pairs of electrons. Following these bonding requirements gives the following two resonance structures for vitamin B_6:



a. 21 σ bonds; 4 π bonds (The electrons in the three π bonds in the ring are delocalized.)

b. Angles a), c), and g): ≈109.5°; angles b), d), e), and f): ≈120°

c. 6 sp^2 carbons; the five carbon atoms in the ring are sp^2 hybridized, as is the carbon with the double bond to oxygen.

d. 4 sp^3 atoms; the two carbons that are not sp^2 hybridized are sp^3 hybridized, and the oxygens marked with angles a and c are sp^3 hybridized.

e. Yes, the π electrons in the ring are delocalized. The atoms in the ring are all sp^2 hybridized. This leaves a p orbital perpendicular to the plane of the ring from each atom. Overlap of all six of these p orbitals results in a π molecular orbital system where the electrons are delocalized above and below the plane of the ring (similar to benzene in Figure 14.50 of the text).