# CHAPTER 3

MOLECULAR SHAPE AND STRUCTURE

3.1 (a) The shape of the thionyl chloride molecule is trigonal pyramidal.

(b) The O—S—Cl angles are identical. (c) The expected bond angle is slightly less than $109.5°$.

3.3 (a) bent, the electron pair on the central atom results in a trigonal planar arrangement . (b) The bond angle will be around $120°$.

3.5 (a) angular or bent; (b) slightly less than $120°$

3.7

(a) Cl–S structure with Cl atoms   (b) Cl–I–Cl structure   (c) $[F–I–F]^-$ structure   (d) O–Xe structure
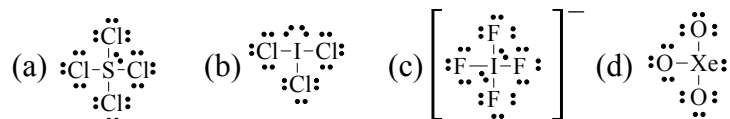
(a) The sulfur atom will have five pairs of electrons about it: one nonbonding pair and four bonding pairs to chlorine atoms. The arrangement of electron pairs will be trigonal bipyramidal; the nonbonding pair of electrons will prefer to lie in an equatorial position, because in that location the e-e repulsions will be lowest. The actual structure is described as a seesaw. AX_4E
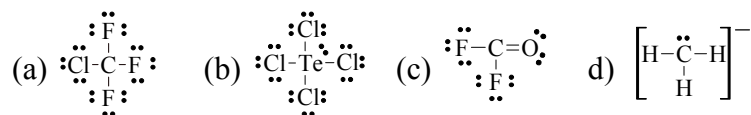
(b) Like the sulfur atom in (a), the iodine in iodine trichloride has five pairs of electrons about it, but here there are two lone pairs and three bonding pairs. The arrangement of electron pairs will be the same as in (a), and again the lone pairs will occupy the equatorial positions. Because the name of the molecule ignores the lone pairs, it will be classified as T-shaped. AX_3E_2

(c) There are six pairs of electrons about the central iodine atom in IF_4^-.

Of these, two are lone pairs and four are bonding pairs. The pairs will be placed about the central atom in an octahedral arrangement with the lone pairs opposite each other. This will minimize repulsions between them. The name given to the structure is square planar. AX_4E_2

(d) In determining the shape of a molecule, double bonds count the same as single bonds. The XeO_3 structure has four "objects" about the central Xe atom: three bonds and one lone pair. These will be placed in a tetrahedral arrangement. Because the lone pair is ignored in naming the molecule, it will be classified as trigonal pyramidal. AX_3E

3.9   (a) The I_3^- molecule is predicted to be linear, so the $< I$—I—I should equal 180°. AX_2E_3

(b) The $SbCl_5$ molecule is trigonal bipyramidal. There should be three Cl—Sb—Cl angles of 120°, and two of 90°. AX_5

(c) The structure of IO_4^- will be tetrahedral, so the O—I—O bond angles should be 109.5°. AX_4

(d) The structure of NO_2^- is bent with a bond angle of around 120°. AX_2E

3.11   The Lewis structures are

(a) :Cl-C-F: with F atoms (b) :Cl-Te-Cl: with Cl atoms   (c) :F—C=O: with F   d) $\left[H-\overset{..}{\underset{H}{C}}-H \right]^-$

(a) The shape of CF_3Cl is tetrahedral; all halogen—C—halogen angles should be approximately 109.5°. AX_4;

(b) $TeCl_4$ molecules will be see saw shaped with Cl—Te—Cl ond angles of approximately 90° and 120°. AX_4E;

(c) COF_2 molecules will be trigonal planar with F—C—F and O—C—F angles of 120°. AX_3;

(d) CH_3^- ions will be trigonal pyramidal with H—C—H angles of slightly less than 109.5°. AX_3E

3.13 (a) a and b are expected to be about 120°, c is expected to be about 109.5° in 2, 4-pentanedione. All of the angles are expected to be about 120° in the acetylacetonate ion.

(b) The major difference arises at the C of the original sp^3-hybridized CH_2 group, which upon deprotonation goes to sp^2 hybrization with only three groups attached.

3.15 (a) slightly less than 120°; (b) 180°; (c) 180°; (d) slightly less then 109.5°

**3.17** The Lewis structures are

(a)   (b)   (c)   (d)
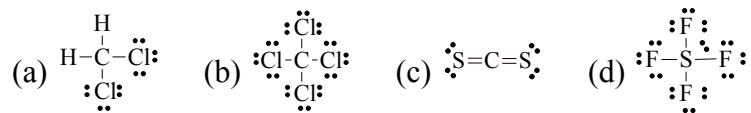
Molecules (a) and (d) are polar; (b) and (c) are nonpolar.

3.19 (a) pyridine: polar
(b) ethane: nonpolar
(c) trichloromethane: polar

3.21 Of the three forms, only **3** is nonpolar. This is because the C—Cl bond dipoles are pointing in exactly opposite directions in **3**. The dipole moment for **1** would be the largest because the C—Cl bond vectors are pointing most nearly in the same direction in **1** (60° apart) whereas in **2**

the C—Cl vectors point more away from each other ($120°$), giving a larger cancellation of dipole.
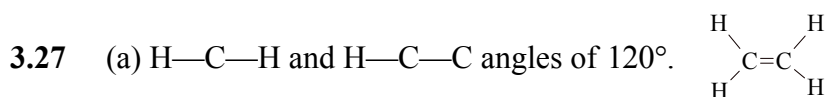
3.23

$$H_2C=CH-C≡N:$$

(H₂C=C(H)-C≡N structure drawn with H's)
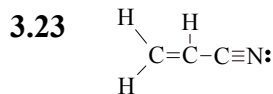
The first two carbons (CH_2 and CH) are sp^2 hybridized with H—C—H and C—C—H angles of $120°$. The third carbon (bonded to N) is sp hybridized with a C—C—N angle of $180°$.

3.25 (a) tetrahedral, bond angle of $109.5°$

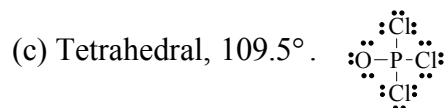(b) Tetrahedral about the carbon atoms ($109.5°$) C—Be—C angle of $180°$.

(c) Bent, H—B—H angle slightly less than $120°$

(d) Bent, Cl—Sn—Cl angle slightly less than $120°$

3.27 (a) H—C—H and H—C—C angles of $120°$.

$$H_2C=CH_2$$

(b) linear, $180°$.   Cl-C≡N:

(c) Tetrahedral, $109.5°$.

(structure: Cl₃P=O, phosphorus with three Cl and one O)

(d) The arrangement of atoms about each N is trigonal pyramidal giving H—N—H and H—N—N bond angles of approximately $107°$.   H–N–N–H (with H's)

3.29 (a) tetrahedral: (O-Sb-Cl₃ structure)   (b) tetrahedral: (O-S-Cl with O structure)

(c) seesaw: $\left[\text{O-I-F structure} \right]^-$
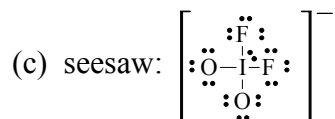
3.31 (a) sp^3, orbitals oriented toward corners of a tetrahedron ($109.5°$ apart); (b) sp, orbitals oriented directly opposite to each other ($180°$ apart); (c) sp^3d^2, orbitals oriented toward the corners of an octahedron (interorbital angles of $90°$ and $180°$); (d) sp^2, orbitals oriented toward the corners of an equilateral triangle trigonal planar array (angles $=120°$); trigonal planar.

3.33 (a) sp^3d; (b) sp^2; (c) sp^3; (d) sp

3.35 (a) sp^2; (b) sp^3; (c) sp^3d; (d) sp^3

3.37 (a) sp^3; (b) sp^3d^2; (c) sp^3d^2; (d) sp^3

3.39 As the s-character of a hybrid orbital increases, the bond angle increases.

3.41 Atomic orbitals a and b are mutually orthogonal if $\int a \cdot b \, d\tau = 0$ (assuming $a \neq b$) where the integration is over all space.

Furthermore, an orbital, a, is normalized if $\int a^2 \, d\tau = 1$.

In this problem, the two hybrid orbitals are: $h_1 = s + p_x + p_y + p_z$ and $h_2 = s - p_x + p_y - p_z$. Therefore, to show these two orbitals are orthogonal we must show $\int h_1 h_2 \, d\tau = 0$.

$$\int h_1 h_2 \, d\tau = \int (s + p_x + p_y + p_z)(s - p_x + p_y - p_z) d\tau =$$

$$\int (s^2 - sp_x + sp_y - sp_z + sp_x - p_x^2 + p_x p_y - p_x p_z + sp_y -$$

$$p_x p_y + p_y^2 - p_y p_z + sp_z - p_z p_x + p_z p_y - p_z^2) d\tau$$

Of course, this integral of a sum may be written as a sum of integrals:

$$\int s^2 d\tau - \int sp_x d\tau + \int sp_y d\tau - \int sp_z d\tau + \ldots$$

Because the hydrogen wavefunctions are mutually orthogonal, the members of this sum which are integrals of a product of two different wavefunctions are zero. Therefore, this sum of integrals simplifies to:

$$\int s^2 d\tau - \int p_x^2 d\tau + \int p_y^2 d\tau - \int p_z^2 d\tau = 1 - 1 + 1 - 1 = 0$$

(recall that the integral of the square of a normalized wavefunction is one.)

3.43 We are given: $\lambda = -\dfrac{\cos\theta}{\cos^2(\frac{1}{2}\theta)}$. In the H_2O molecule, the bond angle is 104.5°. Therefore, $\lambda = 0.67$ and the hybridization is $sp^{0.67}$.

3.45 (a) Li_2 $BO = \frac{1}{2}(2 + 2 - 2) = 1$

diamagnetic, no unpaired electrons

(b) Li_2^+ $BO = \frac{1}{2}(2 + 2 - 2 - 1) = \frac{1}{2}$

paramagnetic, one unpaired electron

(c) Li_2^- $BO = \frac{1}{2}(2 + 2 - 2 - 1) = \frac{1}{2}$

paramagnetic, one unpaired electron

3.47 (a) (1) $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^1$

(2) $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p}^*)^1$

(3) $(\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^2$
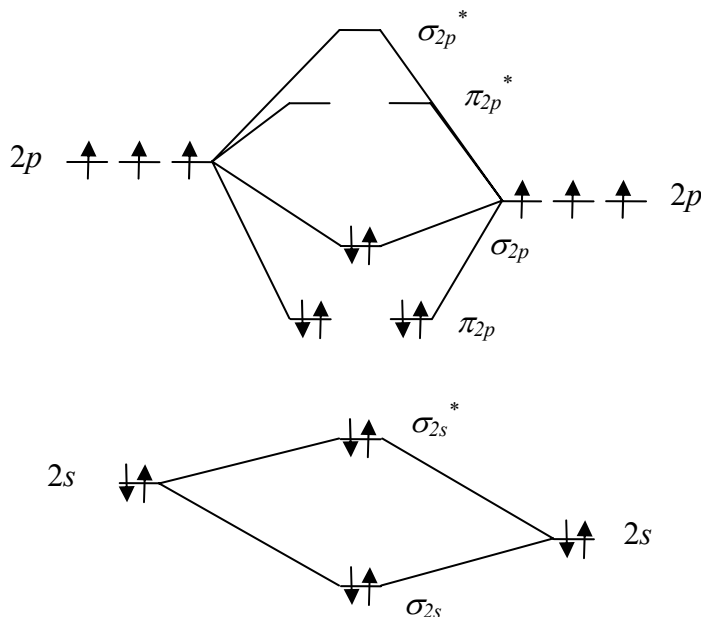
(b) (1) 1.5; (2) 2.5; (3) 1

(c) (1) and (2) are paramagnetic with one unpaired electron each

(d) π in all three cases

3.49 (a) See Figure 3.34 for the energy level diagram for N_2. (b) The nitrogen atom is more electronegative, which will make its orbitals lower in energy than those of C. The revised energy-level diagram is shown below. This will make all of the bonding orbitals closer to N than to C in

energy and will make all the antibonding orbitals closer to C than to N in energy.

Energy level diagram for CN^-

energy levels on C   energy levels on N

(c) The electrons in the bonding orbitals will have a higher probability of being at N because it is the more electronegative atom and its orbitals are lower in energy.

3.51 (a) B_2 (6 valence electrons): $(\sigma_{2s})^2 \, (\sigma_{2s}^*)^2 \, (\sigma_{2p})^2$, bond order = 1.

(b) Be_2 (4 valence electrons): $(\sigma_{2s})^2 \, (\sigma_{2s}^*)^2$, bond order = 0.

(c) F_2 (14 valence electrons):

$(\sigma_{2s})^2 \, (\sigma_{2s}^*)^2 \, (\sigma_{2p})^2 \, (\pi_{2p_x})^2 \, (\pi_{2p_y})^2 \, (\pi_{2p_x}^*)^2 \, (\pi_{2p_y}^*)^1 \, (\sigma_{2p}^*)^1$,

bond order = 1.

3.53 All of these molecules are paramagnetic. O_2^- and O_2^+ have an odd number of electrons and must, therefore, have at least one unpaired

electron. O_2 has an even number of electrons, but in its molecular orbital energy level diagram, the HOMO is a degenerate set of orbitals that are each singly occupied, giving this molecule two unpaired electrons. For O_2^-, one more electron will be placed in this degenerate set of orbitals, causing one of the original unpaired electrons to now be paired. O_2^- will therefore have one unpaired electron. Likewise, O_2^+ will have one less electron than O_2; thus one of the originally unpaired electrons will be removed, leaving one unpaired electron in this molecule.

3.55 (a) F_2 with 14 valence electrons has a valence electron configuration of $(\sigma_{2s})^2 \ (\sigma_{2s}^*)^2 \ (\sigma_{2p})^2 (\pi_{2px})^2 (\pi_{2py})^2 (\pi_{2px}^*)^2 (\pi_{2py}^*)^2$ with a bond order of 1. After forming F_2^- from F_2, an electron is added into a σ_{2p}^* orbital. The addition of an electron to this antibonding orbital will result in a reduction of the bond order to 1/2 (See 51). F_2 will have the stronger bond. (b) B_2 will have an electron configuration of $(\sigma_{2s})^2 \ (\sigma_{2s}^*)^2 \ (\pi_{2px})^1 \ (\pi_{2py})^1$ with a bond order of 1. Removing one electron to form B_2^+ will eliminate one electron in the bonding orbitals, creating a bond order of 1/2. B_2 will have the stronger bond.

3.57 The conductivity of a semiconductor increases with temperature at increasing numbers of electrons are promoted into the conduction band, whereas the conductivity of a metal will decrease as the motion of the atoms will slow down the migration of electrons.
Note: The electron due to the charge has arbitrarily been placed in a $2p$ orbital on C on the left-hand side of the diagram.

3.59 (a) In and Ga; (b) P and Sb

3.61 Given the overlap integral $S = \int \Psi_{A1s}\Psi_{B1s}d\tau$, the bonding orbital

$\Psi = \Psi_{A1s} + \Psi_{B1s}$, and the fact that the individual atomic orbitals are normalized, we are asked to find the normalization constant N which will normalize the bonding orbital Ψ such that:
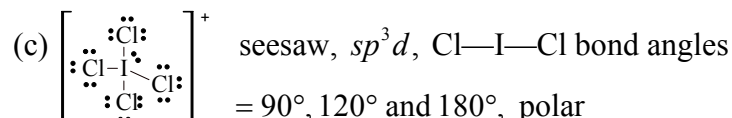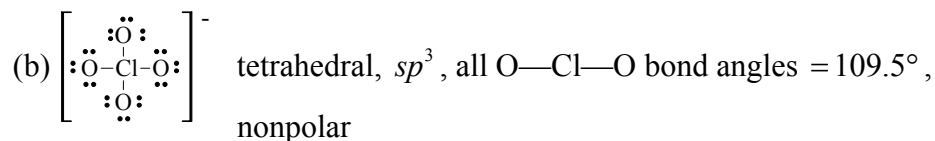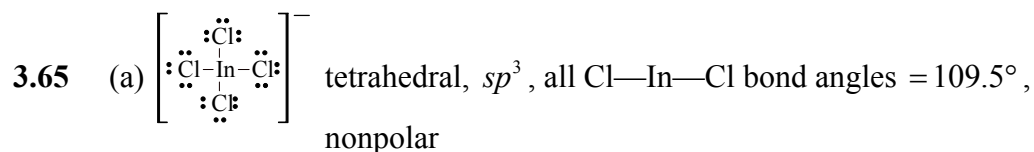
$$\int N^2\Psi^2 d\tau = N^2 \int (\Psi_{A1s} + \Psi_{B1s})^2 d\tau = 1$$

$$N^2 \int (\Psi_{A1s} + \Psi_{B1s})^2 d\tau = N^2 \int (\Psi_{A1s}^2 + 2\Psi_{A1s}\Psi_{B1s} + \Psi_{B1s}^2)d\tau$$

$$= N^2 \left(\int \Psi_{A1s}^2 d\tau + 2\int \Psi_{A1s}\Psi_{B1s}d\tau + \int \Psi_{B1s}^2 d\tau \right)$$
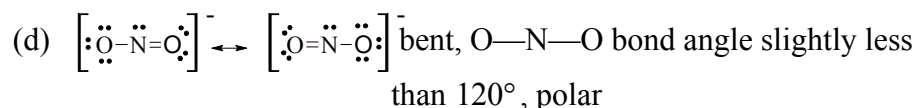
Given the definition of the overlap integral above and the fact that the individual orbitals are normalized, this expression simplifies to:

$$N^2(1 + 2S + 1) = 1$$

Therefore, $\quad N = \sqrt{\dfrac{1}{2 + 2S}}$

3.63 The antibonding molecular orbital is obtained by taking the difference between two atomic orbitals that are proportional to e^{-r/a_o}. Halfway between the two nuclei the distance from the first nucleus, r_1, is equal to the distance to the second nucleus, r_2, and the antibonding orbital is proportional to: $\quad \Psi \propto e^{-r/a_o} - e^{-r/a_o} = 0$

3.65 (a) $\left[\begin{array}{c} :\ddot{C}l: \\ :\ddot{C}l-In-\ddot{C}l: \\ :\ddot{C}l: \end{array} \right]^-$ tetrahedral, sp^3, all Cl—In—Cl bond angles $= 109.5°$, nonpolar

(b) $\left[\begin{array}{c} :\ddot{O}: \\ :\ddot{O}-Cl-\ddot{O}: \\ :\ddot{O}: \end{array} \right]^-$ tetrahedral, sp^3, all O—Cl—O bond angles $= 109.5°$, nonpolar

(c) $\left[\begin{array}{c} :\ddot{C}l: \\ :\ddot{C}l-I\cdot \\ :\ddot{C}l: \quad \ddot{C}l: \end{array} \right]^+$ seesaw, sp^3d, Cl—I—Cl bond angles $= 90°, 120°$ and $180°$, polar

(d) $\left[:\overset{..}{\underset{..}{O}}-\overset{..}{N}=\overset{..}{O}:\right]^{-} \leftrightarrow \left[:\overset{..}{O}=\overset{..}{N}-\overset{..}{\underset{..}{O}}:\right]^{-}$ bent, O—N—O bond angle slightly less

than $120°$, polar

3.67 (a) $SiF_4 : SiF_4$ is nonpolar (tetrahedral AX_4 structure) but PF_3 is polar

(trigonal pyramidal AX_3E structure);

b) $SF_6 : SF_6$ is nonpolar (octahedral AX_6 structure) whereas SF_4 is polar

(seesaw, AX_4E structure);

(c) $AsF_5 : IF_5$ is polar (square pyramidal, AX_5E structure) whereas AsF_5 is

nonpolar (AX_5, trigonal bipyramidal structure).

3.69 The elemental composition gives an empirical formula of CH_4O, which

agrees with the molar mass. There is only one reasonable Lewis structure;

this corresponds to the compound methanol. Both carbon and oxygen are

sp^3 hybridized. All of the bond angles at carbon should be $109.5°$. The

bond angles about oxygen should be close to $109.5°$ but will be somewhat

less, due to the repulsions by the lone pairs. The molecule is polar.

3.71   <u>Bonding</u>   <u>Anti bonding</u>
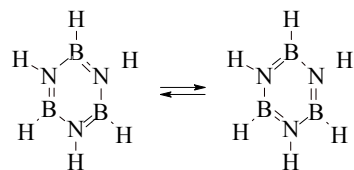
(a)

(b)
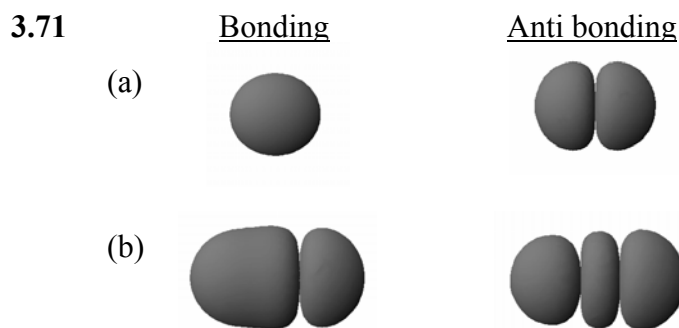
(c) The bonding and antibonding orbitals for HF appear different due to

the fact that a *p*-orbital from the F atom is used to construct bonding and

antibonding orbitals whereas in the H_2 molecule s orbitals on each atom

are used to construct bonding and antibonding orbitals.

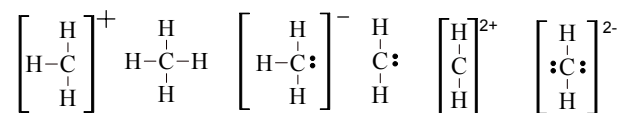**3.73** The expected molecular orbital diagram for CF is
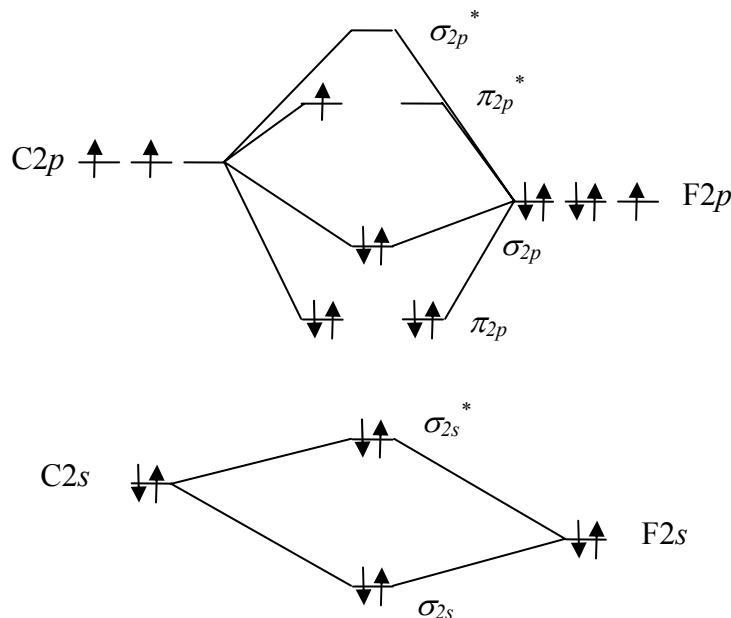
The bond order for the neutral species is 2.5 because one electron occupies a π_{2p}^* orbital. Adding an electron to form CF^- will reduce the bond order by 1/2 to 2, while removing an electron from form CF^+ will increase the bond order to 3. The bond lengths will increase as the bond order decreases: $CF^- < CF < CF^+$. The CF^+ ion will be diamagnetic but both CF and CF^- will have unpaired electrons (one in the case of CF and two in the case of CF^-).

3.75 The Lewis structure of borazine is nearly identical to that of benzene. It is obtained by replacing alternating C atoms in the benzene structure with B and N, as shown. The orbitals at each B and N atom will be sp^2 hybridized.
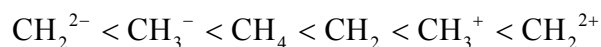
3.77 The Lewis structures are:

$$\left[\begin{array}{c}H\\|\\H-C\\|\\H\end{array}\right]^{+} \quad \begin{array}{c}H\\|\\H-C-H\\|\\H\end{array} \quad \left[\begin{array}{c}H\\|\\H-C{:}\\|\\H\end{array}\right]^{-} \quad \begin{array}{c}H\\|\\C{:}\\|\\H\end{array} \quad \left[\begin{array}{c}H\\|\\C\\|\\H\end{array}\right]^{2+} \quad \left[\begin{array}{c}H\\|\\{:}C{:}\\|\\H\end{array}\right]^{2-}$$

The predicted bond angles in each species based upon the Lewis structure and VSEPR theory will be

CH_3^{+}	AX_3	trigonal planar	120°
CH_4	AX_4	tetrahedral	109.5°
CH_3^{-}	AX_3E	pyramidal	slightly less than 109.5°
CH_2	AX_2E	angular	slightly less than 120°
CH_2^{2+}	AX_2	linear	180°
CH_2^{2-}	AX_2E_2	angular	less than 109.5°, more so than CH_3^{-} due to the presence of two lone pairs

The order of increasing H—C—H bond angle will be

$$CH_2^{2-} < CH_3^{-} < CH_4 < CH_2 < CH_3^{+} < CH_2^{2+}$$

All of these species are expected to be diamagnetic. None are radicals.

3.79 Acetylene : $H-C{\equiv}C-H$ Polymer: $\left[\begin{array}{c}H \quad\;\; H \quad\;\; H\\|\qquad|\qquad|\\{=}C-C{=}C-C{=}C-\\|\qquad|\\H \qquad H\end{array}\right]$

Polyacetylene retains multiple bonds along the chain. It is through the series of orbitals that electrons can be conducted. A resonance form of the Lewis structure can be drawn showing that the electrons may be delocalized along the polyacetylene chain. No such resonance form is possible for polyethylene.

Note: The dark color of the material results from the formation of a large number of molecular orbitals that are not very different in energy. These molecular orbitals are made up of combinations of the *p*-orbitals on the

carbons that make up the double bonds. Because the orbitals are closely spaced in energy, electrons in them can readily absorb visible light to be promoted to a higher energy orbital. See section 3.13.

3.81   The energy of an electron in the nth quantum state of a one-dimensional box is given by: $E = n^2 h^2 / (8mL^2)$, where h is Plank's constant, m is the mass of the electron and L is the length of the box (recall n must be an integer). The lowest energy transition for this system will be from the highest occupied quantum state, which we will identify with the quantum number n_{HO}, to the next highest state or the lowest unoccupied quantum state, n_{LU}. Since each quantum state can hold 2 electrons and each carbon atom contributes one electron, $n_{HO} = N/2$ and $n_{LU} = (N/2) + 1$. (In the case N is odd, $N/2$ must be rounded up to the nearest integer) Also, the length of the box is given by $L = NR$ where R is the average C—C bond length. Therefore, the lowest energy transition is given by:
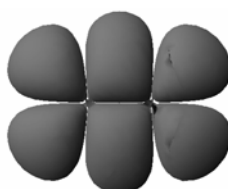
$$\Delta E = E_{LU} - E_{HO} = \frac{n_{LU} h^2}{8mN^2 R^2} - \frac{n_{HO} h^2}{8mN^2 R^2} = \frac{h^2}{8mN^2 R^2}\left[\left(\frac{N}{2}+1\right)^2 - \left(\frac{N}{2}\right)^2\right]$$

$$= \frac{h^2 (N+1)}{8mN^2 R^2}$$

To shift the wavelength of the absorption to longer wavelengths (lower energies) the length of the carbon chain, N, must increase.
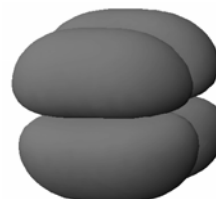
3.83   (a) σ π δ
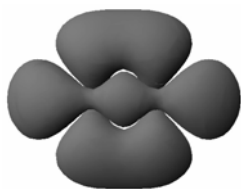
(b) The overlap between the orbitals will decrease as one goes from σ to π to δ, so we expect the bond strengths to decline in the same order.

3.85 The effect of changes (a) and (b) will be similar. The overall bond order will change. In the first case, electrons will be removed from π orbitals so that the net π-bond order will drop from three to two. The same thing will happen in (b), but because two electrons are added to antibonding orbitals, a net total of one π-bond will be broken. Based on this simple model, the ions formed should be paramagnetic because the electrons are added to or taken from doubly degenerate orbitals.

**3.87** (a) The Lewis structure of benzyne is
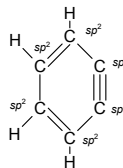
(b) Benzyne would be highly reactive because the two carbon atoms that are sp hybridized are constrained to have a very strained structure compared to what their hybridization would like to adopt—namely a linear arrangement. Instead of $100°$ angles at these carbon atoms, the angles by necessity of being in a six-membered ring are constrained to be close to $120°$. A possibility that allows the carbon atoms to adopt more reasonable angles is the formation of a diradical:
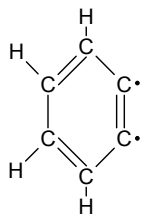
3.89 (a) The carbon atoms are all sp^3 hybridized.   (b) The C—C—C, H—C—H and H—C—C bond angles should be $109.5°$ based upon the answer to (a).   (c) Because of the ring structure, however, the C—C—C bond angles must be $60°$.   (d) The σ-bond will have the electron density of the bond located on a line between the two atoms that it joins. (e) If the C atoms are truly sp^3 hybridized, then the bonding orbitals will not necessarily point directly between the C atoms.   (f) The sp^3 hybridized orbitals can still overlap even if they do not point directly

between the atoms as shown. Such bonds are sometimes called "bent" bonds, or "banana" bonds. As a result of the situation in the C—C—C bond angles, the H—C—H bond angles are also distorted from 109.5°.
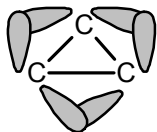
3.91 (a) and (d) have the possibility of n-to-π^* transitions because these molecules possess both an atom with a lone pair of electrons (on O in HCOOH and on N in HCN) and a π-bond to that atom. The other molecules have either a lone pair or a π-bond, but not both.

3.93 (a)

(b)