

# Instructor Supplemental Solutions to Problems

Marc Loudon  
Joseph G. Stowell

to accompany

## Organic Chemistry 5th Edition

This manual provides the solutions to the problems that are not provided in the Study Guide and Solutions Manual. These answers are provided as electronic files in Portable Document Format (PDF). Each chapter is provided as a separate file. For the conventions used in these solutions, see the Preface of the *Study Guide and Solutions Manual*.

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# Chapter 1

## Chemical Bonding and Chemical Structure

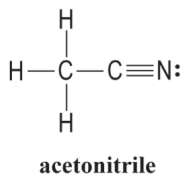
### Solutions to In-Text Problems

- 1.1 (b) The neutral calcium atom has a number of valence electrons equal to its group number, that is, 2.  
(d) Neutral Br, being in Group 7A, has 7 valence electrons; therefore,  $\text{Br}^+$  has 6.

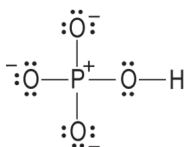
- 1.2 (b) The positive ion isoelectronic with neon must have 10 electrons and 11 protons, and therefore must have an atomic number = 11. This is the sodium ion,  $\text{Na}^+$ .  
(d) Because Ne has atomic number = 10 and F has atomic number = 9, the neon species that has 9 electrons is  $\text{Ne}^+$ .

- 1.3 (b)  $\begin{array}{c} \text{H} - \ddot{\text{N}} - \text{H} \\ | \\ \text{H} \end{array}$       (d)  $\begin{array}{c} \text{H} - \overset{+}{\text{O}} - \text{H} \\ | \\ \text{H} \end{array}$   
ammonia      hydronium ion

- 1.5 The structure of acetonitrile:

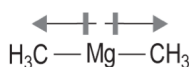


- 1.6 (b) The overall charge is  $-2$ .



- 1.8 (b) Formal charge does not give an accurate picture, because O is more electronegative than H; most of the positive charge is actually on the hydrogens.  
(d) An analysis of relative electronegativities would suggest that, because C is slightly more electronegative than H, a significant amount of the positive charge resides on the hydrogens. However, carbon does not have its full complement of valence electrons—that is, it is short of the octet by 2 electrons. In fact, both C and H share the positive charge about equally.

- 1.9 The bond dipole for dimethylmagnesium should indicate that C is at the negative end of the C—Mg bond, because carbon is more electronegative than magnesium.



- 1.10 (a) Water has bent geometry; that is, the H—O—H bond angle is approximately tetrahedral. Repulsion between the lone pairs and the bonds reduces this bond angle somewhat. (The actual bond angle is  $104.5^\circ$ .)

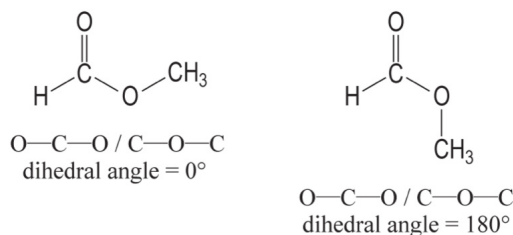
- (c) The formaldehyde molecule has trigonal planar geometry. Thus, both the H—C—H bond angle and the H—C=O bond angle are about 120°.

- 1.11 (a) Bond angles:  $aa$ ,  $ab$ ,  $bc$ ,  $bd$ ,  $cd$ ,  $de$ ,  $df$ , and  $ef$  are all about 120°, because all are centered on atoms with trigonal planar geometry;  $fg$  is predicted to have the tetrahedral value of 109.5. The bond lengths increase in the order

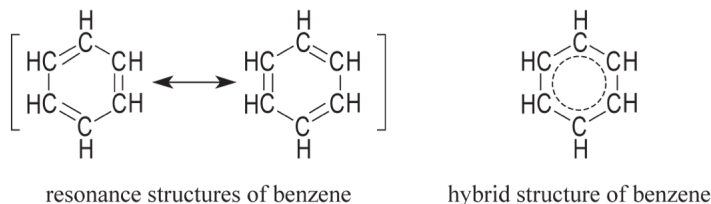
$$a \approx g < e < b < d \approx f < c$$

(In Chapter 4, you'll learn that C—H bonds attached to carbons of double bonds are shorter than C—H bonds attached to carbons of single bonds. For this reason,  $a < g$ .)

- 1.13 (a) Because the carbon has trigonal-planar geometry, the H—C=O bond angle is 120°.  
 (b) The two structures are as follows:

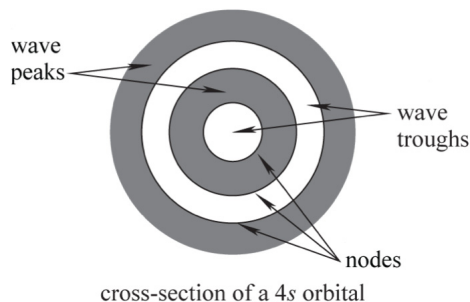


- 1.15 The resonance structures of benzene:



Each bond is a single bond in one structure and a double bond in the other. On average, each bond has a bond order of 1.5.

- 1.17 (b) A 4s orbital is four concentric spheres of electron density, each separated by a node, as shown in “cutaway” diagram (b) in Fig. IS1.1.
- 1.18 (b) The chloride ion,  $\text{Cl}^-$  (atomic number = 17 and one negative charge, therefore 18 electrons): This ion has the same electronic configuration as argon:  $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$ . The valence orbitals are the 3s and 3p orbitals, and the valence electrons are the eight electrons that occupy these orbitals.
- (d) The sodium atom (atomic number = 11) has 11 electrons. Therefore its electronic configuration is  $(1s)^2(2s)^2(2p)^6(3s)^1$ . The valence orbital is the 3s orbital, and the valence electron is the one electron that occupies this orbital.



**Figure IS1.1** Cross section of a 4s orbital in the solution to Problem 1.17b.

- 1.19 The pictures and energy levels of the molecular orbitals for parts (a), (b), (d), and (e) are essentially the same as they are for the dihydrogen molecular orbitals in Fig. 1.14 of the text. For part (c), the atomic orbitals involved are  $2s$  orbitals, which have a node. However, the various species differ in their electron occupancies.
- (b) The  $\text{H}_2^-$  ion contains three electrons. This can be conceived as the combination of a hydrogen atom with a hydride ion ( $\text{H}^-$ ). By the aufbau principle, two occupy the bonding molecular orbital, and one occupies the antibonding molecular orbital. This is shown in the electron-occupancy diagram (b) of Fig. IS1.2. Because the bonding molecular orbital contains a greater number of electrons than the antibonding molecular orbital, this species is stable. Notice that in terms of electron occupancy,  $\text{H}_2^-$  and  $\text{He}_2^+$  are identical.
- (d) The  $\text{H}_2^{2-}$  ion can be conceived to result from the combination of two hydride ions ( $\text{H}^-$ ). This species contains four electrons; two occupy the bonding molecular orbital, and two occupy the antibonding molecular orbital. This is shown in the electron-occupancy diagram (d) of Fig. IS1.2. In this species, the energetic advantage of the electrons in the bonding molecular orbital is cancelled by the energetic disadvantage of the same number of electrons in the antibonding molecular orbital. This species consequently has no energetic advantage over two dissociated hydride ( $\text{H}^-$ ) ions, and therefore it readily dissociates.
- 1.22 (a) The oxygen of the hydronium ion has approximately tetrahedral geometry and is therefore  $sp^3$ -hybridized. Two of the  $sp^3$  hybrid orbitals contain an unshared electron pair. One of these becomes the lone pair in  $\text{H}_3\text{O}^+$ ; the other overlaps with a proton ( $\text{H}^+$ ) to give one of the O—H bonds. The other two  $sp^3$  hybrid orbitals contain one electron each; each of these overlaps with the  $1s$  orbital of a hydrogen atom (which contains one electron) to give the three  $sp^3-1s$   $\sigma$  bonds (the O—H bonds) of  $\text{H}_3\text{O}^+$ .
- (b) The H—O—H bond angles in  $\text{H}_3\text{O}^+$  should be somewhat larger than those in water, because there is one less lone pair and a smaller associated repulsion.

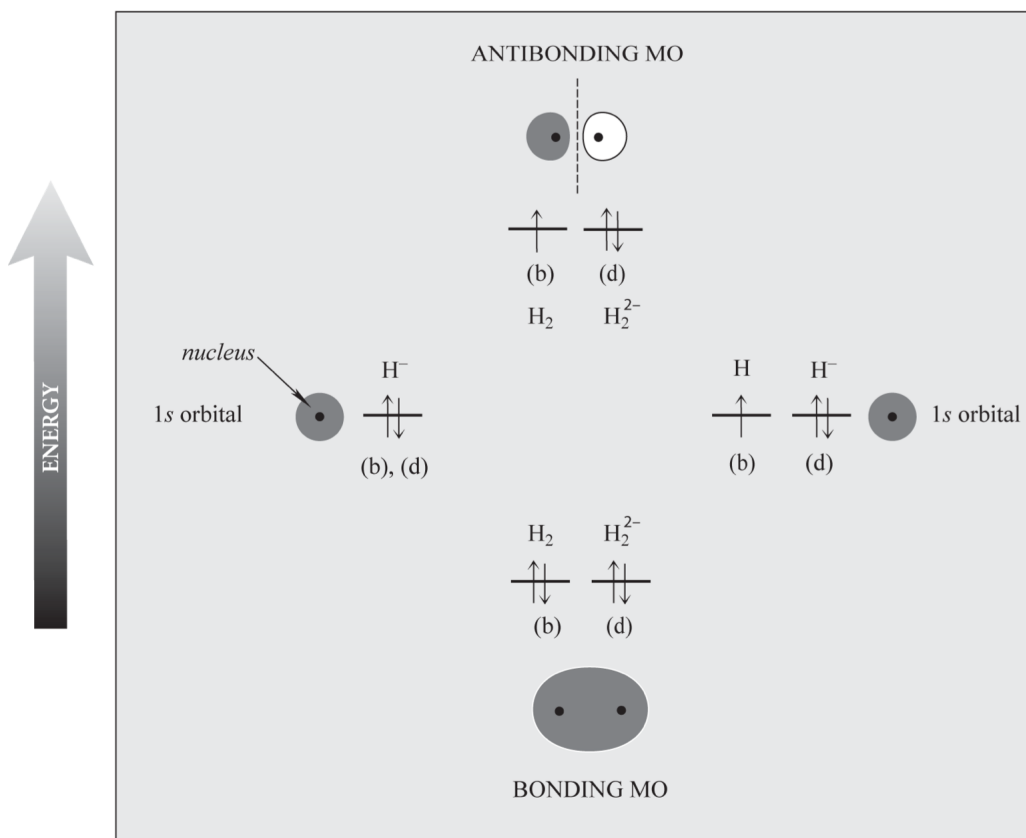
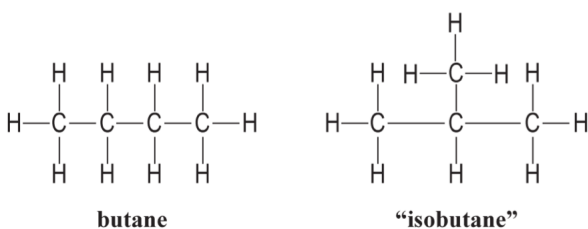
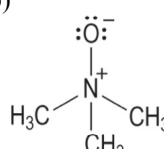
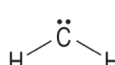
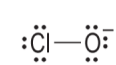


Figure IS1.2 Electron-occupancy diagram for the solution to Problems 1.19b and 1.19d.

## Solutions to Additional Problems

- 1.23 (b) Compound (2), cesium fluoride, would be most likely to exist as an ionic species, because Cs and F come from opposite corners of the periodic table.
- 1.24 The formal charge on all the hydrogens is 0. For the other atoms:
- (b) Nitrogen has a complete octet and a formal charge of 0.  
 (d) Boron has a sextet and a formal charge of 0.  
 (f) Boron has an octet and a formal charge of  $-1$ .
- 1.26 The lengths of the C—C bonds in isobutane have no significance; two are longer merely to accommodate the rest of the structure. Remember that these Lewis structures show only connectivity—not geometry.

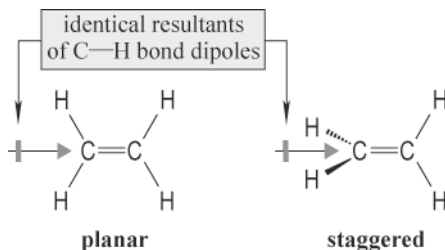


- 1.27 (b)  (d)  (f) 
- trimethylamine oxide**  
overall charge = 0
- methylene**  
overall charge = 0
- hypochlorite**  
overall charge =  $-1$

- 1.29 Silicon atom (atomic number = 14; therefore 14 electrons):  $(1s)^2(2s)^2(2p)^6(3s)^2(3p_x)^1(3p_y)^1$ . The valence electrons are the two  $3s$  and the two  $3p$  electrons.
- 1.31 (b) The beryllium (Be) bears two groups, and therefore has linear geometry. The H—Be—H bond angle is  $180^\circ$ .  
 (d) The silicon is bound to four chlorines, and is therefore tetrahedral. The Cl—Si—Cl bond angle is  $109.5^\circ$ .  
 (f) The terminal carbons are bound to three groups, and are therefore trigonal planar. The central carbon is bound to two groups, and is therefore linear. Hence, the H—C—H and H—C=C bond angles are  $120^\circ$ ; the C=C=C bond angle is  $180^\circ$ .
- 1.32 (b) Using the method in part (a), the hybrid orbitals in the O—H bonds have about 18.6%  $s$  character; they therefore have 81.4%  $p$  character. Two such orbitals account for 37.2% of an  $s$  orbital. The 62.8% remaining  $s$  character is divided equally between the orbitals containing the unshared pairs—that is, 31.4% for each orbital. Therefore, the hybrid orbitals in the bonds are  $s^{18.6}p^{81.4}$ , or  $sp^{4.4}$  hybrids, and the orbitals containing the unshared pairs are  $s^{31.4}p^{68.6}$ , or  $sp^{2.2}$  hybrids.
- 1.34 We use reasoning analogous to that used in the previous problem. This ion is a hybrid of three identical structures. Hence, each property will be the sum of that property in each structure divided by 3.
- (a) Negative charge on each oxygen:  $(-1 + 0 + -1)/3 = -2/3$ .  
 (b) Bond order of each carbon–oxygen bond:  $(1 + 2 + 1)/3 = 4/3$  or 1.33.
- 1.37 (a) The number of equivalent  $f$  orbitals equals the number of possible values of the quantum number  $m_l$ , which is 7 ( $\pm 3, \pm 2, \pm 1, 0$ ). That is, there are  $l + 1 = 7$  equivalent  $f$  orbitals.

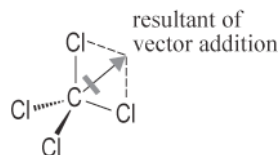
- (b) The orbital designation  $f$  means  $l = 3$ . Orbitals with  $l = 3$  (that is,  $f$  orbitals) first appear in principal quantum level 4.
- (c) There are  $n - 1 = 5 - 1 = 4$  nodes. (Three of them are planar, and one is spherical; see Problem 1.35. Can you sketch a  $4f$  orbital?)

1.40 No matter how any  $\text{CH}_2$  group is turned, the resultant bond dipole is the same:

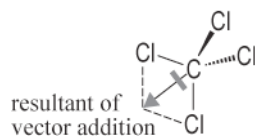


Hence, ethylenes with the two different dihedral angles should both have zero dipole moment because the resultants of the two  $\text{CH}_2$  groups cancel each other in either arrangement. The observation of zero dipole moment does not permit a choice between these two dihedral angles.

1.42 To solve this problem, we first have to know the geometry of  $\text{CCl}_4$ . This should be easy: it's tetrahedral, because the carbon is bonded to four identical groups. Now, as suggested in the hint, let's do a vector addition for the bond dipoles of each  $\text{Cl}-\text{C}-\text{Cl}$  pair. (Use a dipole arrow of arbitrary length as long as it is the same for both. We'll use an arrow with the length of the  $\text{C}-\text{Cl}$  bonds.) Here's the result of the vector addition, which we've done graphically, for the first pair. Notice that, because the  $\text{C}-\text{Cl}$  bonds are identical, the resultant must *bisect* the angle between the two bonds.



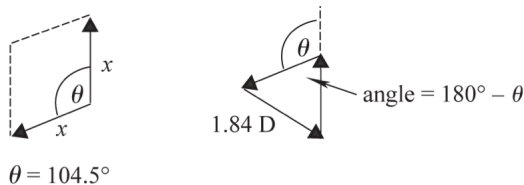
Now let's do the resultant for the second pair. Because the  $\text{C}-\text{Cl}$  bonds are identical to those of the first pair, it follows that the resultant is the same length, and it again bisects the  $\text{Cl}-\text{C}-\text{Cl}$  bond angle. (We've rotated the molecule about an axis along the dipole so we are viewing the other two chlorines from the perspective we used to view the first two—in the plane of the page.)



The two resultants we have just obtained are oriented at an angle of  $180^\circ$ ; that is, they are pointed in opposite directions. Since they are identical in magnitude, they cancel. Hence the dipole moment of  $\text{CCl}_4$  is zero.



1.44 This problem requires a construction similar to the one used in Problem 1.43 in which the resultant is known and the individual  $\text{O}-\text{H}$  bond dipoles are unknown.



Applying the law of cosines, with  $x$  as the O—H bond dipoles,

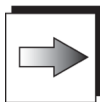
$$1.84^2 = x^2 + x^2 - 2x^2 (\cos (180^\circ - \theta))$$

$$3.39 = 2x^2(1 - \cos 75.5^\circ) = 2x^2(1 - 0.25) = 1.50 x^2$$

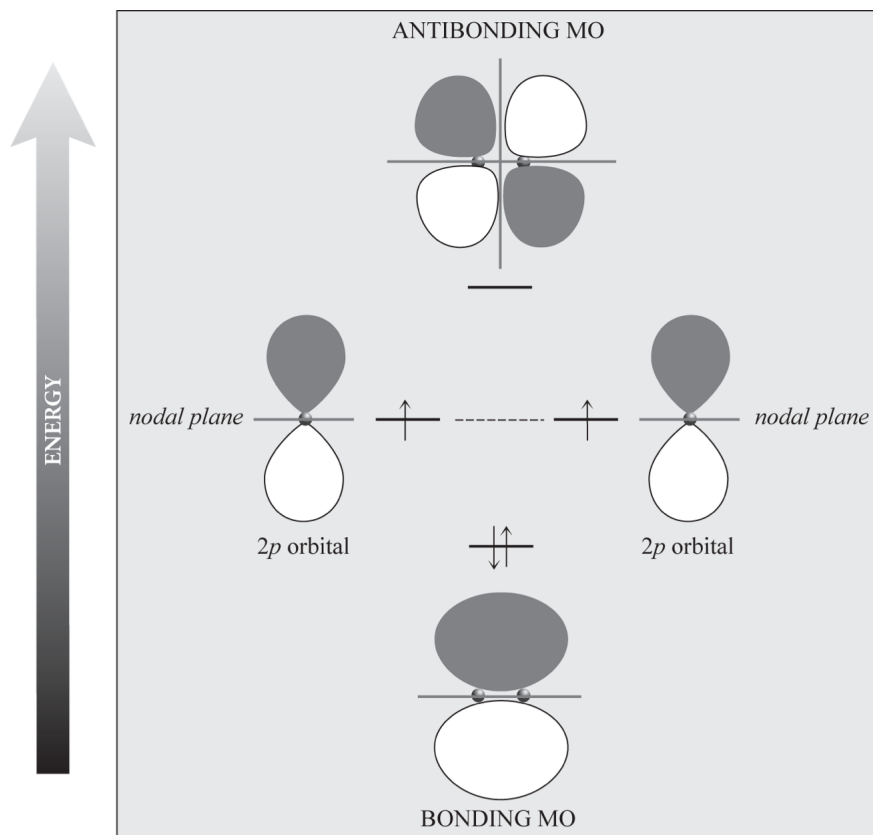
$$x = \sqrt{\frac{3.39}{1.50}} = 1.50 \text{ D}$$

This is the calculated value of the O—H bond dipole, which is very similar to the value assumed in Problem 1.43.

- 1.46 (a) The bonding molecular orbital is derived by the constructive “side-to-side” overlap of peaks with peaks and troughs with troughs. The antibonding molecular orbital is derived by changing the peak to a trough and the trough to a peak in one of the two  $2p$  orbitals. Destructive overlap of troughs with peaks and peaks with troughs gives an additional node in the antibonding orbital. These molecular orbitals are shown in Fig. IS1.3 on the following page.
- (b) The nodes are also shown in Fig. IS1.3. Both of the MOs have the nodes of the original  $2p$  orbitals, which merge into a single node because the nodal plane is common to both orbitals. The antibonding MO has in addition a node between the original orbitals that results from the destructive overlap of a peak and a trough.
- (c) Fig. SG1.8 is the required interaction diagram.
- (d) The resulting bond is *not* a  $\sigma$  bond because it is not cylindrically symmetrical about the internuclear axis.



This type of bond, called a pi ( $\pi$ ) bond, is important in the carbon–carbon double bond. Pi bonds are discussed in Chapter 4.



**Figure IS1.3** An orbital interaction diagram for the side-to-side interaction of two  $2p$  orbitals. The small spheres are nuclei, and the gray lines are nodal planes viewed end-on.