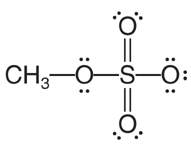
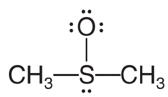
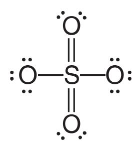
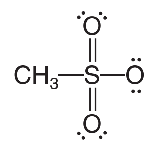
LEWIS STRUCTURES

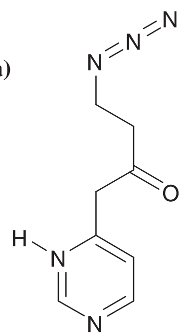
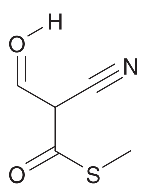
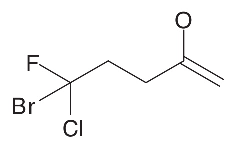
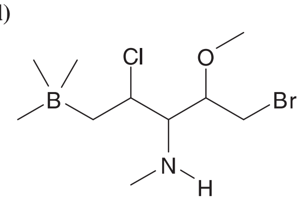
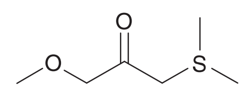
1.30 Write a Lewis structure for each of the following:

(a) $SOCl_2$ **(b)** $POCl_3$ **(c)** PCl_5 **(d)** $HONO_2$ (HNO_3)

1.31 Give the formal charge (if one exists) on each atom of the following:

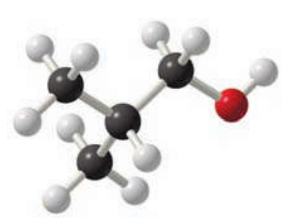
(a) 
(b) 
(c) 
(d) 

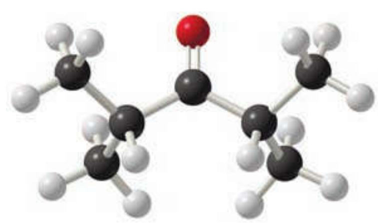
1.32 Add any unshared electrons to give each element an octet in its valence shell in the formulas below and indicate any formal charges. Note that all of the hydrogen atoms that are attached to heteroatoms have been drawn if they are present.

(a) 
(b) 
(c) 
(d) 
(e) 

STRUCTURAL FORMULAS AND ISOMERISM

1.33 Write a condensed structural formula for each compound given here.


(a)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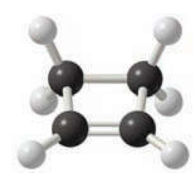
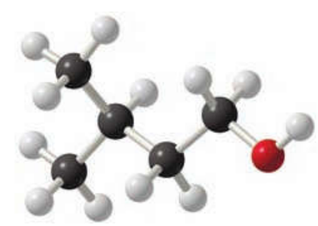
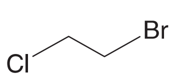
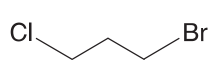
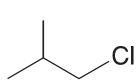

(c)

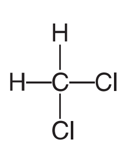
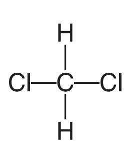

(d)

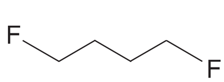
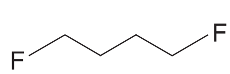
1.34 What is the molecular formula for each of the compounds given in Exercise 1.33?

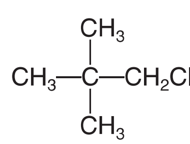
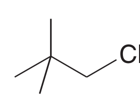
1.35 Consider each pair of structural formulas that follow and state whether the two formulas represent the same compound, whether they represent different compounds that are constitutional isomers of each other, or whether they represent different compounds that are not isomeric.

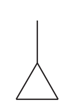
(a)  and 

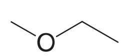
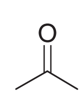
(b)  and $ClCH_2CH(CH_3)_2$

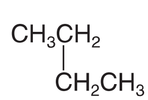
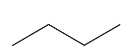
(c)  and 

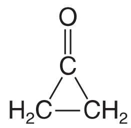
(d)  and 

(e)  and 

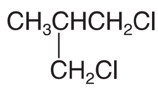
(f) $CH_2{=}CHCH_2CH_3$ and 

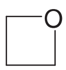
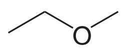
(g)  and 

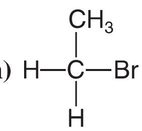
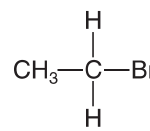
(h)  and 

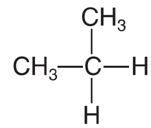
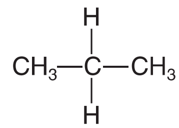
(i) $CH_3OCH_2CH_3$ and 

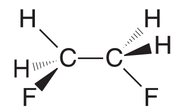
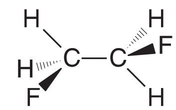
(j) $CH_2ClCHClCH_3$ and $CH_3CHClCH_2Cl$

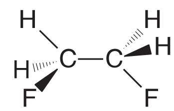
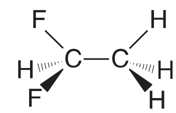
(k) $CH_3CH_2CHClCH_2Cl$ and 

(l)  and 

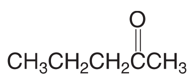
(m)  and 

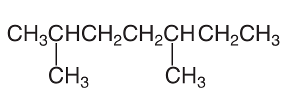
(n)  and 

(o)  and 

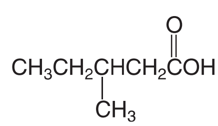
(p)  and 

1.36 Rewrite each of the following using bond-line formulas:

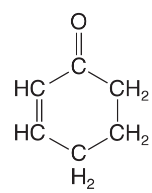
(a) 

(b) 

(c) $(CH_3)_3CCH_2CH_2CH_2OH$

(d) 

(e) $CH_2{=}CHCH_2CH_2CH{=}CHCH_3$

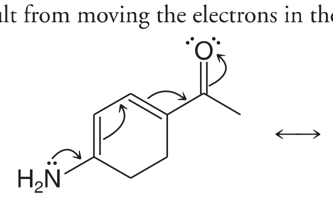
(f) 

1.37 Write bond-line formulas for all of the constitutional isomers with the molecular formula C_4H_8.

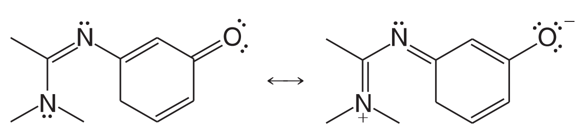
1.38 Write structural formulas for at least three constitutional isomers with the molecular formula CH_3NO_2. (In answering this question you should assign a formal charge to any atom that bears one.)

RESONANCE STRUCTURES

1.39 Write the resonance structure that would result from moving the electrons in the way indicated by the curved arrows.

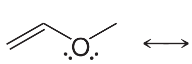


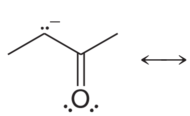
1.40 Show the curved arrows that would convert **A** into **B**.

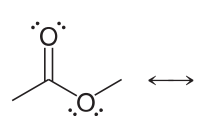


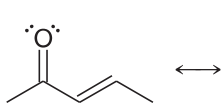
A **B**

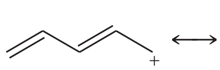
1.41 For the following write all possible resonance structures. Be sure to include formal charges where appropriate.

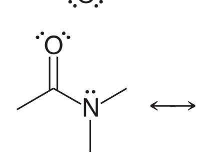
(a) 

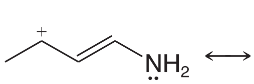
(d) 

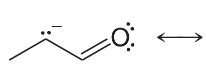
(g) 

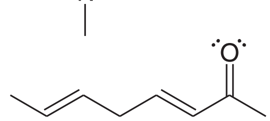
(b) 

(e) 

(h) 

(c) 

(f) 

(i) 

1.42 **(a)** Cyanic acid (H—O—C≡N) and isocyanic acid (H—N=C=O) differ in the positions of their electrons but their structures do not represent resonance structures. Explain. **(b)** Loss of a proton from cyanic acid yields the same anion as that obtained by loss of a proton from isocyanic acid. Explain.

1.43 Consider a chemical species (either a molecule or an ion) in which a carbon atom forms three single bonds to three hydrogen atoms and in which the carbon atom possesses no other valence electrons. **(a)** What formal charge would the carbon atom have? **(b)** What total charge would the species have? **(c)** What shape would you expect this species to have? **(d)** What would you expect the hybridization state of the carbon atom to be?

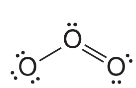
1.44 Consider a chemical species like the one in the previous problem in which a carbon atom forms three single bonds to three hydrogen atoms, but in which the carbon atom possesses an unshared electron pair. **(a)** What formal charge would the carbon atom have? **(b)** What total charge would the species have? **(c)** What shape would you expect this species to have? **(d)** What would you expect the hybridization state of the carbon atom to be?

1.45 Consider another chemical species like the ones in the previous problems in which a carbon atom forms three single bonds to three hydrogen atoms but in which the carbon atom possesses a single unpaired electron. **(a)** What formal charge would the carbon atom have? **(b)** What total charge would the species have? **(c)** Given that the shape of this species is trigonal planar, what would you expect the hybridization state of the carbon atom to be?

1.46 Draw a three-dimensional orbital representation for each of the following molecules, indicate whether each bond in it is a σ or π bond, and provide the hybridization for each non-hydrogen atom.

(a) CH_2O **(b)** $H_2C{=}CHCH{=}CH_2$ **(c)** $H_2C{=}C{=}C{=}CH_2$

1.47 Ozone (O_3) is found in the upper atmosphere where it absorbs highly energetic ultraviolet (UV) radiation and thereby provides the surface of Earth with a protective screen (cf. Section 10.11E). One possible resonance structure for ozone is the following:

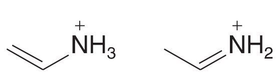


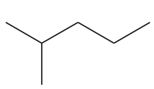
(a) Assign any necessary formal charges to the atoms in this structure. **(b)** Write another equivalent resonance structure for ozone. **(c)** What do these resonance structures predict about the relative lengths of the two oxygen–oxygen bonds of ozone? **(d)** In the structure above, and the one you have written, assume an angular shape for the ozone molecule. Is this shape consistent with VSEPR theory? Explain your answer.

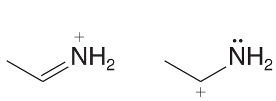
1.48 Write resonance structures for the azide ion, N_3^-. Explain how these resonance structures account for the fact that both bonds of the azide ion have the same length.

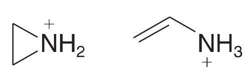
1.49 Write structural formulas of the type indicated: **(a)** bond-line formulas for seven constitutional isomers with the formula $C_4H_{10}O$; **(b)** condensed structural formulas for two constitutional isomers with the formula C_2H_7N; **(c)** condensed structural formulas for four constitutional isomers with the formula C_3H_9N; **(d)** bond-line formulas for three constitutional isomers with the formula C_5H_{12}.

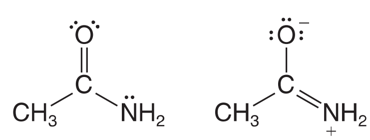
1.50 What is the relationship between the members of the following pairs? That is, are they constitutional isomers, the same, or something else (specify)?

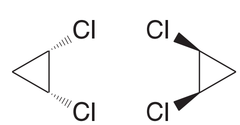
(a) 

(b)  $CH_3CH_2CH_2CH(CH_3)_2$

(c) 

(d) 

(e) 

(f) 

CHALLENGE PROBLEMS

1.51 In Chapter 15 we shall learn how the nitronium ion, NO_2^+, forms when concentrated nitric and sulfuric acids are mixed. **(a)** Write a Lewis structure for the nitronium ion. **(b)** What geometry does VSEPR theory predict for the NO_2^+ ion? **(c)** Give a species that has the same number of electrons as NO_2^+.

1.52 Given the following sets of atoms, write bond-line formulas for all of the possible constitutionally isomeric compounds or ions that could be made from them. Show all unshared electron pairs and all formal charges, if any.

Set	C atoms	H atoms	Other
A	3	6	2 Br atoms
B	3	9	1 N atom and 1 O atom (not on same C)
C	3	4	1 O atom
D	2	7	1 N atom and 1 proton
E	3	7	1 extra electron

1.53 **(a)** Consider a carbon atom in its ground state. Would such an atom offer a satisfactory model for the carbon of methane? If not, why not? (*Hint:* Consider whether a ground state carbon atom could be tetravalent, and consider the bond angles that would result if it were to combine with hydrogen atoms.)

(b) Consider a carbon atom in the excited state:

C ↿⇂ ↿ ↿ ↿ ↿
$1s$ $2s$ $2p_x$ $2p_y$ $2p_z$

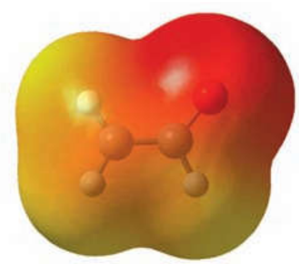
Excited state of a carbon atom

Would such an atom offer a satisfactory model for the carbon of methane? If not, why not?

1.54 Open computer molecular models for dimethyl ether, dimethylacetylene, and *cis*-1,2-dichloro-1,2-difluoroethene from the 3D Molecular Models section of the book's website. By interpreting the computer molecular model for each one, draw **(a)** a dash formula, **(b)** a bond-line formula, and **(c)** a three-dimensional dashed-wedge formula. Draw the models in whatever perspective is most convenient—generally the perspective in which the most atoms in the chain of a molecule can be in the plane of the paper.

1.55 Boron is a group IIIA element. Open the molecular model for boron trifluoride from the 3D Molecular Models section of the book's website. Near the boron atom, above and below the plane of the atoms in BF_3, are two relatively large lobes. Considering the position of boron in the periodic table and the three-dimensional and electronic structure of BF_3, what type of orbital does this lobe represent? Is it a hybridized orbital or not?

1.56 There are two contributing resonance structures for an anion called acetaldehyde enolate, whose condensed molecular formula is CH_2CHO^-. Draw the two resonance contributors and the resonance hybrid, then consider the map of electrostatic potential (MEP) shown below for this anion. Comment on whether the MEP is consistent or not with predominance of the resonance contributor you would have predicted to be represented most strongly in the hybrid.



LEARNING GROUP PROBLEMS

Consider the compound with the following condensed molecular formula:

$$CH_3CHOHCH{=}CH_2$$

Helpful Hint

Your instructor will tell you how to work these problems as a Learning Group.

1. Write a full dash structural formula for the compound.

2. Show all nonbonding electron pairs on your dash structural formula.

3. Indicate any formal charges that may be present in the molecule.

4. Label the hybridization state at every carbon atom and the oxygen.

5. Draw a three-dimensional perspective representation for the compound showing approximate bond angles as clearly as possible. Use ordinary lines to indicate bonds in the plane of the paper, solid wedges for bonds in front of the paper, and dashed wedges for bonds behind the paper.

6. Label all the bond angles in your three-dimensional structure.

7. Draw a bond-line formula for the compound.

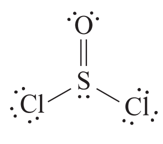
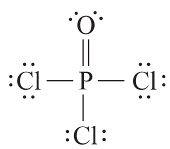
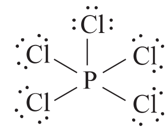
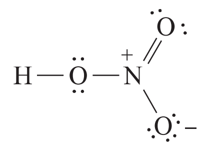
8. Devise two structures, each having two *sp*-hybridized carbons and the molecular formula C_4H_6O. Create one of these structures such that it is linear with respect to all carbon atoms. Repeat parts 1–7 above for both structures.

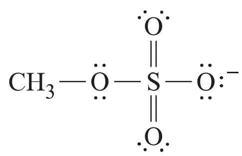
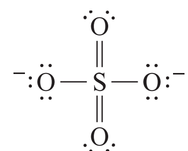
(e) Ca^{2+} has the electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$, of Ar.

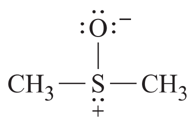
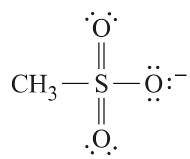
(f) S^{2-} has the electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$, of Ar.

(g) O^{2-} has the electronic configuration, $1s^2 2s^2 2p^6$, of Ne.

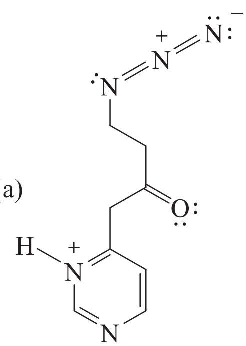
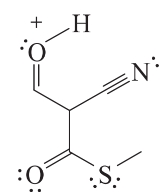
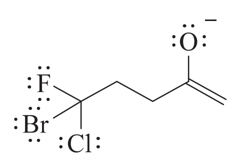
Lewis Structures

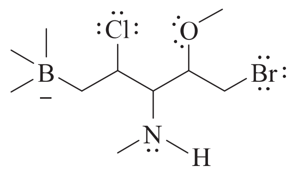
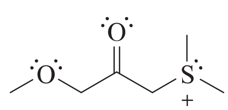
1.30 (a)  (b)  (c)  (d) 

1.31 (a)  (c) 

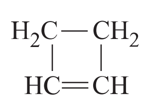
(b)  (d) 

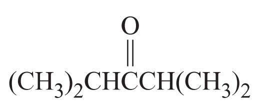
1.32

(a)  (b)  (c) 

(d)  (e) 

Structural Formulas and Isomerism

1.33 (a) $(CH_3)_2CHCH_2OH$ (c) 

(b)  (d) $(CH_3)_2CHCH_2CH_2OH$

1.34 (a) $C_4H_{10}O$ (c) C_4H_6

(b) $C_7H_{14}O$ (d) $C_5H_{12}O$

1.35 (a) Different compounds, not isomeric

(b) Same compound

(c) Same compound

(d) Same compound

(e) Same compound

(f) Constitutional isomers

(g) Different compounds, not isomeric

(h) Same compound

(i) Different compounds, not isomeric

(j) Same compound

(k) Constitutional isomers

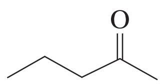
(l) Different compounds, not isomeric

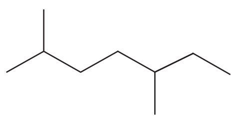
(m) Same compound

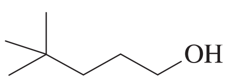
(n) Same compound

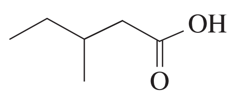
(o) Same compound

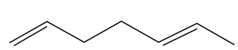
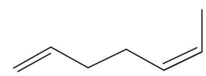
(p) Constitutional isomers

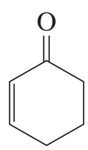
1.36 (a) 

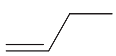
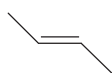
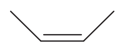
(b) 

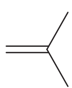
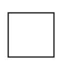
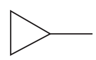
(c) 

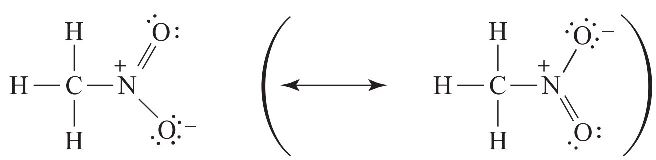
(d) 

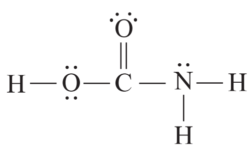
(e)  or 

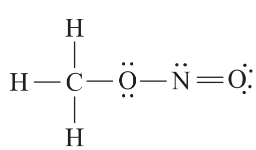
(f) 

1.37   

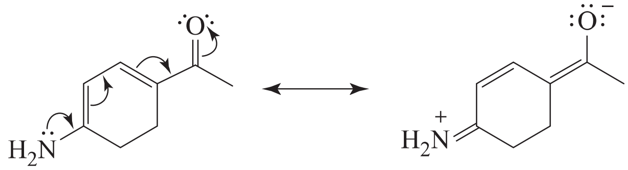
1.38 

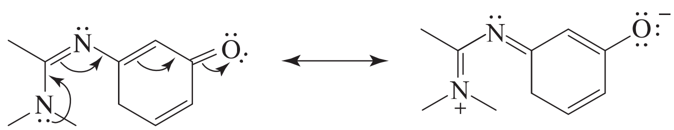


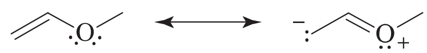


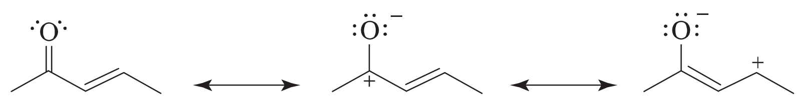
(Other structures are possible.)

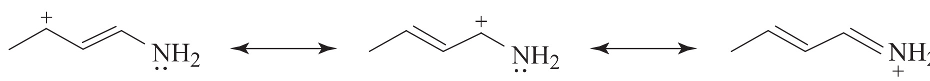
Resonance Structures

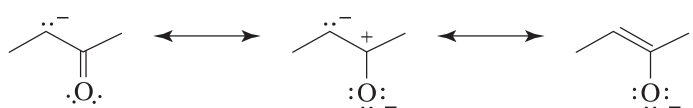
1.39 

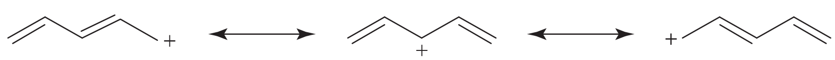
1.40 

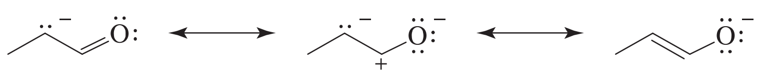
1.41 (a) 

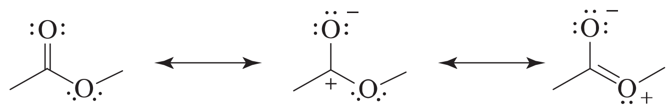
(b) 

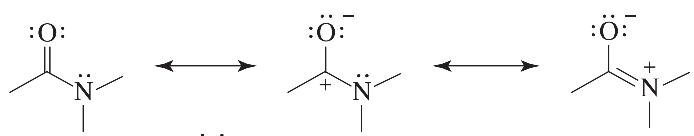
(c) 

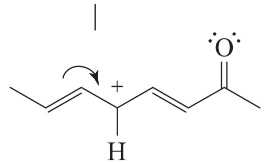
(d) 

(e) 

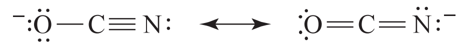
(f) 

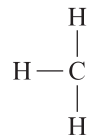
(g) 

(h) 

(i) 

1.42 (a) While the structures differ in the position of their electrons, they also differ in the positions of their nuclei and thus *they are not resonance structures*. (In cyanic acid the hydrogen nucleus is bonded to oxygen; in isocyanic acid it is bonded to nitrogen.)

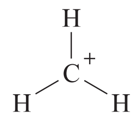
(b) The anion obtained from either acid is a resonance hybrid of the following structures: 

1.43 

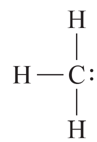
(a) A +1 charge. (F— 4 − $^6/_2$ − 2 = +1)

(b) A +1 charge. (It is called a methyl cation.)

(c) Trigonal planar, that is,



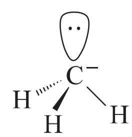
(d) sp^2

1.44 

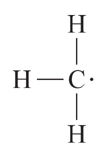
(a) A −1 charge. (F = 4 − 6/2 − 2 = −1)

(b) A −1 charge. (It is called a methyl anion.)

(c) Trigonal pyramidal, that is



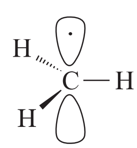
(d) sp^3

1.45 

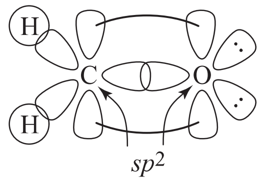
(a) No formal charge. (F = 4 − $^6/_2$ − 1 = 0)

(b) No charge.

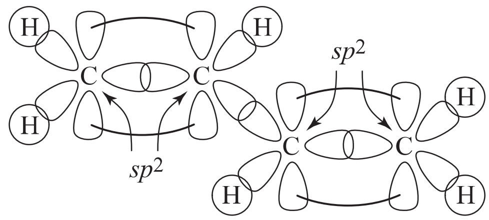
(c) sp^2, that is,



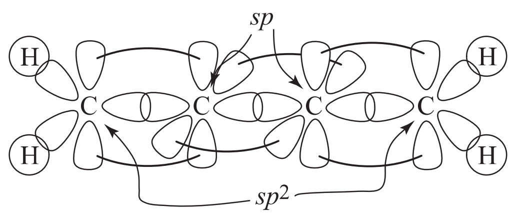
1.46 (a) H_2CO or CH_2O



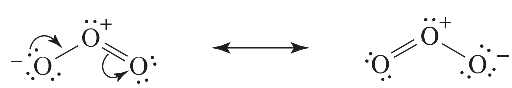
(b) $H_2C=CHCH=CH_2$



(c) $H_2C=C=C=CH_2$

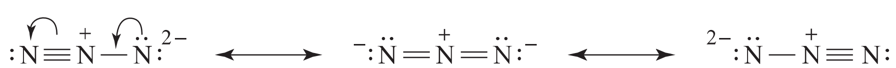


1.47 (a) and (b)



(c) Because the two resonance structures are equivalent, they should make equal contributions to the hybrid and, therefore, the bonds should be the same length.

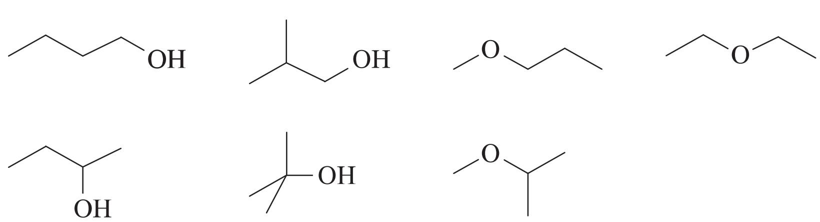
(d) Yes. We consider the central atom to have two groups or units of bonding electrons and one unshared pair.

1.48 

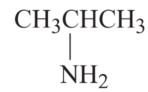
A **B** **C**

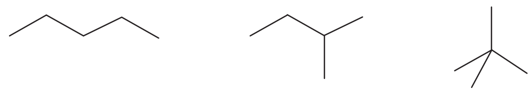
Structures **A** and **C** are equivalent and, therefore, make equal contributions to the hybrid. The bonds of the hybrid, therefore, have the same length.

1.49 (a)



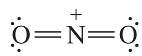
(b) $(CH_3)_2NH$ $CH_3CH_2NH_2$

(c) $(CH_3)_3N$ $CH_3CH_2NHCH_3$ $CH_3CH_2CH_2NH_2$ 

(d) 

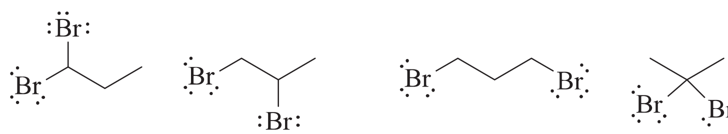
1.50 (a) constitutional isomers (b) the same
(c) resonance forms (d) constitutional isomers
(e) resonance forms (f) the same

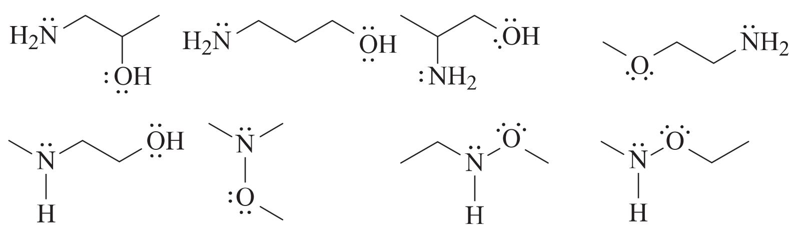
Challenge Problems

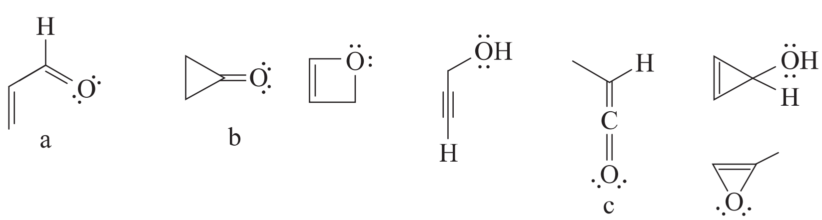
1.51 (a) 

(b) Linear

(c) Carbon dioxide

1.52 Set A: 

Set B: 

Set C: 

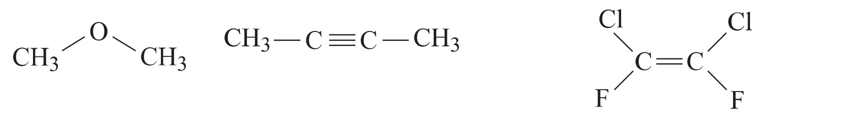
[and unstable enol forms of a, b, and c]

Set D: 

Set E:  (i.e., $CH_3CH_2\overset{-}{\ddot{C}}H_2$ and $CH_3\overset{-}{\ddot{C}}HCH_3$)

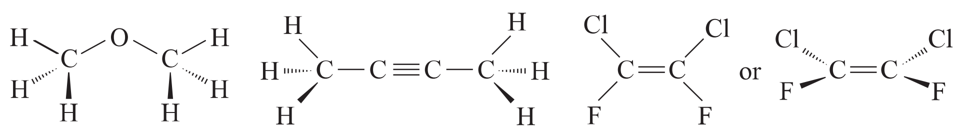
1.53 (a) No, a carbon atom in its ground state would have 2 electrons in the 1*s* orbital, 2 electrons in the 2*s* orbital, and only 2 unpaired electrons in the degenerate $2p_x$,$2p_y$, and $2p_z$ orbitals. So the two unpaired electrons can pair with only 2 hydrogen atoms with their one unpaired electron, respectively to form the compound CH_2 , which would be divalent and have 180 degree bond angles.
(b) In this case 4 unpaired electrons can combine with 4 hydrogen atoms to give CH_4, the correct bonding for methane, a tetravalent compound. However, the tetrahedral geometry known to exist for methane would not result from bonding at the 2*s* and three 2*p* orbitals in the excited state. Hybridized sp^3 orbitals are required for tetrahedral geometry.

1.54 (a) Dimethyl ether Dimethylacetylene *cis*-1,2-Dichloro-1,2-difluoroethene



(b)

(c)



1.55 The large lobes centered above and below the boron atom represent the 2*p* orbital that was not involved in hybridization to form the three $2sp^2$ hybrid orbitals needed for the three boron-fluorine covalent bonds. This orbital is not a pure 2*p* atomic orbital, since it is not an isolated atomic *p* orbital but rather part of a molecular orbital. Some of the other lobes in this molecular orbital can be seen near each fluorine atom.

1.56 The two resonance forms for this anion are $^{-}{:}CH_2{-}CH{=}\ddot{O}{:}$ and $CH_2{=}CH{-}\ddot{O}{:}^{-}$. The MEP indicates that the resonance contributor where the negative charge on the anion is on the oxygen is more important, which is what we would predict based on the fact that oxygen is more electronegative than carbon.

Resonance hybrid, $\overset{\delta-}{CH_2}\cdots CH \cdots \overset{\delta-}{O}$

QUIZ

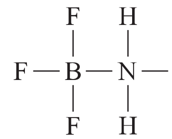
1.1 Which of the following is a valid Lewis dot formula for the nitrite ion (NO_2^-)?

(a) $^{-}{:}\ddot{\underset{..}{O}}{-}\ddot{N}{=}\ddot{O}{:}$ (b) ${:}\ddot{O}{=}\ddot{N}{-}\ddot{\underset{..}{O}}{:}^{-}$ (c) ${:}\ddot{\underset{..}{O}}{-}\ddot{N}{\equiv}\ddot{O}{:}$ (d) Two of these

(e) None of the above

1.2 What is the hybridization state of the boron atom in BF_3?

(a) *s* (b) *p* (c) *sp* (d) sp^2 (e) sp^3

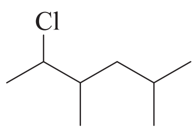
1.3 BF_3 reacts with NH_3 to produce a compound,  F—B—N—H. The hybridization state of B is

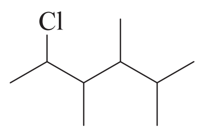
(a) *s* (b) *p* (c) *sp* (d) sp^2 (e) sp^3

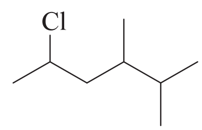
1.4 The formal charge on N in the compound given in Problem 1.3 is

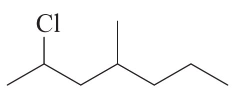
(a) −2 (b) −1 (c) 0 (d) +1 (e) +2

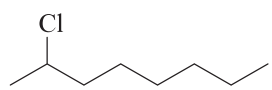
1.5 The correct bond-line formula of the compound whose condensed formula is $CH_3CHClCH_2CH(CH_3)CH(CH_3)_2$ is

(a) 

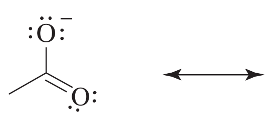
(b) 

(c) 

(d) 

(e) 

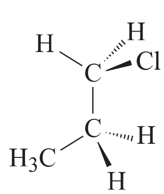
1.6 Write another resonance structure for the acetate ion.



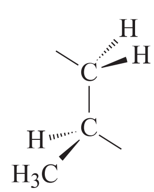
Acetate ion

1.7 In the boxes below write condensed structural formulas for constitutional isomers of $CH_3(CH_2)_3CH_3$.

1.8 Write a three-dimensional formula for a constitutional isomer of compound **A** given below. Complete the partial structure shown.



A



Constitutional isomer of A

1.9 Consider the molecule $(CH_3)_3B$ and give the following:

(a) Hybridization state of boron

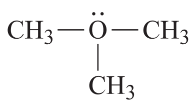
(b) Hybridization state of carbon atoms

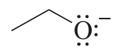
(c) Formal charge on boron

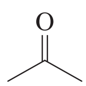
(d) Orientation of groups around boron

(e) Dipole moment of $(CH_3)_3B$

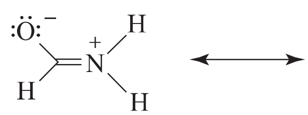
1.10 Give the formal charge on oxygen in each compound.

(a) 

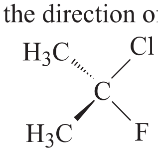
(c) 

(b) 

1.11 Write another resonance structure in which all of the atoms have a formal charge of zero.



1.12 Indicate the direction of the net dipole moment of the following molecule.



1.13 Write bond-line formulas for all compounds with the formula C_3H_6O.