1 THE BASICS: BONDING AND MOLECULAR STRUCTURE

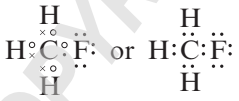
SOLUTIONS TO PROBLEMS

Another Approach to Writing Lewis Structures

When we write Lewis structures using this method, we assemble the molecule or ion from the constituent atoms showing only the valence electrons (i.e., the electrons of the outermost shell). By having the atoms share electrons, we try to give each atom the electronic structure of a noble gas. For example, we give hydrogen atoms two electrons because this gives them the structure of helium. We give carbon, nitrogen, oxygen, and fluorine atoms eight electrons because this gives them the electronic structure of neon. The number of valence electrons of an atom can be obtained from the periodic table because it is equal to the group number of the atom. Carbon, for example, is in Group IVA and has four valence electrons; fluorine, in Group VIIA, has seven; hydrogen, in Group 1A, has one. As an illustration, let us write the Lewis structure for CH_3F. In the example below, we will at first show a hydrogen's electron as x, carbon's electrons as o's, and fluorine's electrons as dots.

Example A

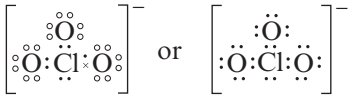
3 $H^{\times}$, $\cdot\overset{\circ}{\underset{\circ}{C}}\cdot$, and $\cdot\ddot{F}:$ are assembled as



If the structure is an ion, we add or subtract electrons to give it the proper charge. As an example, consider the chlorate ion, ClO_3^-.

Example B

$:\ddot{Cl}\cdot$, $:\overset{\circ}{\underset{\circ}{O}}:$, and an extra electron $\times$ are assembled as



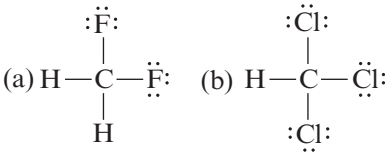
1.1 ^{14}N, seven protons and seven neutrons; ^{15}N, seven protons and eight neutrons

1.2 (a) one (b) seven (c) four (d) three (e) eight (f) five

1.3 (a) O (b) N (c) Cl (d) S

1.4 (a) ionic (b) covalent (c) covalent (d) covalent

1.5



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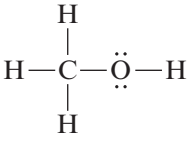

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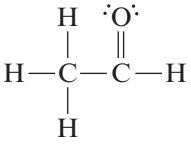

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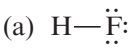
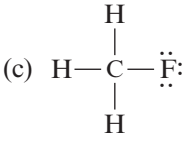


(b)

(c)



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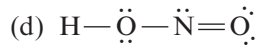

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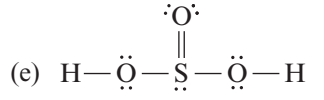

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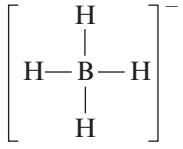

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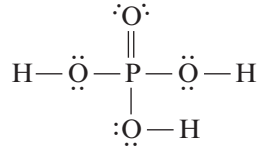

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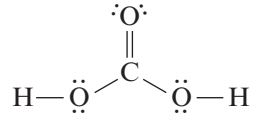

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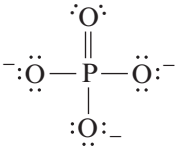
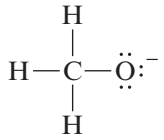
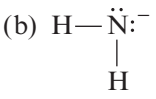
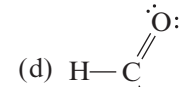


1.10 (a) 

(b) 

(c) 

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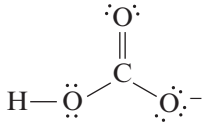
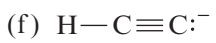
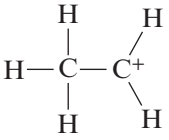
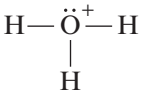
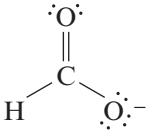
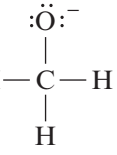
(e) 

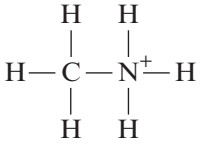
(f) 

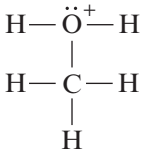
1.11 (a) 

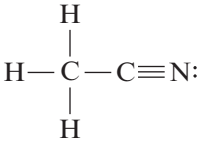
(b) 

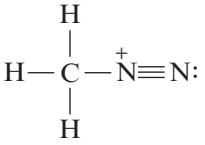
(c) 

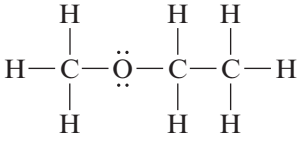
(d) 

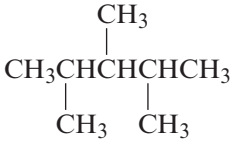
(e) 

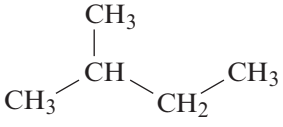
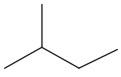
(f) 

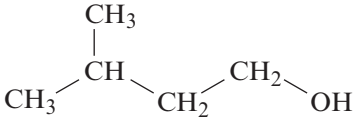
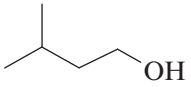
(g) 

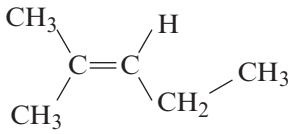
(h) 

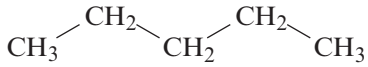
1.12 

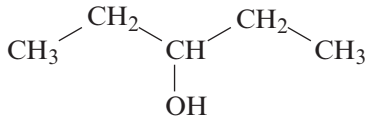
1.13  or $(CH_3)_2CHCH(CH_3)CH(CH_3)_2$

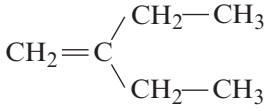
1.14 (a)  = 

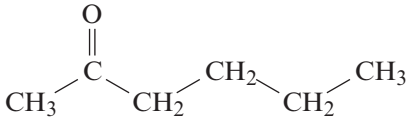
(b)  = 

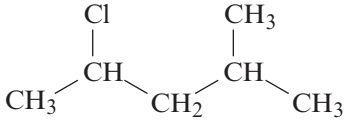
(c)  =

(d)  =

(e)  =

(f)  =

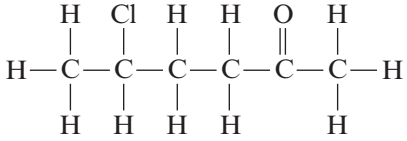
(g)  =

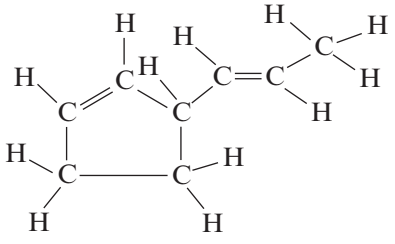
(h)  =

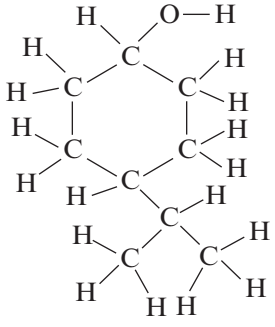
1.15 (a) and (d) are constitutional isomers with the molecular formula C_5H_{12}.

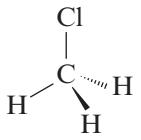
(b) and (e) are constitutional isomers with the molecular formula $C_5H_{12}O$.

(c) and (f) are constitutional isomers with the molecular formula C_6H_{12}.

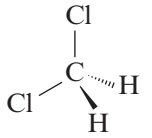
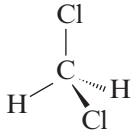
1.16 (a) 

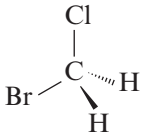
(c) 

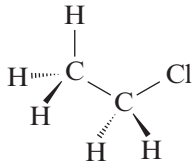
(b) 

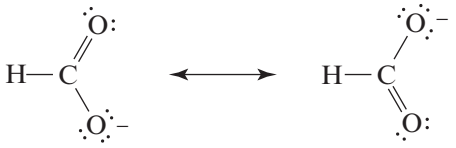
1.17 (a) 

(Note that the **Cl** atom and the three **H** atoms may be written at any of the four positions.)

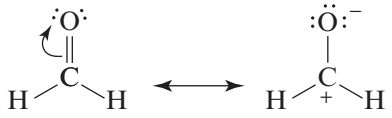
(b)  or  and so on

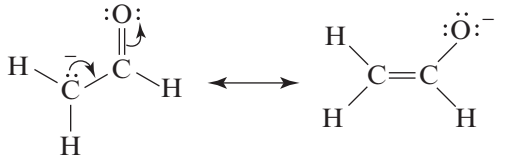
(c)  and others

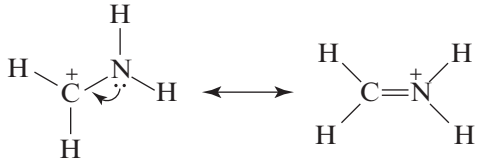
(d)  and others

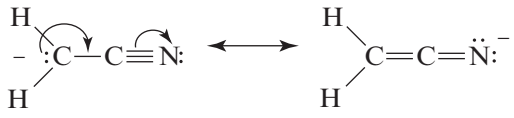
1.18 (a) 

(b) and (c). Since the two resonance structures are equivalent, each should make an equal contribution to the overall hybrid. The C—O bonds should therefore be of equal length (they should be of bond order 1.5), and each oxygen atom should bear a 0.5 negative charge.

1.19 (a) 

(b) 

(c) 

(d) 

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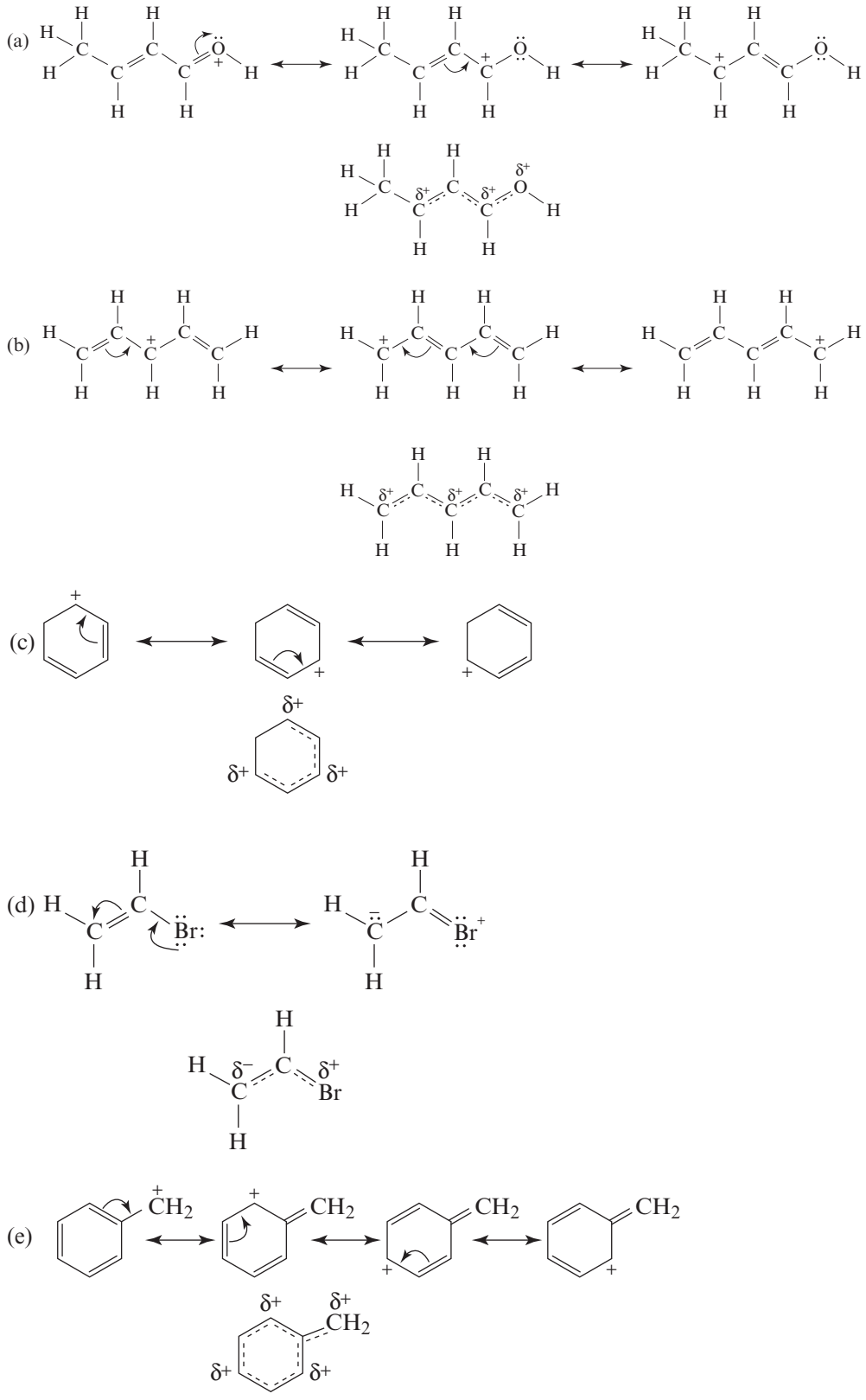

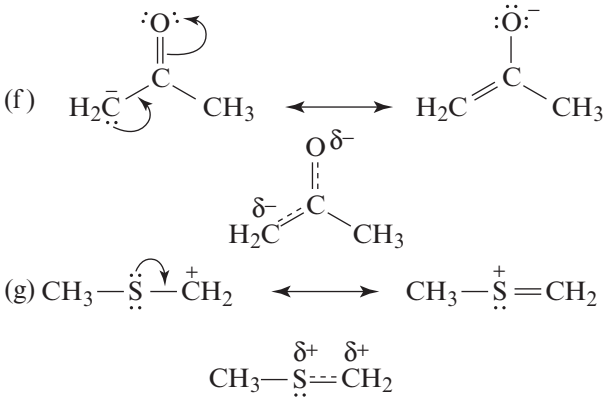

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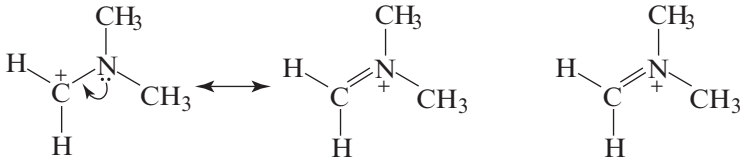
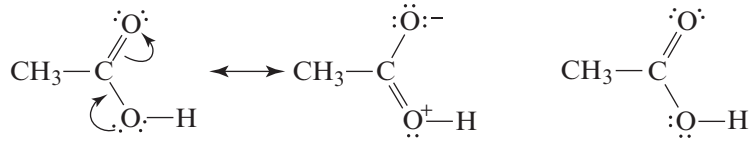


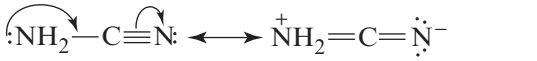
because all atoms have a complete octet (rule 3), and there are more covalent bonds (rule 1).

(b)



because it has no charge separation (rule 2).

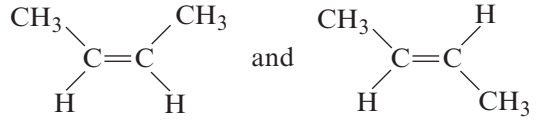
(c)



because it has no charge separation (rule 2).

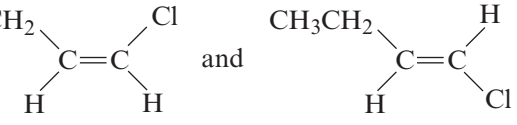
1.22 (a) Cis-trans isomers are not possible.

(b)



(c) Cis-trans isomers are not possible.

(d)



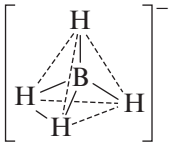
1.23 sp^3

1.24 sp^3

1.25 sp^2

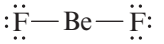
1.26 *sp*

1.27 (a)



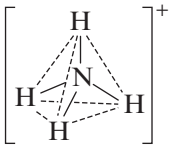
There are four bonding pairs.
The geometry is tetrahedral.

(b)



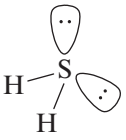
There are two bonding pairs about the central atom. The geometry is linear.

(c)



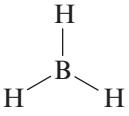
There are four bonding pairs.
The geometry is tetrahedral.

(d)



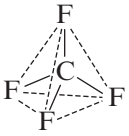
There are two bonding pairs and two nonbonding pairs.
The geometry is tetrahedral and the shape is angular.

(e)



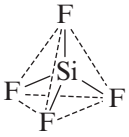
There are three bonding pairs. The geometry is trigonal planar.

(f)



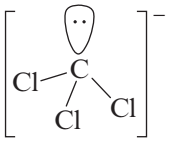
There are four bonding pairs around the central atom. The geometry is tetrahedral.

(g)



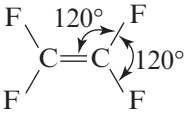
There are four bonding pairs around the central atom.
The geometry is tetrahedral.

(h)



There are three bonding pairs and one nonbonding pair around the central atom. The geometry is tetrahedral and the shape is trigonal pyramidal.

1.28 (a)



trigonal planar at each carbon atom

(b) $CH_3-C\equiv C-CH_3$ linear (c) $H-C\equiv N:$ linear

Problems

Electron Configuration

1.29 (a) Na^+ has the electronic configuration, $1s^2 2s^2 2p^6$, of Ne.

(b) Cl^- has the electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$, of Ar.

(c) F^+ and (h) Br^+ do not have the electronic configuration of a noble gas.

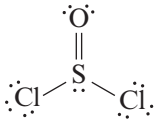
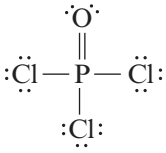
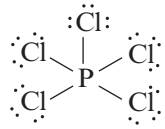
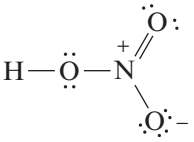
(d) H^- has the electronic configuration, $1s^2$, of He.

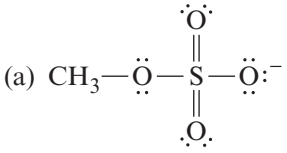
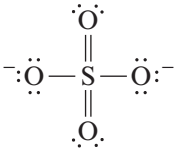
(e) Ca^{2+} has the electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$, of Ar.

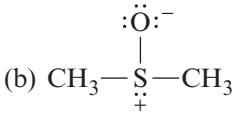
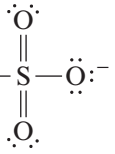
(f) S^{2-} has the electronic configuration, $1s^2 2s^2 2p^6 3s^2 3p^6$, of Ar.

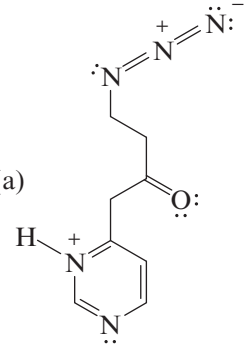
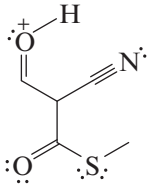
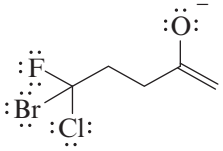
(g) O^{2-} has the electronic configuration, $1s^2 2s^2 2p^6$, of Ne.

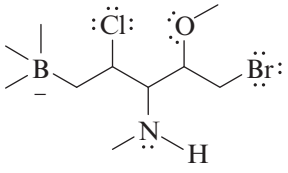
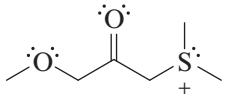
Lewis Structures

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) $(CH_3)_2CHCH_2\ddot{O}H$

(b) $(CH_3)_2CH\overset{\cdot\cdot}{\underset{\|}{C}}CH(CH_3)_2$

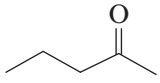
(c) $H_2C(-CH_2)-HC=CH$

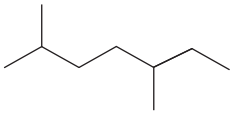
(d) $(CH_3)_2CHCH_2CH_2\ddot{O}H$

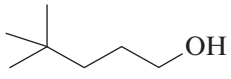
1.34 (a) $C_4H_{10}O$ (c) C_4H_6

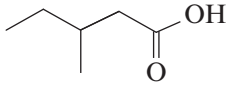
(b) $C_7H_{14}O$ (d) $C_5H_{12}O$

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

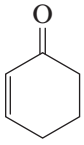
1.36 (a) 

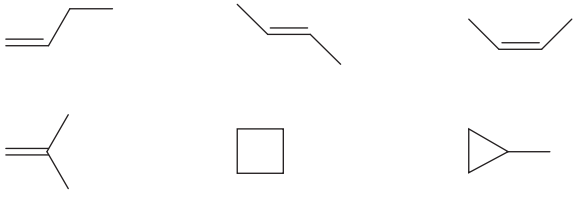
(b) 

(c) 

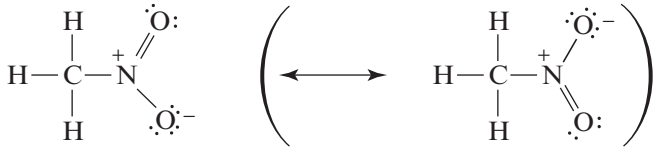
(d) 

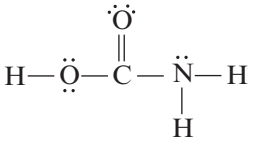
(e) 

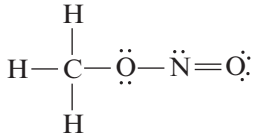
(f) 

1.37 

1.38



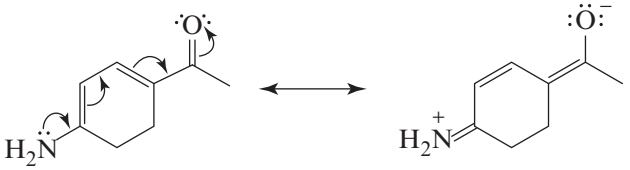




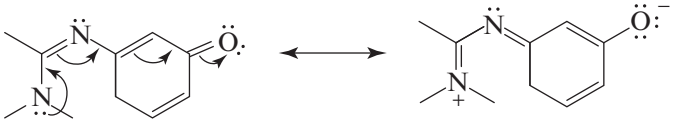
(Other structures are possible.)

Resonance Structures

1.39



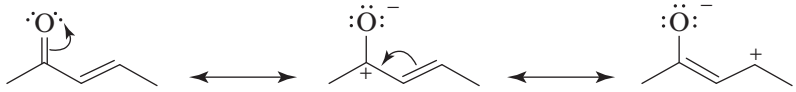
1.40



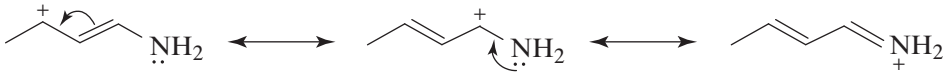
1.41

(a)

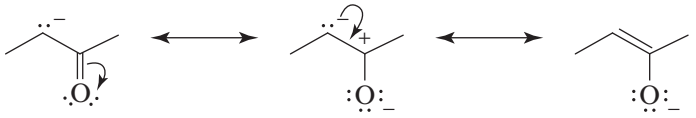
(b)



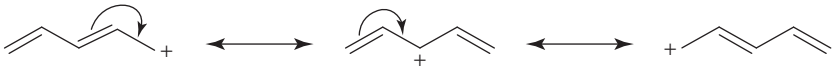
(c)



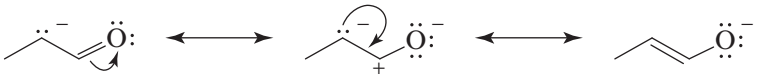
(d)



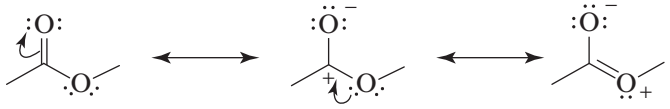
(e)



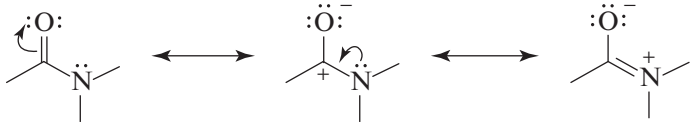
(f)



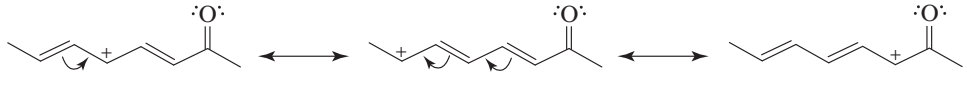
(g)



(h)



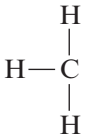
(i)



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:

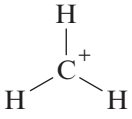
1.43



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

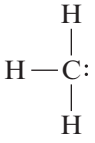
(b) A +1 charge. (It is called a methyl cation.)

(c) Trigonal planar, that is,



(d) sp^2

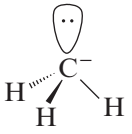
1.44



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

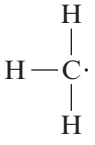
(b) A −1 charge. (It is called a methyl anion.)

(c) Trigonal pyramidal, that is



(d) sp^3

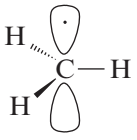
1.45



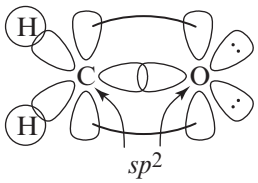
(a) No formal charge. ($F = 4 - 6/2 - 1 = 0$)

(b) No charge.

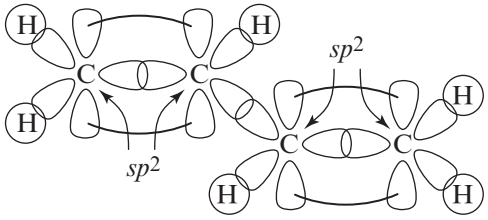
(c) sp^2, that is,



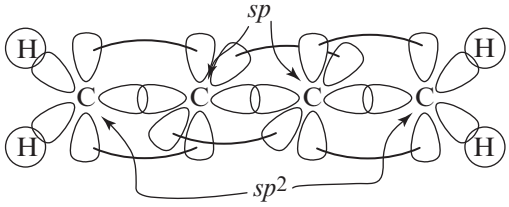
1.46 (a) H_2CO or CH_2O



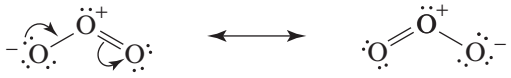
(b) $H_2C=CHCH=CH_2$



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



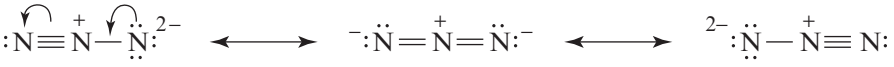
1.47 (a) and (b)



(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.

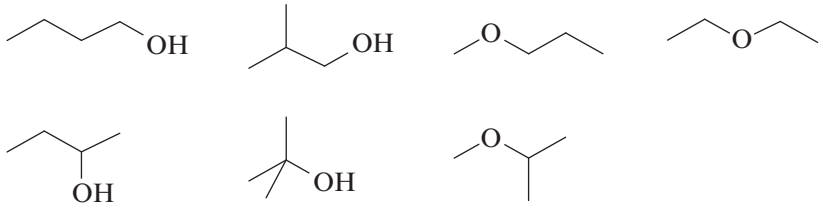
1.48



A **B** **C**

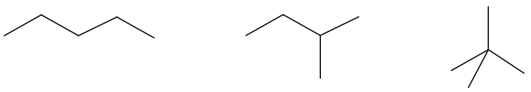
Structures **A** and **C** are equivalent and, therefore, make equal contributions to the hybrid. The bonds of the hybrid, therefore, have the same length.

1.49 (a)



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

(c) $(CH_3)_3N$ $CH_3CH_2NHCH_3$ $CH_3CH_2CH_2NH_2$ CH_3CHCH_3 (NH$_2$)

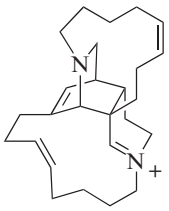
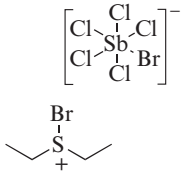
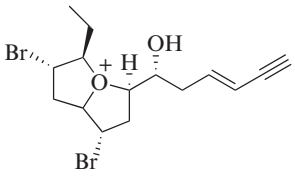
(d) 

1.50 (a) constitutional isomers (b) the same

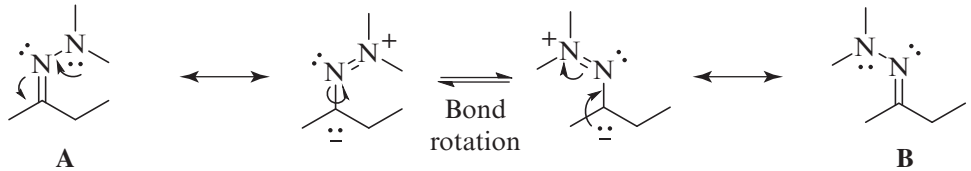
(c) resonance forms (d) constitutional isomers

(e) resonance forms (f) the same

Chemical Consultant Needed

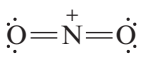
1.51 (a)  (b)  (c) 

1.52 The reason for the equilibration is to relieve steric strain. A methyl group is smaller than an ethyl group in terms of the atoms to which the main functional group (a hydrazone) is attached, so that is why **B** is preferred. The shown movement of electrons by simple resonance can allow for equilibration by scrambling the initial stereochemical disposition of **A**.



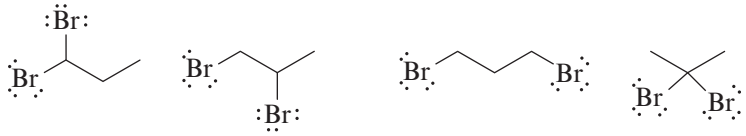
A **B**

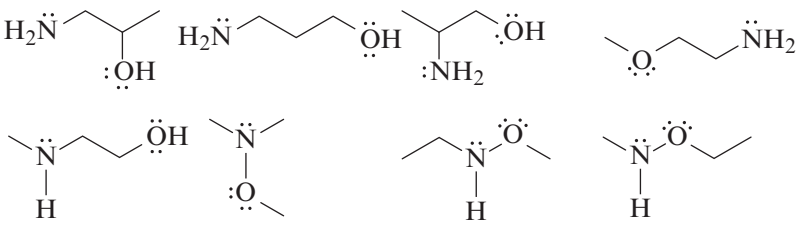
Challenge Problems

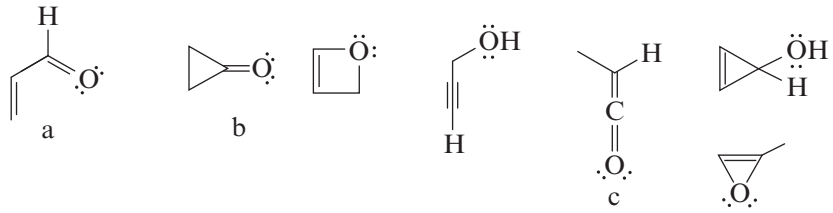
1.53 (a) 

(b) Linear

(c) Carbon dioxide

1.54 Set A: 

Set B: 

Set C: 

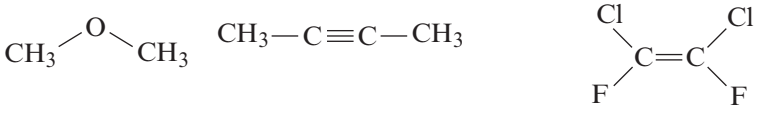
[and unstable enol forms of a, b, and c]

Set D: 

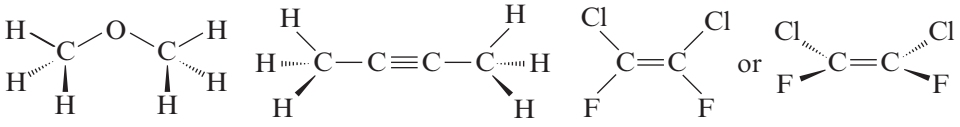
Set E:  (i.e., $CH_3CH_2\ddot{C}H_2$ and $CH_3\ddot{C}HCH_3$)

1.55 (a) No, a carbon atom in its ground state would have two electrons in the 1*s* orbital, two electrons in the 2*s* orbital, and only two unpaired electrons in the degenerate $2p_x$, $2p_y$, and $2p_z$ orbitals. So the two unpaired electrons can pair with only two hydrogen atoms with their one unpaired electron, respectively, to form the compound CH_2, which would be divalent and have 180° bond angles.
(b) In this case four unpaired electrons can combine with four 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.

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



(b) 

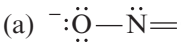
(c) 

1.57 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.

1.58 The two resonance forms for this anion are $^{-}{:}CH_2{-}CH{=}\ddot{O}{:}$ and $CH_2{=}CH{-}\ddot{\underset{\cdot\cdot}{O}}{:}^{-}$.
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, $\overset{\delta-}{C}H_2{-}CH{-}\overset{\delta-}{O}$

QUIZ

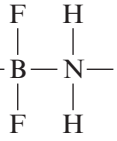
1.1 Which of the following is a valid Lewis dot formula for the nitrite ion (NO_2^-)?

(a)  (b) (c) (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

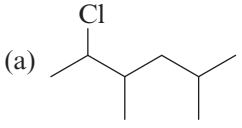
1.3 BF_3 reacts with NH_3 to produce a compound,  . The hybridization state of B is

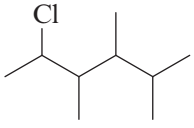
(a) *s* (b) *p* (c) *sp* (d) sp^2 (e) sp^3

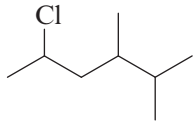
1.4 The formal charge on N in the compound given in Problem 1.3 is

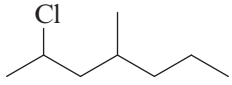
(a) -2 (b) -1 (c) 0 (d) $+1$ (e) $+2$

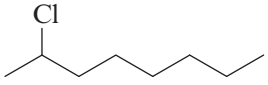
1.5 The correct bond-line formula of the compound whose condensed formula is $CH_3CHClCH_2CH(CH_3)CH(CH_3)_2$ is

(a) 

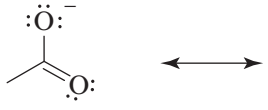
(b) 

(c) 

(d) 

(e) 

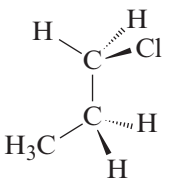
1.6 Write another resonance structure for the acetate ion.



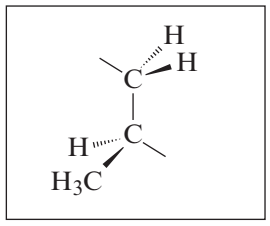
Acetate ion

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

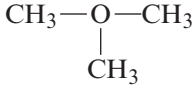
(b) Hybridization state of carbon atoms

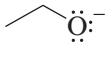
(c) Formal charge on boron

(d) Orientation of groups around boron

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

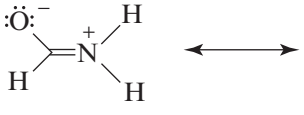
1.10 Give the formal charge on oxygen in each compound.

(a) 

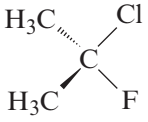
(c) 

(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.