

1 THE BASICS: BONDING AND MOLECULAR STRUCTURE

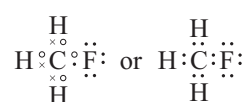
SOLUTIONS TO PROBLEMS

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 IA, 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

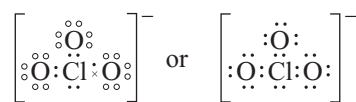
3H^x , ${}^{\circ}\text{C}^{\circ}$, and ${}^{\cdot}\text{F}^{\cdot}$ are assembled as



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

${}^{\cdot}\text{Cl}^{\cdot}$, and ${}^{\circ}\text{O}^{\circ}$ and an extra electron \times are assembled as

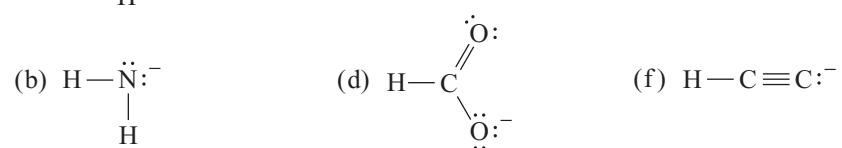
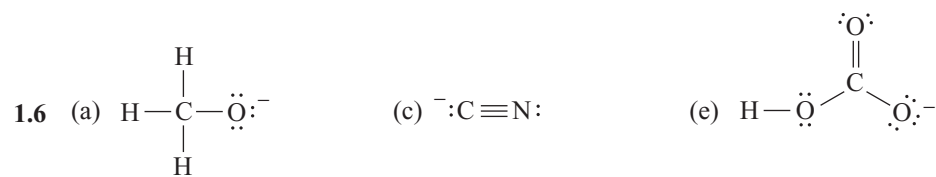
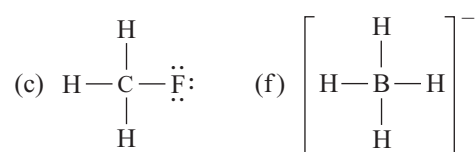
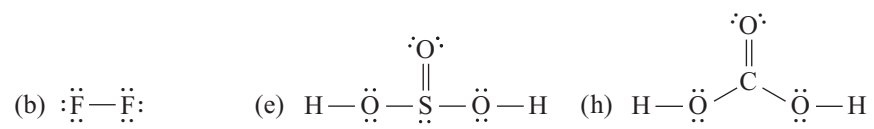
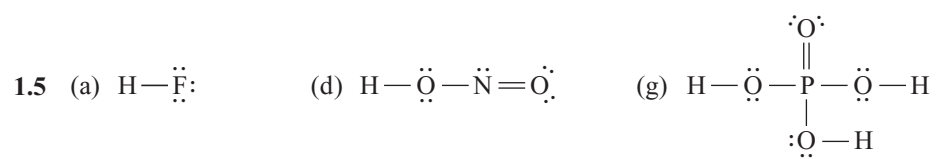
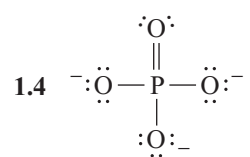


2 THE BASICS: BONDING AND MOLECULAR STRUCTURE

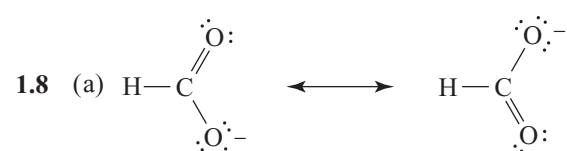
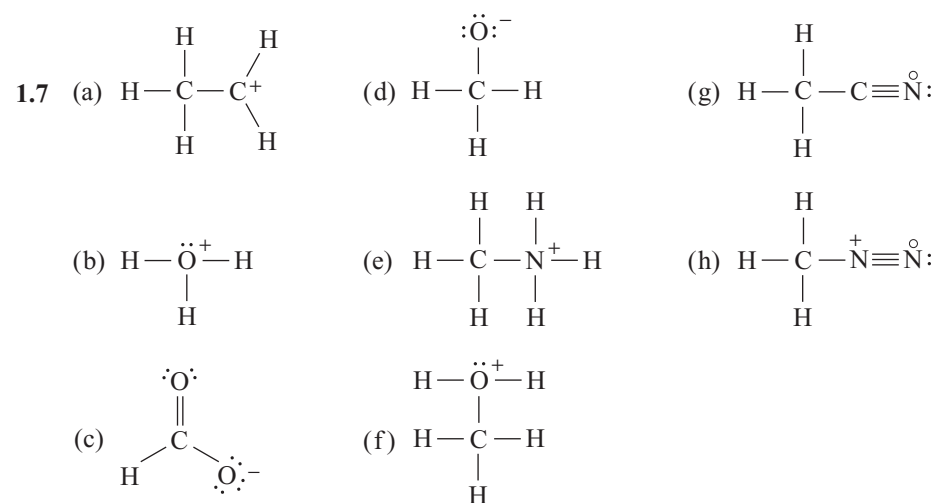
1.1 ^{14}N , 7 protons and 7 neutrons; ^{15}N , 7 protons and 8 neutrons

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

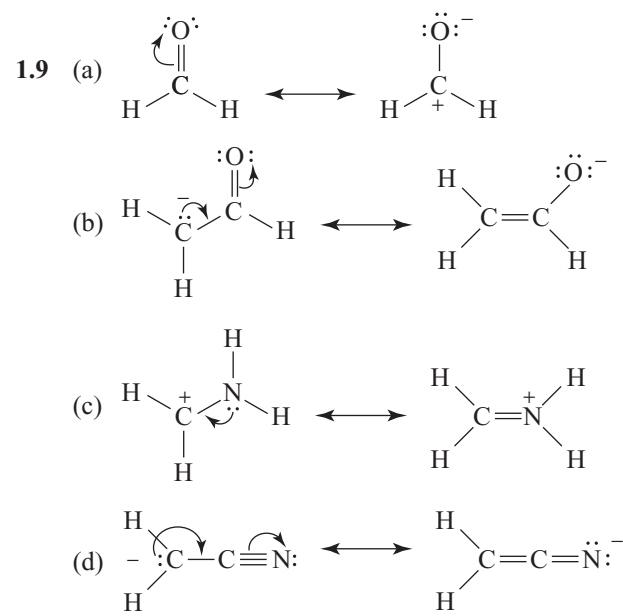
1.3 (a) covalent (b) ionic (c) covalent (d) covalent



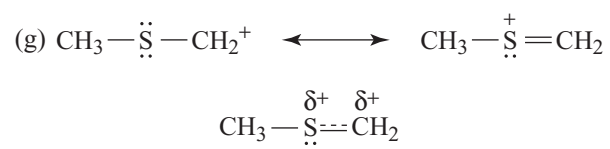
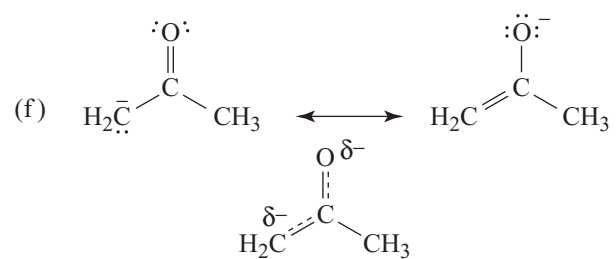
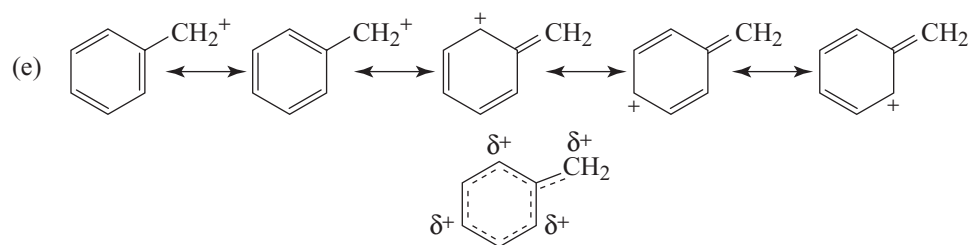
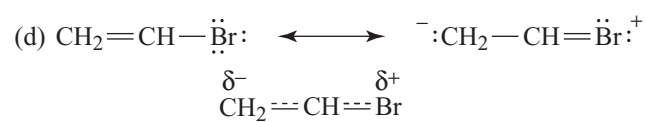
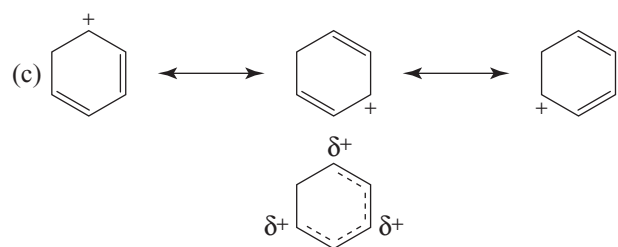
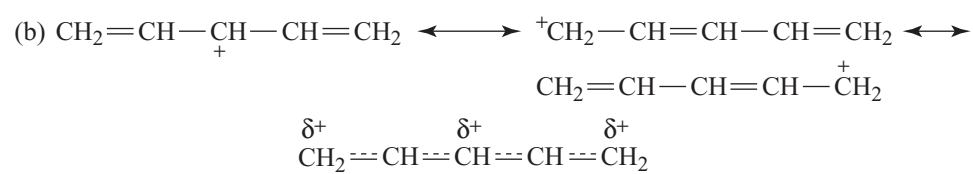
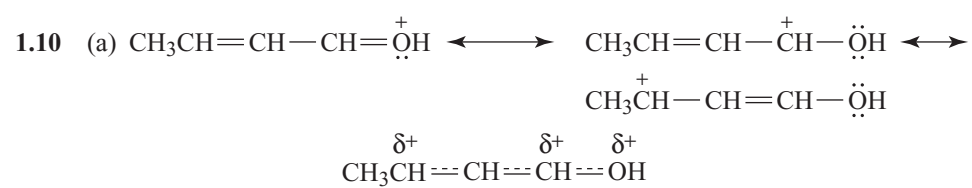
THE BASICS: BONDING AND MOLECULAR STRUCTURE 3



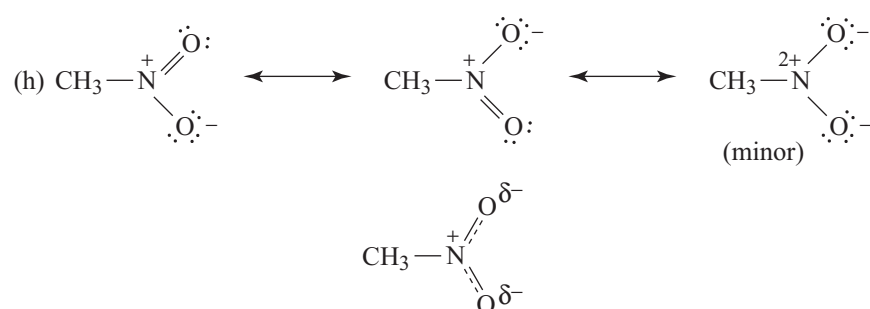
(b) and (c). Since the two resonance structures are equivalent, each should make an equal contribution to the overall hybrid. The C—O bonds should therefore be of equal length (they should be of bond order 1.5), and each oxygen atom should bear a 0.5 negative charge.



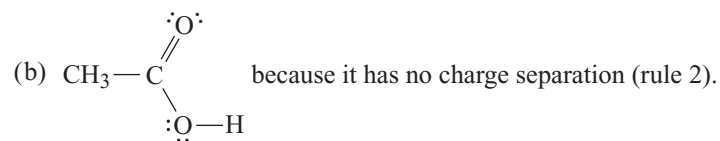
4 THE BASICS: BONDING AND MOLECULAR STRUCTURE



THE BASICS: BONDING AND MOLECULAR STRUCTURE 5

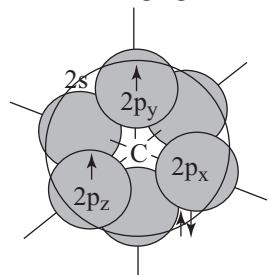


- 1.11 (a) $\text{CH}_2=\overset{+}{\text{N}}(\text{CH}_3)_2$ because all atoms have a complete octet (rule 3), and there are more covalent bonds (rule 1).



- (c) $:\text{NH}_2-\text{C}\equiv\text{N}:$ because it has no charge separation (rule 2).

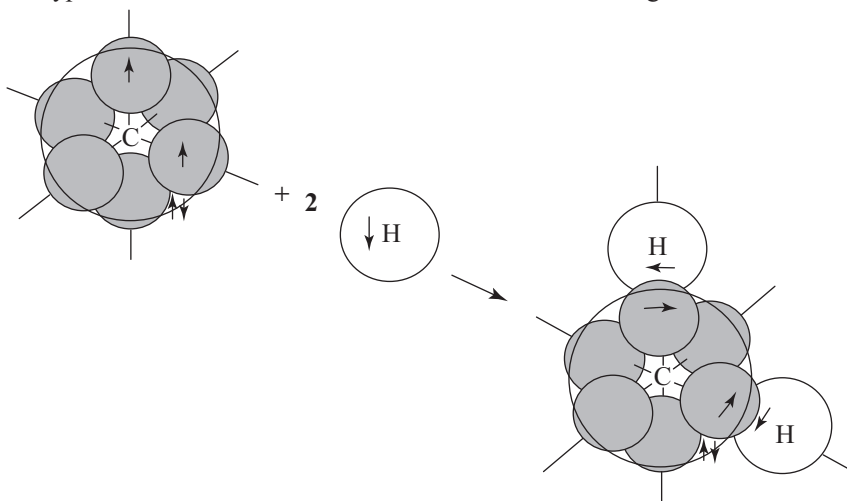
- 1.12 (a) In its ground state, the valence electrons of carbon might be disposed as shown in the following figure.



The electronic configuration of a ground state carbon atom: The p orbitals are designated $2p_x$, $2p_y$, and $2p_z$ to indicate their respective orientations along the x , y , and z axes. The assignment of the unpaired electrons to the $2p_y$ and $2p_x$ orbitals is arbitrary. They could also have been placed in the $2p_x$ and $2p_z$ or $2p_y$ and $2p_z$ orbitals. (To have placed them both in the same orbital would not have been correct, however, for this would have violated Hund's rule.) (Section 1.10A)

The formation of the covalent bonds of methane from individual atoms requires that the carbon atom overlap its orbitals containing single electrons with $1s$ orbitals of hydrogen atoms (which also contain a single electron). If a ground state carbon atom were to combine with hydrogen atoms in this way, the result would be that depicted below. Only two carbon-hydrogen bonds would be formed, and these would be at right angles to each other.

The hypothetical formation of CH_2 from a carbon atom in its ground state:

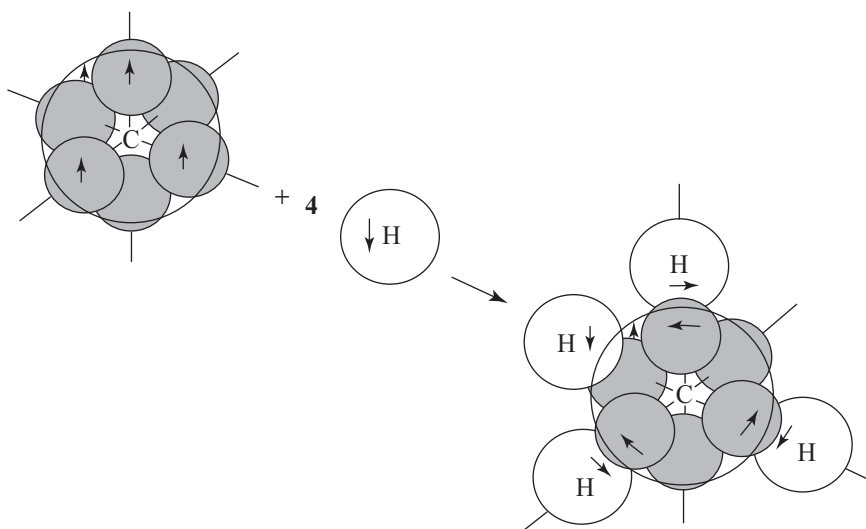


6 THE BASICS: BONDING AND MOLECULAR STRUCTURE

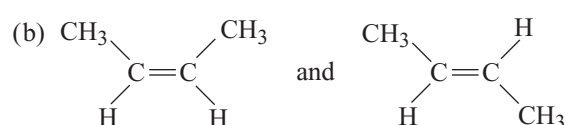
- (b) An excited-state carbon atom might combine with four hydrogen atoms as shown in the figure above.

The promotion of an electron from the $2s$ orbital to the $2p_z$ orbital requires energy. The amount of energy required has been determined and is equal to 400 kJ mol^{-1} . This expenditure of energy can be rationalized by arguing that the energy released when two additional covalent bonds form would more than compensate for that required to excite the electron. No doubt this is true, but it solves only one problem. The problems that cannot be solved by using an excited-state carbon as a basis for a model of methane are the problems of the carbon-hydrogen bond angles and the apparent equivalence of all four carbon-hydrogen bonds. Three of the hydrogens—those overlapping their $1s$ orbitals with the three p orbitals—would, in this model, be at angles of 90° with respect to each other; the fourth hydrogen, the one overlapping its $1s$ orbital with the $2s$ orbital of carbon, would be at some other angle, probably as far from the other bonds as the confines of the molecule would allow. Basing our model of methane on this excited state of carbon gives us a carbon that is tetravalent *but one that is not tetrahedral*, and it predicts a structure for methane in which one carbon-hydrogen bond differs from the other three.

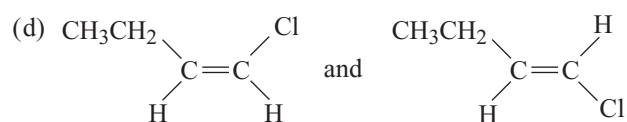
The hypothetical formation of CH_4 from an excited-state carbon atom:



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



- (c) Cis-trans isomers are not possible.



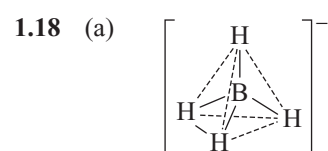
THE BASICS: BONDING AND MOLECULAR STRUCTURE 7

1.14 sp^3

1.15 sp^3

1.16 sp^2

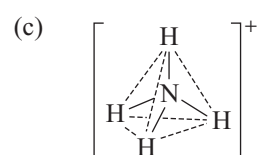
1.17 sp



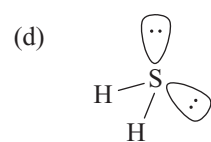
There are four bonding pairs.
The geometry is tetrahedral.



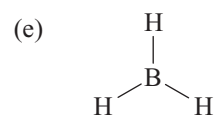
There are two bonding pairs about
the central atom. The geometry is linear.



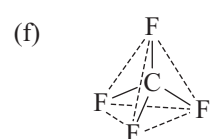
There are four bonding pairs.
The geometry is tetrahedral.



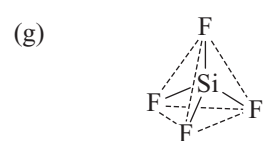
There are two bonding pairs and two
nonbonding pairs. The geometry is angular.



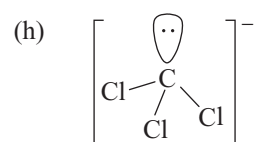
There are three bonding pairs. The geometry
is trigonal planar.



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

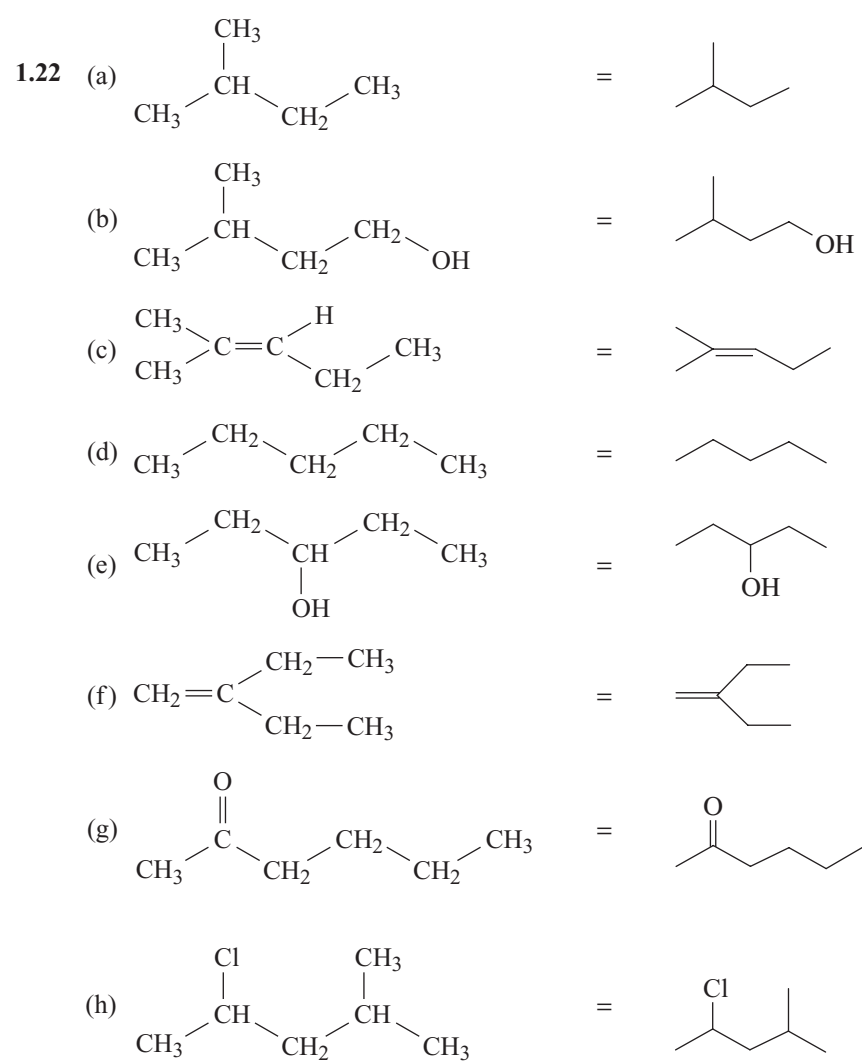
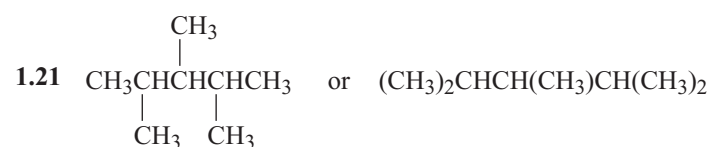
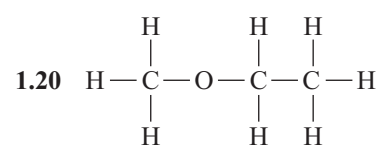
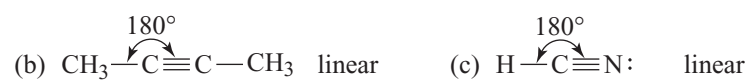


There are four bonding pairs around the central atom.
The geometry is tetrahedral.



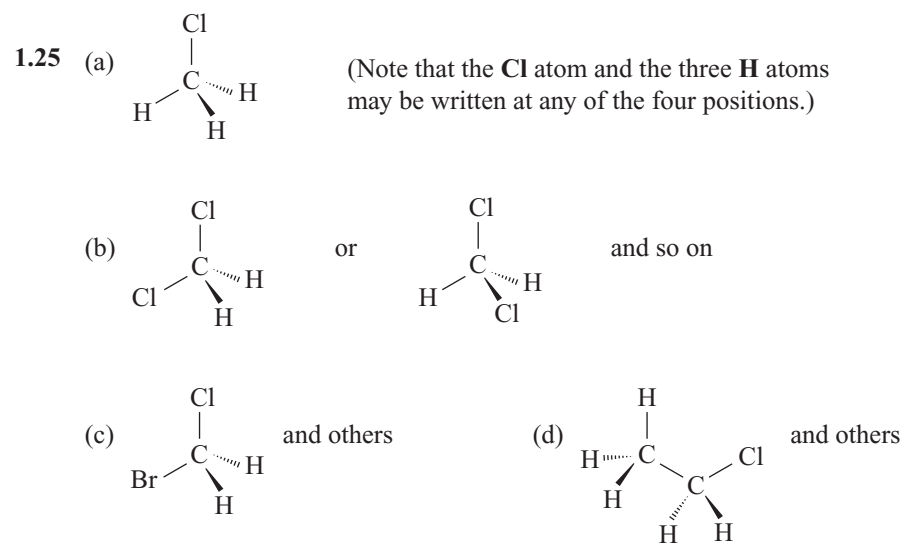
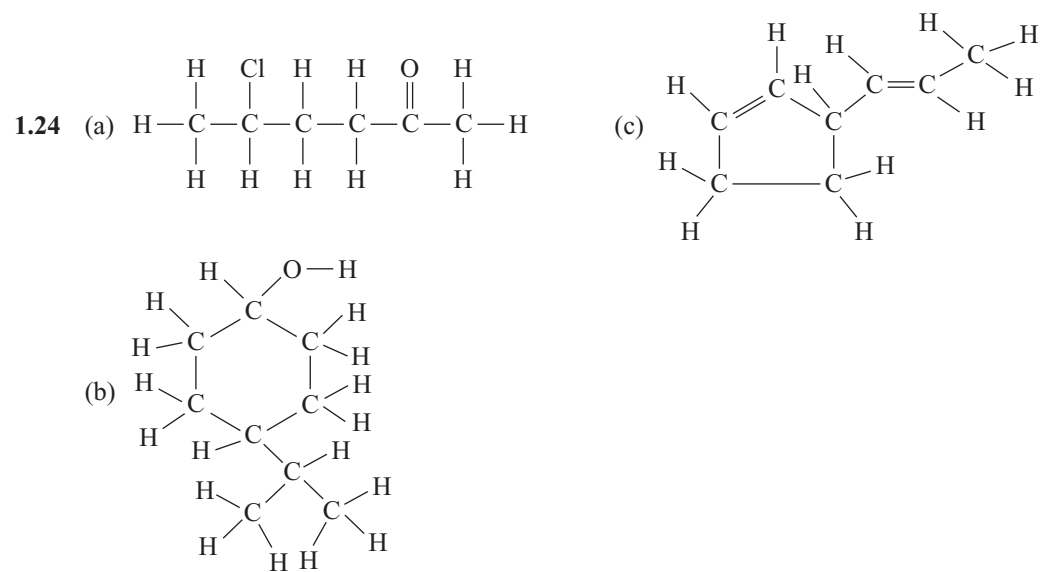
There are three bonding pairs and one nonbonding pair
around the central atom. The geometry is trigonal pyramidal.

8 THE BASICS: BONDING AND MOLECULAR STRUCTURE



THE BASICS: BONDING AND MOLECULAR STRUCTURE 9

- 1.23 (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} .



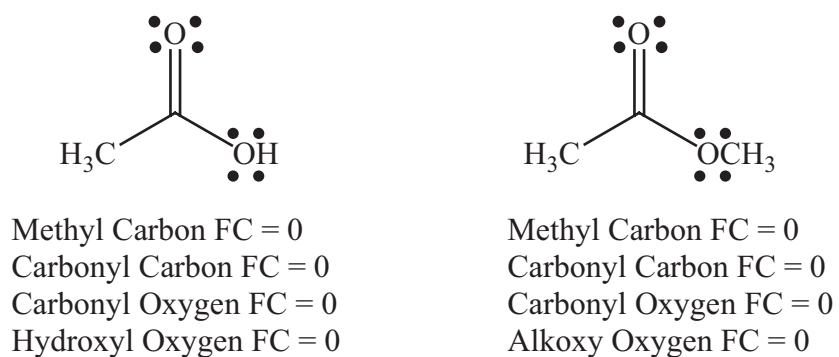
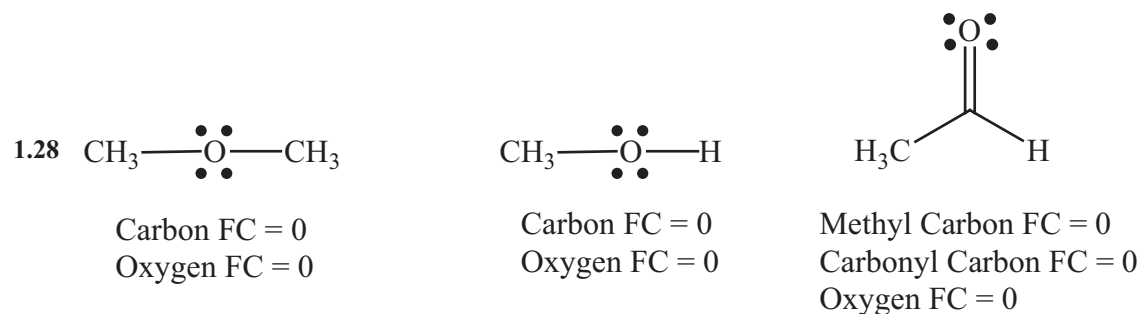
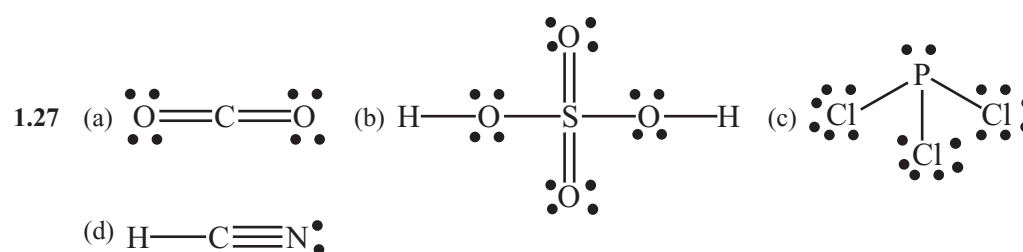
10 THE BASICS: BONDING AND MOLECULAR STRUCTURE

Problems

Electron Configuration

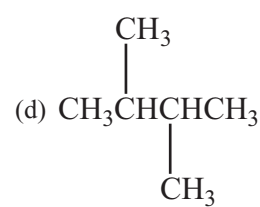
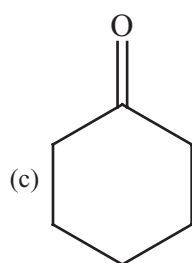
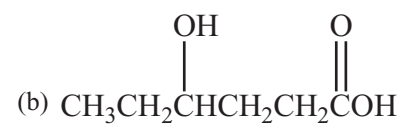
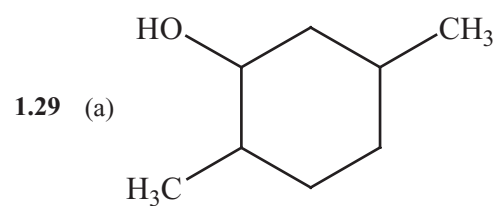
1.26 (a) no (b) yes (c) yes (d) no (e) yes (f) yes (g) yes (h) yes

Lewis Structures



THE BASICS: BONDING AND MOLECULAR STRUCTURE 11

Structural Formulas and Isomerism

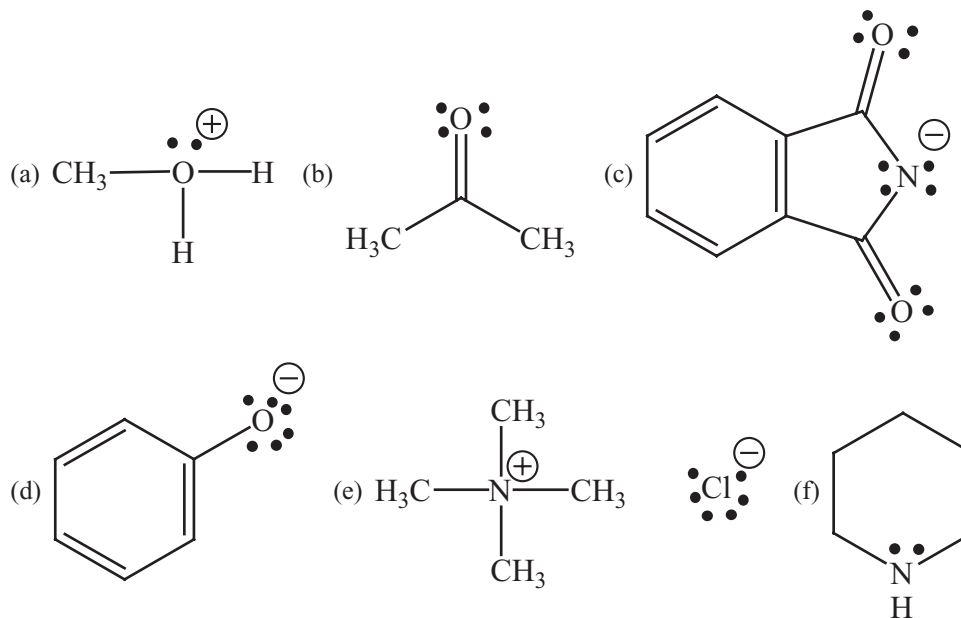


- 1.30 (a) $\text{C}_8\text{H}_{16}\text{O}$ (c) $\text{C}_6\text{H}_{10}\text{O}$
(b) $\text{C}_6\text{H}_{12}\text{O}_3$ (d) C_6H_{14}

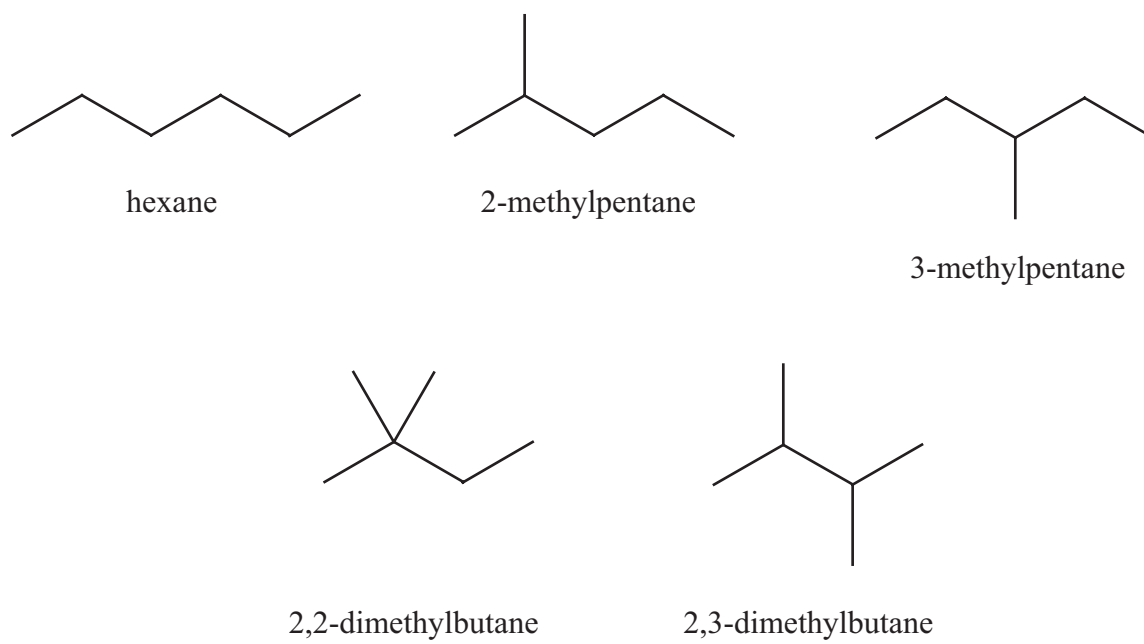
- 1.31 (a) Different compounds, not isomeric (i) Different compounds, not isomeric
(b) Constitutional isomers (j) Same compound
(c) Same compound (k) Constitutional isomers
(d) Same compound (l) Different compounds, not isomeric
(e) Same compound (m) Same compound
(f) Constitutional isomers (n) Same compound
(g) Different compounds, not isomeric (o) Same compound
(h) Same compound (p) Constitutional isomers

12 THE BASICS: BONDING AND MOLECULAR STRUCTURE

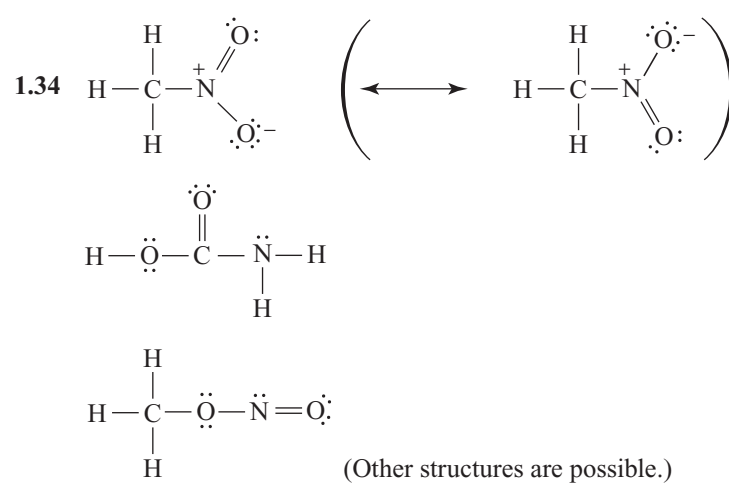
1.32 In each of the following structural formulas, place the appropriate number of lone pairs of electrons on each heteroatom and indicate the charge on the heteroatom, if any.



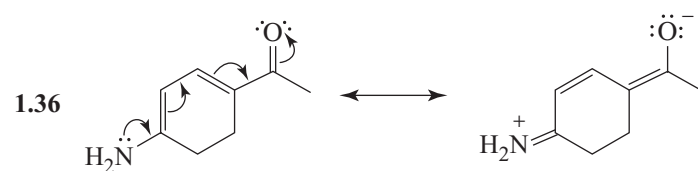
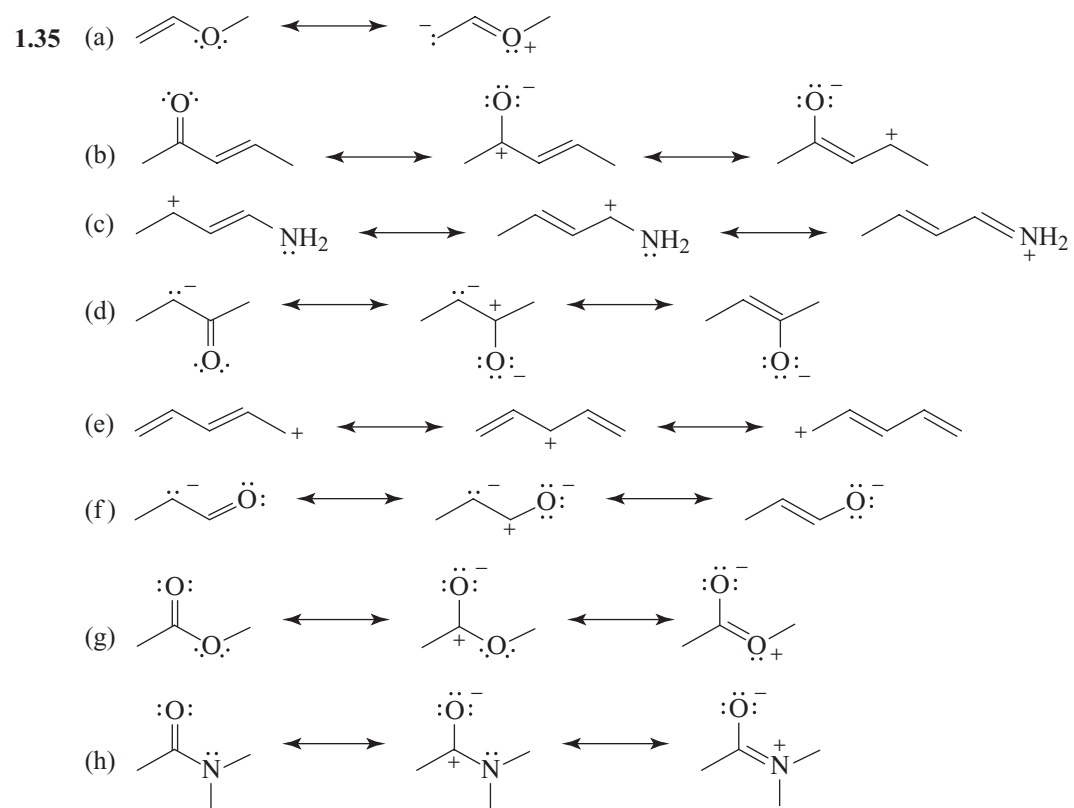
1.33 Write structural formulas for the constitutional isomers with the molecular formula C_6H_{14} .



THE BASICS: BONDING AND MOLECULAR STRUCTURE 13

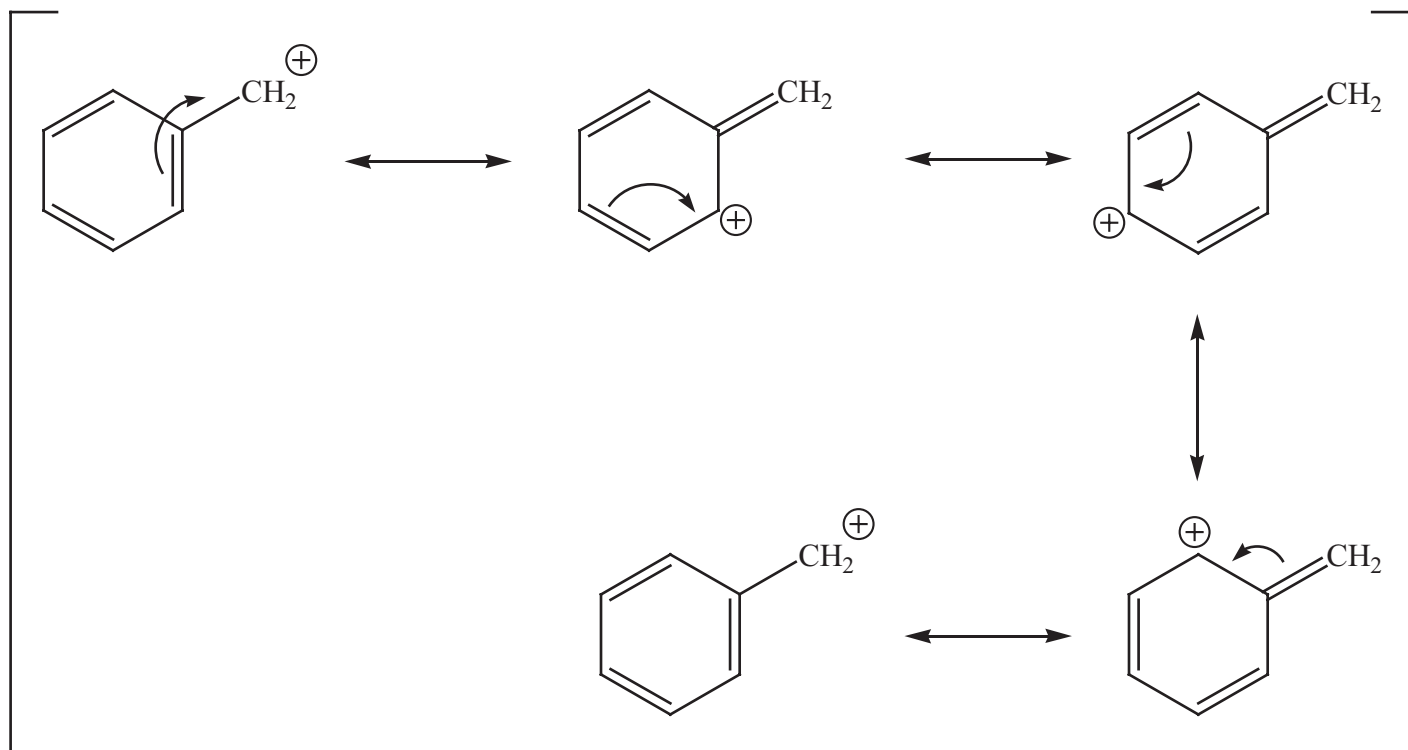


Resonance Structures

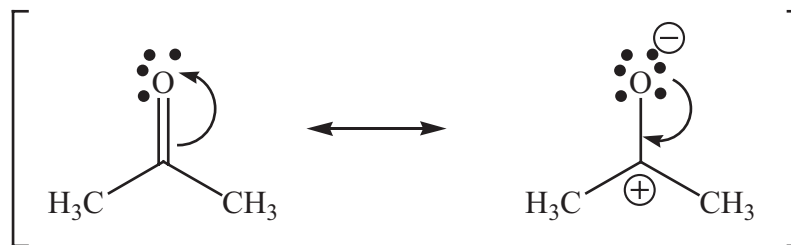


14 THE BASICS: BONDING AND MOLECULAR STRUCTURE

1.37 Draw resonance structures for the benzyl cation, shown below, used curved arrows.



1.38 Which resonance structure shown below for acetone would contribute more to the overall structure of acetone? Explain.

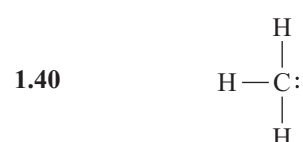


The resonance structure on the left would be the major contributor. There are two contributing factors; first, the resonance structure on the left has one more formal bond, the C=O, compared to the one on the right. Second, in the resonance structure on the left there is no formal charge separation as there is in the one on the right.

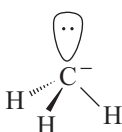
1.39 Indicate the number of bonds and lone pairs of electrons on each of the following atoms:

- A neutral carbon – four bonds and zero lone pairs
- A positively charged oxygen – three bonds and one lone pair
- A negatively charged nitrogen – two bonds and two lone pairs
- A positively charged carbon – three bonds and zero lone pairs

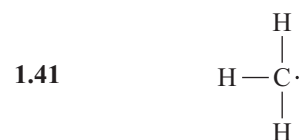
THE BASICS: BONDING AND MOLECULAR STRUCTURE 15



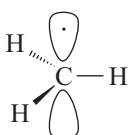
- (a) A -1 charge. ($F = 4 - 6/2 - 2 = -1$)
 (b) A -1 charge. (It is called a methyl anion.)
 (c) Trigonal pyramidal, that is



- (d) sp^3



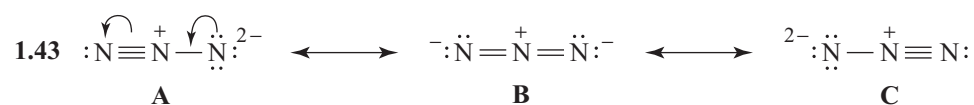
- (a) No formal charge. ($F = 4 - 6/2 - 1 = 0$)
 (b) No charge.
 (c) sp^2 , that is,



- 1.42 (a) and (b)

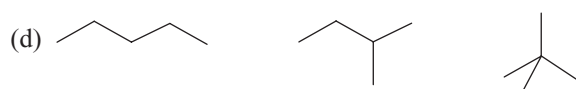
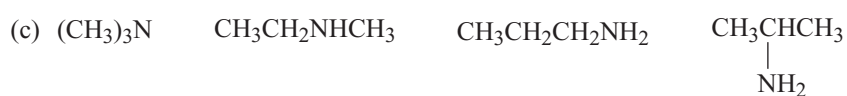
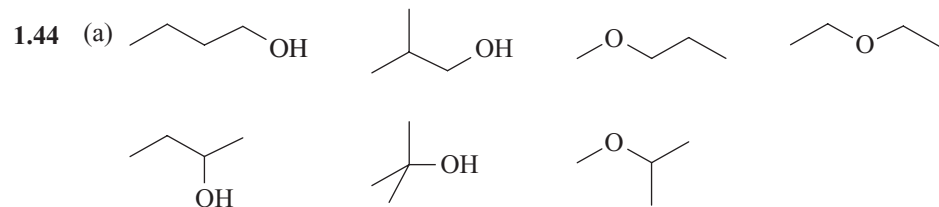


- (c) Because the two resonance structures are equivalent, they should make equal contributions to the hybrid and, therefore, the bonds should be the same length.
 (d) Yes. We consider the central atom to have two groups or units of bonding electrons and one unshared pair.



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

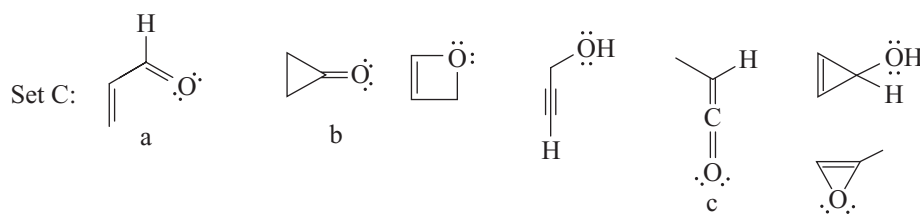
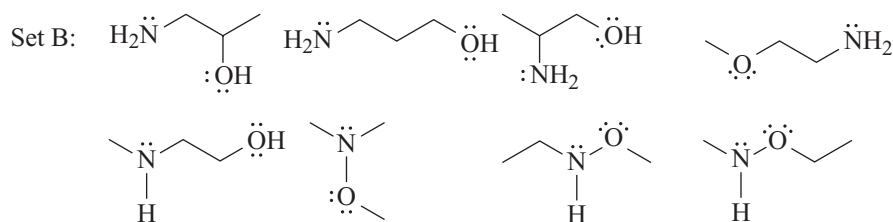
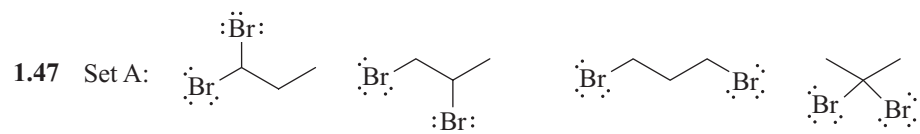
16 THE BASICS: BONDING AND MOLECULAR STRUCTURE



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

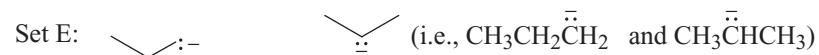
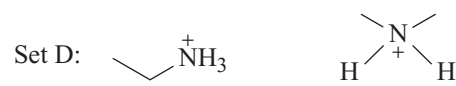
Challenge Problems

- 1.46 (a) $\ddot{\text{O}}=\overset{+}{\text{N}}=\ddot{\text{O}}$
 (b) Linear
 (c) Carbon dioxide

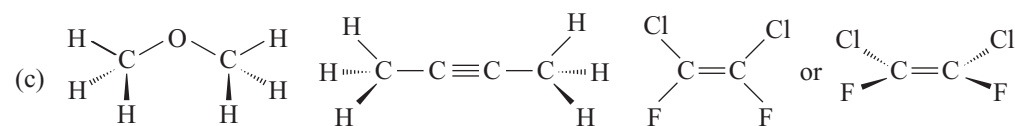
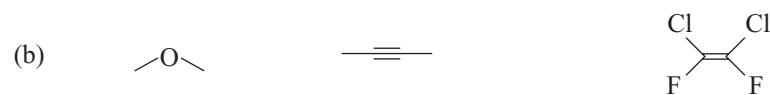
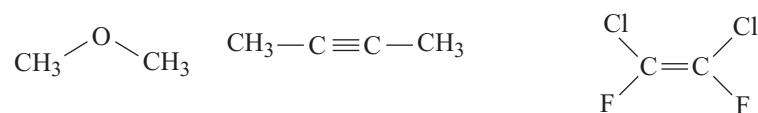


[and unstable enol forms of a, b, and c]

THE BASICS: BONDING AND MOLECULAR STRUCTURE 17

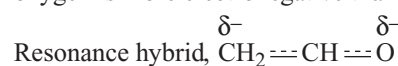


- 1.48 (a) Dimethyl ether Dimethylacetylene *cis*-1,2-Dichloro-1,2-difluoroethene



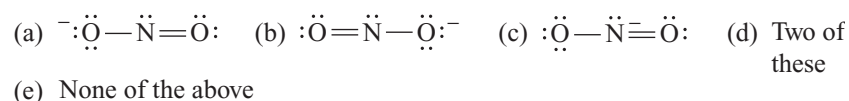
- 1.49 The large lobes centered above and below the boron atom represent the $2p$ orbital that was not involved in hybridization to form the three $2sp^2$ hybrid orbitals needed for the three boron-fluorine covalent bonds. This orbital is not a pure $2p$ atomic orbital, since it is not an isolated atomic 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.

- 1.50 The two resonance forms for this anion are $^-\text{CH}_2-\text{CH}=\ddot{\text{O}}:$ and $\text{CH}_2=\text{CH}-\ddot{\text{O}}:^-$. 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.

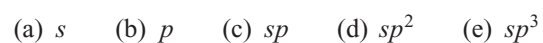


QUIZ

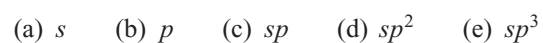
- 1.1 Which of the following is a valid Lewis dot formula for the nitrite ion (NO_2^-)?



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



- 1.3 BF_3 reacts with NH_3 to produce a compound, $\text{F}-\text{B}(\text{F})_2-\text{N}(\text{H})_3$. The hybridization state of B is

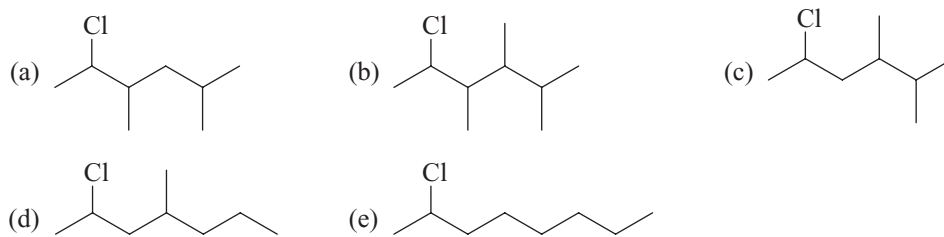


18 THE BASICS: BONDING AND MOLECULAR STRUCTURE

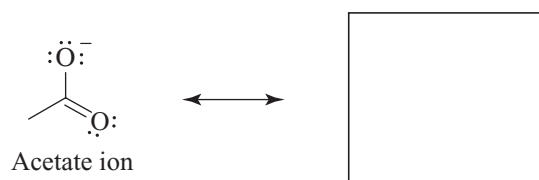
1.4 The formal charge on N in the compound given in Problem 1.3 is

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

1.5 The correct bond-line formula of the compound whose condensed formula is $\text{CH}_3\text{CHClCH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{CH}_3)_2$ is

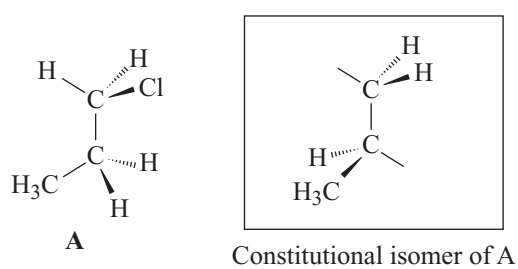


1.6 Write another resonance structure for the acetate ion.



1.7 In the boxes below write condensed structural formulas for constitutional isomers of $\text{CH}_3(\text{CH}_2)_3\text{CH}_3$.

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

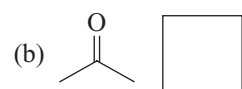


THE BASICS: BONDING AND MOLECULAR STRUCTURE 19

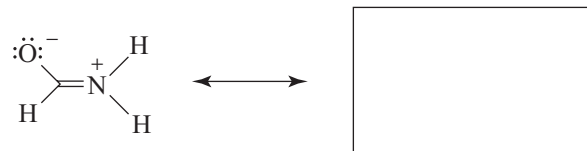
1.9 Consider the molecule $(\text{CH}_3)_3\text{B}$ and give the following:

- (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 $(\text{CH}_3)_3\text{B}$

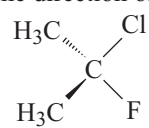
1.10 Give the formal charge on oxygen in each compound.



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 $\text{C}_3\text{H}_6\text{O}$.