14. Given a simple molecular formula, draw the electron-dot formula and determine whether each atom in the structure carries a formal charge.
15. Draw the electron-dot formulas that show all important contributors to a resonance hybrid and show their electronic relationship using curved arrows.
16. Predict the geometry of bonds around an atom, knowing the electron distribution in the orbitals.
17. Draw in three dimensions, with solid, wedged, and dashed bonds, the tetrahedral bonding around sp^3-hybridized carbon atoms.
18. Distinguish between acyclic, carbocyclic, and heterocyclic structures.
19. Given a series of structural formulas, recognize compounds that belong to the same class (same functional group).
20. Begin to recognize the important functional groups: alkene, alkyne, alcohol, ether, aldehyde, ketone, carboxylic acid, ester, amine, nitrile, amide, thiol, and thioether.

ANSWERS TO PROBLEMS

Problems Within the Chapter

1.1 The lithium atom donates its valence electron to the bromine atom to form the ionic compound, lithium bromide.

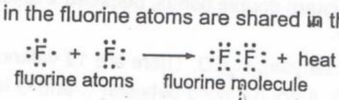
1.2 Elements with fewer than four valence electrons tend to give them up and form positive ions: Al^{3+}, Li^{+}. Elements with more than four valence electrons tend to gain electrons to complete the valence shell, becoming negative ions: S^{2-}, O^{2-}.

1.3 Within any horizontal row in the periodic table, the most electropositive element appears farthest to the left. Na is more electropositive than Al, and B is more electropositive than C. In a given column in the periodic table, the lower the element, the more electropositive it is. Al is more electropositive than B.

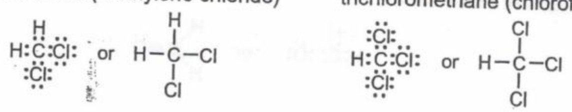
1.4 Within any horizontal row in the periodic table, the most electronegative element appears farthest to the right. F is more electronegative than O, and O more than N. In a given column, the higher the element, the more electronegative it is. F is more electronegative than Cl.

1.5 As will be explained in Sec. 1.3, carbon is in Group IV and has a half-filled (or half-empty) valence shell. It is neither strongly electropositive nor strongly electronegative.

1.6 The unpaired electrons in the fluorine atoms are shared in the fluorine molecule.

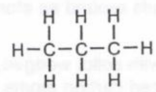


1.7 dichloromethane (methylene chloride) trichloromethane (chloroform)



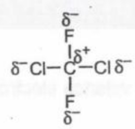
1.8 If the C–C bond length is 1.54 Å and the Cl–Cl bond length is 1.98 Å, we expect the C–Cl bond length to be about 1.76 Å: (1.54 + 1.98)/2. In fact, the C–Cl bond (1.75 Å) is longer than the C–C bond.

1.9 Propane

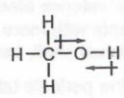


1.10 $P^{\delta+}$–$Cl^{\delta-}$; $S^{\delta+}$–$O^{\delta-}$ The key to predicting bond polarities is to determine the relative electronegativities of the elements in the bond. The polarity of the P–Cl bond is easy to predict because both elements are in the same row of the periodic table and the more electronegative atom appears nearer the right. The polarity of the S–O bond is predicted in much the same way. Both elements are in the same column, and the more electronegative atom appears nearer the top.

1.11 Both Cl and F are more electronegative than C.



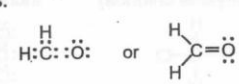
1.12 Both the C–O and H–O bonds are polar, and the oxygen is more electronegative than either carbon or hydrogen.



1.13 H:C:::N: H:C:::N: H:C:::N:

1.14 a. The carbon shown has 12 electrons around it, 4 more than are allowed.
b. There are 20 valence electrons shown, whereas there should only be 16 (6 from each oxygen and 4 from the carbon).
c. There is nothing wrong with this formula, but it does place a formal charge of –1 on the "left" oxygen and +1 on the "right" oxygen (see Sec. 1.11). This formula is one possible contributor to the resonance hybrid structure for carbon dioxide (see Sec. 1.12); it is less important than the structure with two carbon–oxygen double bonds, because it takes energy to separate the + and – charges.

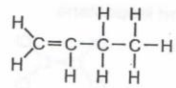
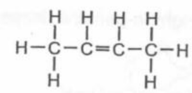
1.15 Methanal (formaldehyde), H_2CO. There are 12 valence electrons altogether (C = 4, H = 1, and O = 6). A double bond between C and O is necessary to put 8 electrons around each of these atoms.



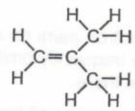
1.16 There are 10 valence electrons, 4 from C and 6 from O. An arrangement that puts 8 electrons around each atom is shown below. This structure puts a formal charge of –1 on C and +1 on O (see Sec. 1.11).

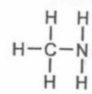
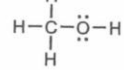
:C:::O: or :C≡O:

1.17 If the carbon chain is linear, there are two possibilities:

 and 

But the carbon chain can be branched, giving a third possibility:

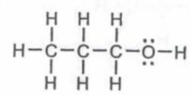
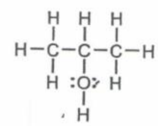


1.18 a.  b. 

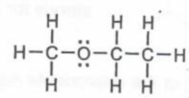
Notice that the nitrogen has one non-bonded electron pair (part a) and the oxygen has two non-bonded electron pairs (part b).

1.19 No, it does not. We cannot draw any structure for C_2H_5 that has four bonds to each carbon and one bond to each hydrogen.

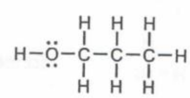
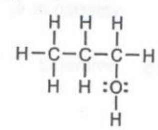
1.20 First write the alcohols (compounds with an O–H group).

 and 

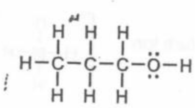
Then write the structures with a C–O–C bond (ethers).



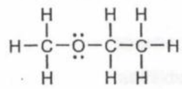
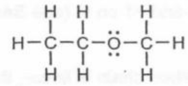
There are no other possibilities. For example,

 and 

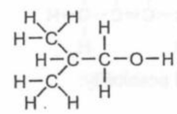
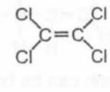
are the same as



They all have the same bond connectivities and represent a single structure. Similarly,

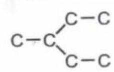
 is the same as 

1.21 From left to right: *n*-pentane, isopentane, and isopentane.

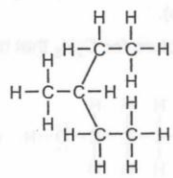
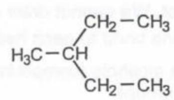
1.22 a.  b. 

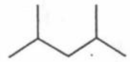
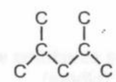
Notice that the non-bonded electron pairs on oxygen and chlorine are not shown. Non-bonded electron pairs are frequently omitted from organic structures, but it is important to know that they are there.

1.23 First draw the carbon skeleton showing all bonds between carbons.

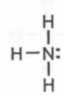


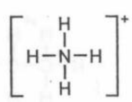
Then add hydrogens to satisfy the valency of four at each carbon.

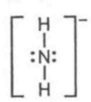
 or 

1.24  stands for the carbon skeleton 

Addition of the appropriate number of hydrogens on each carbon completes the valence of 4.

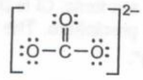
1.25 ammonia  formal charge on nitrogen = 5 – (2 + 3) = 0

ammonium ion  formal charge on nitrogen = 5 – (0 + 4) = +1

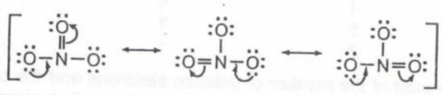
amide ion  formal charge on nitrogen = 5 – (4 + 2) = –1

The formal charge on hydrogen in all three cases is zero [1 – (0 + 1) = 0].

1.26 For the singly bonded oxygens, formal charge = 6 – (6 + 1) = –1.
For the doubly bonded oxygen, formal charge = 6 – (4 + 2) = 0.
For the carbon, formal charge = 4 – (0 + 4) = 0.

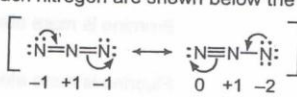


1.27 There are 24 valence electrons to use in bonding (6 from each oxygen, 5 from the nitrogen, and one more because of the negative charge). To arrange the atoms with 8 valence electrons around each atom, we must have one nitrogen–oxygen double bond:



The formal charge on nitrogen is 5 – (0 + 4) = +1.
The formal charge on singly bonded oxygen is 6 – (6 + 1) = –1.
The formal charge on doubly bonded oxygen is 6 – (4 + 2) = 0.
The net charge of the ion is –1 because each resonance structure has one positively charged nitrogen atom and two negatively charged oxygen atoms. In the resonance hybrid, the formal charge on the nitrogen is +1; on the oxygens, the charge is –2/3 at each oxygen, because each oxygen has a –1 charge in two of the three structures and a zero charge in the third structure.

1.28 There are 16 valence electrons (five from each N plus one for the negative charge). The formal charges on each nitrogen are shown below the structures.

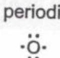
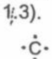


1.29 In tetrahedral methane, the H–C–H bond angle is 109.5°. In "planar" methane, this angle would be 90° and bonding electrons would be closer together. Thus, repulsion between electrons in different bonds would be greater in "planar" methane than in tetrahedral methane. Consequently, "planar" methane would be less stable than tetrahedral methane.

1.30 a. C=C, alkene; O–H, alcohol
b. C=O, carbonyl group, ketone
c. C=C, alkene
d. C=C, alkene; C=O, ketone; O–H, alcohol

ADDITIONAL PROBLEMS

1.31 The number of valence electrons is the same as the number of the group to which the element belongs in the periodic table (Table 1.3).

a.  b.  c.  d. 

e.  f. 

1.32

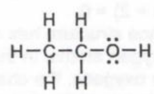
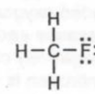
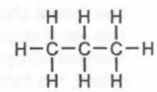
a.	covalent	b.	ionic	c.	covalent	d.	covalent
e.	ionic	f.	covalent	g.	ionic	h.	covalent

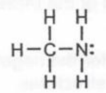
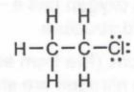
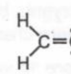
1.33 The bonds in sodium chloride are ionic; Cl is present as chloride ion (Cl^-); Cl^- reacts with Ag^+ to give AgCl, a white precipitate. The C–Cl bonds in CCl_4 are covalent, no Cl^- is present to react with Ag^+.

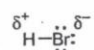
1.34

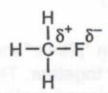
		Valence Electrons	Common Valence
a.	O	6	2
b.	H	1	1
c.	S	6	2
d.	C	4	4
e.	N	5	3
f.	Cl	7	1

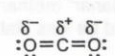
Note that the *sum* of the number of valence electrons and the common valence is 8 in each case (except for H, where it is 2, the number of electrons in the completed first shell).

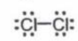
1.35 a.  b.  c. 

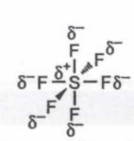
d.  e.  f. 

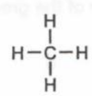
1.36 a.  Bromine is more electronegative than hydrogen.

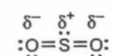
b.  Fluorine is more electronegative than carbon.

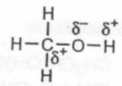
c.  The C=O bond is polar, and the oxygen is more electronegative than carbon.

d.  Since the bond is between identical atoms, it is pure covalent (nonpolar).

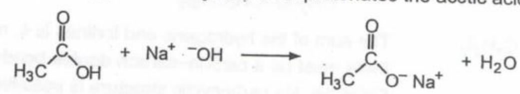
e.  Fluorine is more electronegative than sulfur. Indeed, it is the most electronegative element. Note that the S has 12 electrons around it. Elements below the first full row sometimes have more than 8 valence electrons around them.

f.  Carbon and hydrogen have nearly identical electronegativities, and the bonds are essentially nonpolar.

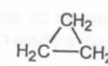
g.  Oxygen is more electronegative than sulfur.

h.  Oxygen is more electronegative than carbon, or hydrogen, so the C–O and O–H bonds are polar covalent.

1.37 The O–H bond is polar (there is a big difference in electronegativity between oxygen and hydrogen), with the hydrogen δ^+. The C–H bonds in acetic acid are not polar (there is little electronegativity difference between carbon and hydrogen). The negatively charged oxygen of the hydroxide deprotonates the acetic acid.



1.38 a. C_3H_6 There must be a double bond or, with three carbons, a ring:

$CH_3CH{=}CH_2$ or 

b. C_3H_7Cl The chlorine can replace a hydrogen on an end carbon or on the middle carbon in the answer to a: $CH_3CH_2CH_2Cl$ or $CH_3CH(Cl)CH_3$

c. $C_2H_4F_2$ The fluorines can either be attached to the same carbon or to different carbons:

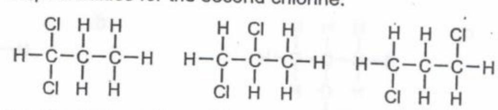
CH_3CHF_2 or CH_2FCH_2F

d. C_3H_8 The only possible structure is $CH_3CH_2CH_3$.

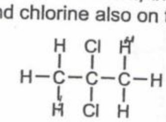
e. C_4H_9F The carbon chain may be either linear or branched. In each case there are two possible positions for the fluorine.

$CH_3CH_2CH_2CH_2F$ $CH_3CH(F)CH_2CH_3$
$(CH_3)_2CHCH_2F$ $(CH_3)_3CF$

f. $C_3H_6Cl_2$ Be systematic. With one chlorine on an end carbon, there are three possibilities for the second chlorine.



If one chlorine is on the middle atom, the only new structure arises with the second chlorine also on the middle carbon:



g. $C_4H_{10}O$ With an O–H bond, there are four possibilities:

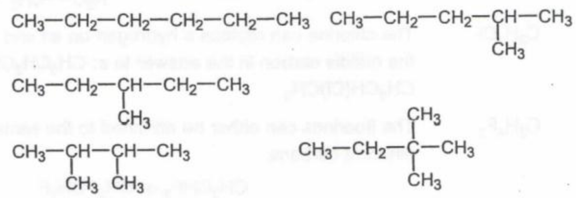
$CH_3CH_2CH_2CH_2$–OH $CH_3CH(OH)CH_2CH_3$
$(CH_3)_2CHCH_2$–OH $(CH_3)_3C$–OH

There are also three possibilities in a C–O–C arrangement:

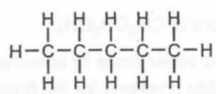
CH_3–O–$CH_2CH_2CH_3$ CH_3CH_2–O–CH_2CH_3
CH_3–O–$CH(CH_3)_2$

h. $C_2H_2I_2$ The sum of the hydrogens and iodines is 4, not 6. Therefore there must be a carbon–carbon double bond: $I_2C{=}CH_2$ or CHI=CHI. No carbocyclic structure is possible because there are only two carbon atoms.

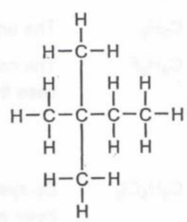
1.39 The problem can be approached systematically. Consider first a chain of six carbons, then a chain of five carbons with a one-carbon branch, and so on.



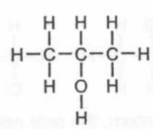
1.40 a.



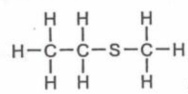
b.



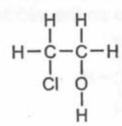
c.



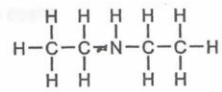
d.



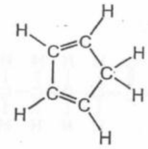
e.



f.



1.41 a. $CH_3CH_2C(CH_3){=}CH_2$

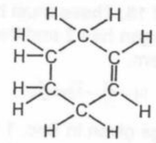
b. 

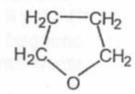
c. $(CH_3)_3CCH(CH_3)_2$

d. $CH_3CH_2CH_2CHCH_2CHCH_2CH_2CH_3$ (branches: CH_3 on the first CH, CH_2CH_3 on the second CH)

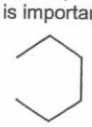
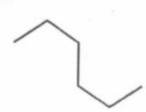
e. $CH_3CH_2OCH_2CH_3$

f. $(CH_3)_2CHCH_2CH_2CH_3$

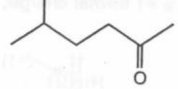
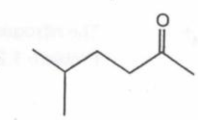
g. 

h. 

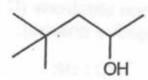
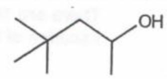
1.42 a. In line formulas, each line segment represents a C–C bond, and C–H bonds are not shown (see Sec. 1.10). There are a number of acceptable line structures for $CH_3(CH_2)_4CH_3$, three of which are shown here. The orientation of the line segments on the page is not important, but the number of line segments connected to each point is important.

 or  or 

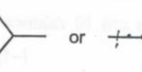
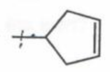
b. Bonds between carbon atoms and non-carbon atoms are indicated by line segments that terminate with the symbol for the non-carbon atom. In this case the non-carbon atom is an oxygen.

 or 

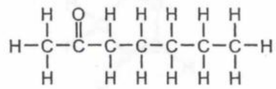
c. Bonds between hydrogens and non-carbon atoms are shown.

 or 

d. The same rules apply for cyclic structures.

 or 

1.43 a. 7 b. $C_7H_{14}O$

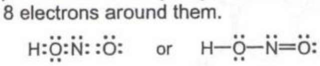
c. 

1.44 First count the carbons, then the hydrogens, and finally the remaining atoms.

a. C_6H_6 b. $C_{19}H_{28}O_2$ c. $C_{10}H_{16}$

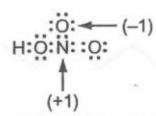
d. $C_{16}H_{18}N_2O_4$ e. $C_9H_6O_2$ f. $C_{10}H_{14}N_2$

1.45 a. HONO First determine the total number of valence electrons; H = 1, O = 2 x 6 = 12, N = 5, for a total of 18. These must be arranged in pairs so that the hydrogen has 2 and the other atoms have 8 electrons around them.

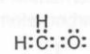


Using the formula for formal charge given in Sec. 1.11, it can be determined that none of the atoms has a formal charge.

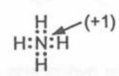
b. $HONO_2$ There are 24 valence electrons. The nitrogen has a +1 formal charge [5 – (0 + 4) = +1], and the singly bonded oxygen has a –1 formal charge [6 – (6 + 1)] = –1. The whole molecule is neutral.



c. H_2CO There are no formal charges.



d. NH_4^+ The nitrogen has a +1 formal charge; see the answer to Problem 1.25.

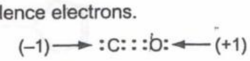


e. CN^- There are 10 valence electrons (C = 4, N = 5, plus 1 more because of the negative charge).

$^-$:C:::N:

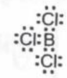
The carbon has a –1 formal charge [4 – (2 + 3) = –1].

f. CO There are 10 valence electrons.



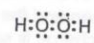
The carbon has a –1 formal charge, and the oxygen has a +1 formal charge. Carbon monoxide is isoelectronic with cyanide ion but has no net charge (–1 + 1 = 0).

g. BCl_3 There are 24 valence electrons (B = 3, Cl = 7). The structure is usually written with only 6 electrons around the boron.

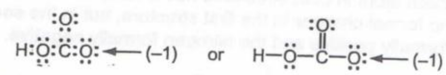


In this case, there are no formal charges. This structure shows that BCl_3 is a Lewis acid, which readily accepts an electron pair to complete the octet around the boron.

h. H_2O_2 There are 14 valence electrons and an O–O bond. There are no formal charges.

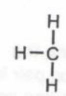


i. HCO_3^- There are 24 valence electrons involved. The hydrogen is attached to an oxygen, not to carbon.



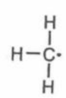
The indicated oxygen has a formal charge: 6 – (6 + 1) = –1. All other atoms are formally neutral.

1.46 This is a methyl carbocation, CH_3^+.



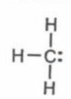
formal charge = 4 – (0 + 3) = +1

This is a methyl free radical, $\cdot CH_3$.



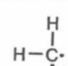
formal charge = 4 – (1 + 3) = 0

This is a methyl carbanion, $:CH_3^-$.



formal charge = 4 – (2 + 3) = –1

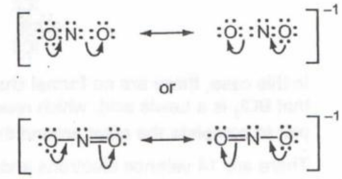
This is a methylene or carbene, $:CH_2$.



formal charge = 4 – (2 + 2) = 0

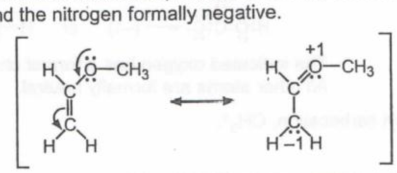
All of these fragments are extremely reactive. They may act as intermediates in organic reactions.

1.47 There are 18 valence electrons (6 from each of the oxygens, 5 from the nitrogen, and 1 from the negative charge).

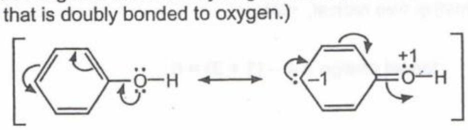


The negative charge in each contributor is on the singly bonded oxygen [6 – (6 + 1) = –1. The other oxygen and the nitrogen have no formal charge. In the resonance hybrid, the negative charge is spread equally over the two oxygens; the charge on each is –1/2.

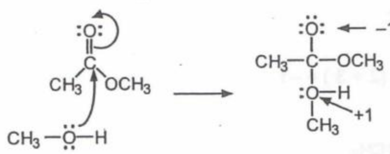
1.48 Each atom in both structures has a complete valence shell of electrons. There are no formal charges in the first structure, but in the second structure the oxygen is formally positive and the nitrogen formally negative.



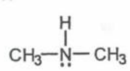
1.49 In the first structure, there are no formal charges. In the second structure, the oxygen is formally +1, and the ring carbon bearing the unshared electron pair is formally –1. (Don't forget to count the hydrogen that is attached to each ring carbon except the one that is doubly bonded to oxygen.)



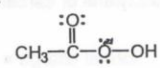
1.50



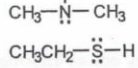
1.51 a.



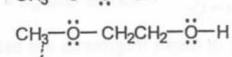
b.



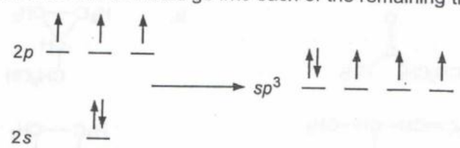
c.



d.



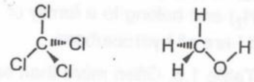
1.52 If the s and p orbitals were hybridized to sp^3, two electrons would go into one of these orbitals and one electron would go into each of the remaining three orbitals.



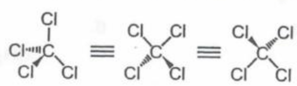
The predicted geometry of ammonia would then be tetrahedral, with one hydrogen at each of three corners, and the unshared pair at the fourth corner. In fact, ammonia has a pyramidal shape, a somewhat flattened tetrahedron. The H–N–H bond angle is 107°.

1.53 The ammonium ion is in fact isoelectronic (the same arrangement of electrons) with methane, and consequently has the same geometry. Four sp^3 orbitals of nitrogen each contain one electron. These orbitals then overlap with the 1s hydrogen orbitals, as in Figure 1.9.

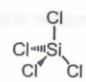
1.54



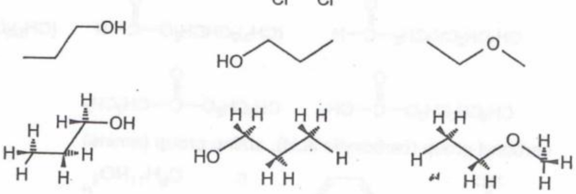
The geometry is tetrahedral at carbon. It does not matter whether we draw the wedge bonds to the right or to the left of the carbon, or indeed "up" or "down".



1.55 The bonding is exactly as in carbon tetrachloride. The geometry of silicon tetrachloride is tetrahedral.



1.56 a.

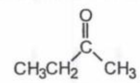


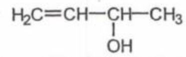
A B C

b. Structures **A** and **B** are identical. Structures **A** and **C** are isomers. They both have the molecular formula C_3H_8O, but **A** is an alcohol and **C** is an ether.

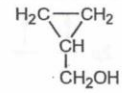
1.57 Many correct answers are possible; a few are given here.

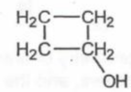
a.



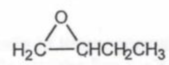
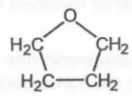


b.





c.

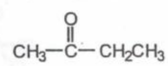
 

1.58 Compounds c, e, f, and j all have hydroxyl groups (—OH) and belong to a class of compounds called alcohols. Compound d is an ether. It has C—O—C unit. Compounds b, g and l contain amino groups (—NH_2) and belong to a family of compounds called amines. Compounds a, f, k, and l are all hydrocarbons.

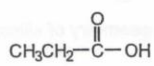
1.59 The more common functional groups are listed in Table 1.6. Often more than one answer is possible.

a. $CH_3CH_2CH_2CH_2OH$ b. $CH_3OCH_2CH_3$

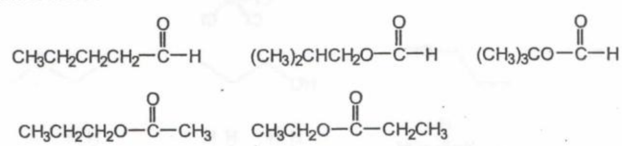
c. $CH_3CH_2CH{=}O$ d.



e.

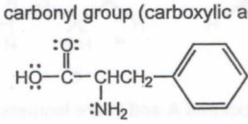


f. There are a number of possible answers. Five are shown below. Can you think of more?



1.60 a. carbonyl group (carboxylic acid), amino group (amine)

b.



c. $C_9H_{11}NO_2$

d. The isomer of phenylalanine shown below is both an alcohol and an amide.