

# Student Study Guide and Solutions Manual

# ORGANIC CHEMISTRY

THIRD EDITION



# DAVID KLEIN

WILEY



# **Student Study Guide and Solutions Manual, 3e**

for  
Organic Chemistry, 3e

David Klein  
*Johns Hopkins University*

**WILEY**

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## HOW TO USE THIS BOOK

Organic chemistry is much like bicycle riding. You cannot learn how to ride a bike by watching other people ride bikes. Some people might fool themselves into believing that it's possible to become an expert bike rider without ever getting on a bike. But you know that to be incorrect (and very naïve). In order to learn how to ride a bike, you must be willing to get on the bike, and you must be willing to fall. With time (and dedication), you can quickly train yourself to avoid falling, and to ride the bike with ease and confidence. The same is true of organic chemistry. In order to become proficient at solving problems, you must "ride the bike". You must try to solve the problems yourself (*without* the solutions manual open in front of you). Once you have solved the problems, this book will allow you to check your solutions. If, however, you don't attempt to solve each problem on your own, and instead, you read the problem statement and then immediately read the solution, you are only hurting yourself. You are not learning how to avoid falling. Many students make this mistake every year. They use the solutions manual as a crutch, and then they never really attempt to solve the problems on their own. It really is like believing that you can become an expert bike rider by watching hundreds of people riding bikes. The world doesn't work that way!

The textbook has thousands of problems to solve. Each of these problems should be viewed as an opportunity to develop your problem-solving skills. By reading a problem statement and then reading the solution immediately (without trying to solve the problem yourself), you are robbing yourself of the opportunity provided by the problem. If you repeat that poor study habit too many times, you will not learn how to solve problems on your own, and you will not get the grade that you want.

Why do so many students adopt this bad habit (of using the solutions manual too liberally)? The answer is simple. Students often wait until a day or two before the exam, and then they spend all night cramming. Sound familiar? Unfortunately, organic chemistry is the type of course where cramming is insufficient, because you need time in order to ride the bike yourself. You need time to think about each problem until you have developed a solution *on your own*. For some problems, it might take days before you think of a solution. This process is critical for learning this subject. Make sure to allot time every day for studying organic chemistry, and use this book to check your solutions. This book has also been designed to serve as a study guide, as described below.

## WHAT'S IN THIS BOOK

This book contains more than just solutions to all of the problems in the textbook. Each chapter of this book also contains a series of exercises that will help you review the concepts, skills and reactions presented in the corresponding chapter of the textbook. These exercises

are designed to serve as study tools that can help you identify your weak areas. Each chapter of this solutions manual/study guide has the following parts:

- **Review of Concepts.** These exercises are designed to help you identify which concepts are the least familiar to you. Each section contains sentences with missing words (blanks). Your job is to fill in the blanks, demonstrating mastery of the concepts. To verify that your answers are correct, you can open your textbook to the end of the corresponding chapter, where you will find a section entitled *Review of Concepts and Vocabulary*. In that section, you will find each of the sentences, verbatim.
- **Review of Skills.** These exercises are designed to help you identify which skills are the least familiar to you. Each section contains exercises in which you must demonstrate mastery of the skills developed in the *SkillBuilders* of the corresponding textbook chapter. To verify that your answers are correct, you can open your textbook to the end of the corresponding chapter, where you will find a section entitled *SkillBuilder Review*. In that section, you will find the answers to each of these exercises.
- **Review of Reactions.** These exercises are designed to help you identify which reagents are not at your fingertips. Each section contains exercises in which you must demonstrate familiarity with the reactions covered in the textbook. Your job is to fill in the reagents necessary to achieve each reaction. To verify that your answers are correct, you can open your textbook to the end of the corresponding chapter, where you will find a section entitled *Review of Reactions*. In that section, you will find the answers to each of these exercises.
- **Common Mistakes to Avoid.** This is a new feature to this edition. The most common student mistakes are described, so that you can avoid them when solving problems.
- **A List of Useful Reagents.** This is a new feature to this edition. This list provides a review of the reagents that appear in each chapter, as well as a description of how each reagent is used.
- **Solutions.** At the end of each chapter, you'll find detailed solutions to all problems in the textbook, including all *SkillBuilders*, conceptual checkpoints, additional problems, integrated problems, and challenge problems.

The sections described above have been designed to serve as useful tools as you study and learn organic chemistry. Good luck!

David Klein  
Senior Lecturer, Department of Chemistry  
Johns Hopkins University





# Chapter 1

## A Review of General Chemistry: Electrons, Bonds and Molecular Properties

### Review of Concepts

Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 1. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

- \_\_\_\_\_ **isomers** share the same molecular formula but have different connectivity of atoms and different physical properties.
- Second-row elements generally obey the \_\_\_\_\_ **rule**, bonding to achieve noble gas electron configuration.
- A pair of unshared electrons is called a \_\_\_\_\_.
- A **formal charge** occurs when an atom does not exhibit the appropriate number of \_\_\_\_\_.
- An **atomic orbital** is a region of space associated with \_\_\_\_\_, while a **molecular orbital** is a region of space associated with \_\_\_\_\_.
- Methane's tetrahedral geometry can be explained using four degenerate \_\_\_\_\_-**hybridized orbitals** to achieve its four single bonds.
- Ethylene's planar geometry can be explained using three degenerate \_\_\_\_\_-**hybridized orbitals**.
- Acetylene's linear geometry is achieved via \_\_\_\_\_-**hybridized** carbon atoms.
- The geometry of small compounds can be predicted using valence shell electron pair repulsion (**VSEPR**) theory, which focuses on the number of \_\_\_\_\_ bonds and \_\_\_\_\_ exhibited by each atom.
- The physical properties of compounds are determined by \_\_\_\_\_ forces, the attractive forces between molecules.
- **London dispersion forces** result from the interaction between transient \_\_\_\_\_ and are stronger for larger alkanes due to their larger surface area and ability to accommodate more interactions.



### Review of Skills

Fill in the blanks and empty boxes below. To verify that your answers are correct, look in your textbook at the end of Chapter 1. The answers appear in the section entitled *SkillBuilder Review*.



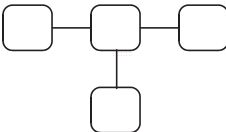

#### SkillBuilder 1.1 Drawing Constitutional Isomers of Small Molecules

<p><b>STEP 1</b> DETERMINE THE VALENCY OF EACH ATOM IN <math>C_3H_8O</math>.</p> <div style="text-align: center;"> </div>	<p><b>STEP 2</b> CONNECT THE ATOMS OF HIGHEST VALENCY, AND PLACE THE MONOVALENT ATOMS AT THE PERIPHERY.</p> <div style="text-align: center;"> </div>	<p><b>STEP 3</b> CONSIDER OTHER WAYS TO CONNECT THE ATOMS.</p> <div style="text-align: center;"> </div>
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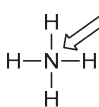
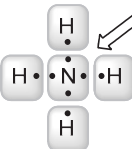

**SkillBuilder 1.2 Drawing the Lewis Dot Structure of an Atom**

<p><b>STEP 1 - DETERMINE THE NUMBER OF VALENCE ELECTRONS</b></p> <p>Nitrogen is in Group ___ of the periodic table, and is expected to have ___ valence electrons.</p>	<p><b>STEP 2 - PLACE ONE ELECTRON BY ITSELF ON EACH SIDE OF THE ATOM</b></p> 	<p><b>STEP 3 - IF THE ATOM HAS MORE THAN FOUR VALENCE ELECTRONS, PAIR THE REMAINING ELECTRONS WITH THE ELECTRONS ALREADY DRAWN</b></p> 
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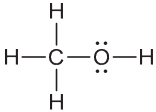
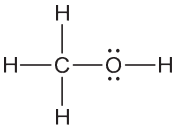
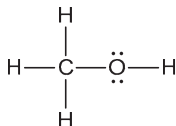
**SkillBuilder 1.3 Drawing the Lewis Structure of a Small Molecule**

<p><b>STEP 1 - DRAW THE LEWIS DOT STRUCTURE OF EACH ATOM IN CH<sub>2</sub>O</b></p> 	<p><b>STEP 2 - FIRST CONNECT ATOMS THAT FORM MORE THAN ONE BOND</b></p> 	<p><b>STEP 3 - CONNECT THE HYDROGEN ATOMS</b></p> 	<p><b>STEP 4 - PAIR ANY UNPAIRED ELECTRONS, SO THAT EACH ATOM ACHIEVES AN OCTET</b></p> 
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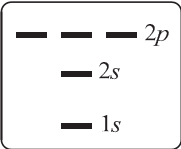
**SkillBuilder 1.4 Calculating Formal Charge**

<p><b>STEP 1 - DETERMINE THE APPROPRIATE NUMBER OF VALENCE ELECTRONS</b></p>  <p>Nitrogen is in Group ___ of the periodic table, and is expected to have ___ valence electrons.</p>	<p><b>STEP 2 - DETERMINE THE NUMBER OF VALENCE ELECTRONS IN THIS CASE</b></p>  <p>In this case, the nitrogen atom is using only ___ valence electrons.</p>	<p><b>STEP 3 - ASSIGN A FORMAL CHARGE TO THE NITROGEN ATOM IN THIS CASE</b></p> 
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


**SkillBuilder 1.5 Locating Partial Charges Resulting from Induction**

<p><b>STEP 1 - CIRCLE THE BONDS BELOW THAT ARE POLAR COVALENT</b></p> 	<p><b>STEP 2 - FOR EACH POLAR COVALENT BOND, DRAW AN ARROW THAT SHOWS THE DIRECTION OF THE DIPOLE MOMENT</b></p> 	<p><b>STEP 3 - INDICATE THE LOCATION OF ALL PARTIAL CHARGES (δ+ and δ-)</b></p> 
---	--	---

**SkillBuilder 1.6 Identifying Electron Configurations**

<p><b>STEP 1 - IN THE ENERGY DIAGRAM SHOWN HERE, DRAW THE ELECTRON CONFIGURATION OF NITROGEN (USING ARROWS TO REPRESENT ELECTRONS).</b></p>	 <p>Nitrogen</p>	<p><b>STEP 2 - FILL IN THE BOXES BELOW WITH THE NUMBERS THAT CORRECTLY DESCRIBE THE ELECTRON CONFIGURATION OF NITROGEN</b></p> <p>1s <input type="text"/> 2s <input type="text"/> 2p <input type="text"/></p>
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**SkillBuilder 1.7 Identifying Hybridization States**

<p>A CARBON ATOM WITH FOUR SINGLE BONDS WILL BE ___ HYBRIDIZED</p> 	<p>A CARBON ATOM WITH ONE DOUBLE BOND WILL BE ___ HYBRIDIZED</p> 	<p>A CARBON ATOM WITH A TRIPLE BOND WILL BE ___ HYBRIDIZED</p> 
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## SkillBuilder 1.8 Predicting Geometry

<p><b>STEP 1 - DETERMINE THE STERIC NUMBER OF THE NITROGEN ATOM BELOW BY ADDING THE NUMBER OF SINGLE BONDS AND LONE PAIRS</b></p> $\begin{array}{c} \text{H}-\ddot{\text{N}}-\text{H} \\   \\ \text{H} \end{array}$ <p># of single bonds = <input type="text"/></p> <p># of lone pairs = <input type="text"/></p> <p><b>Steric Number</b> = <input type="text"/></p>	<p><b>STEP 2 - THE STERIC NUMBER DETERMINES THE ARRANGEMENT OF ELECTRON PAIRS. FILL IN THE CHART BELOW:</b></p> <table border="1"> <thead> <tr> <th>Steric #</th> <th>Arrangement of Electron Pairs</th> </tr> </thead> <tbody> <tr> <td>4</td> <td></td> </tr> <tr> <td>3</td> <td></td> </tr> <tr> <td>2</td> <td></td> </tr> </tbody> </table>	Steric #	Arrangement of Electron Pairs	4		3		2		<p><b>STEP 3 - IDENTIFY THE GEOMETRY IN EACH CASE BELOW:</b></p> <div style="text-align: center;"> <p><i>tetrahedral</i> arrangement of electron pairs</p> </div>
Steric #	Arrangement of Electron Pairs									
4										
3										
2										

## SkillBuilder 1.9 Identifying the Presence of Molecular Dipole Moments

<p><b>STEP 1 - IDENTIFY THE GEOMETRY OF THE OXYGEN ATOM BELOW</b></p> $\begin{array}{c} \text{H} & & \text{H} \\ & \diagdown & / \\ & \text{O} & \\ & / & \diagdown \\ \text{H}_3\text{C}-\text{C} & & \text{C}-\text{CH}_3 \\   & &   \\ \text{H} & & \text{H} \end{array}$ <p>Geometry = <input type="text"/></p>	<p><b>STEP 2 - REDRAW THE COMPOUND. DRAW AN ARROW FOR EACH DIPOLE MOMENT (SHOWING ITS DIRECTION).</b></p> <div style="border: 1px solid black; height: 60px; width: 100%;"></div>	<p><b>STEP 3 - REDRAW THE COMPOUND, AND DRAW THE NET DIPOLE MOMENT</b></p> <div style="border: 1px solid black; height: 60px; width: 100%;"></div>
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## SkillBuilder 1.10 Predicting Physical Properties

<p><b>Dipole-Dipole Interactions</b> CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT</p> $\begin{array}{c} \text{CH}_2 \\    \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\   \\ \text{H} \end{array} \quad \begin{array}{c} \text{O} \\ \cdot \\    \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\   \\ \text{H} \end{array}$	<p><b>H-Bonding Interactions</b> CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT</p> $\begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C}-\ddot{\text{O}}-\text{C}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array} \quad \begin{array}{c} \text{H} & \text{H} \\   &   \\ \text{H}-\text{C}-\text{C}-\ddot{\text{O}}-\text{H} \\   &   \\ \text{H} & \text{H} \end{array}$	<p><b>Carbon Skeleton</b> CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT</p> $\begin{array}{c} \text{H} & \text{H} & \text{H} \\   &   &   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   &   \\ \text{H} & \text{H} & \text{H} \end{array} \quad \begin{array}{c} \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\   &   &   &   &   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{C}-\text{H} \\   &   &   &   &   \\ \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \end{array}$
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A Common Mistake to Avoid

When drawing a structure, don't forget to draw formal charges, as forgetting to do so is a common error. If a formal charge is present, it **MUST** be drawn. For example, in the following case, the nitrogen atom bears a positive charge, so the charge must be drawn:

INCORRECT



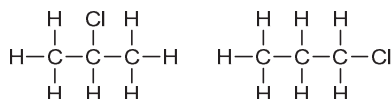
CORRECT



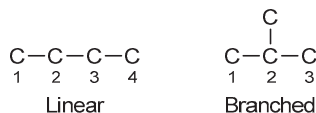
As we progress through the course, we will see structures of increasing complexity. If formal charges are present, failure to draw them constitutes an error, and must be scrupulously avoided. If you have trouble drawing formal charges, go back and master that skill. You can't go on without it. Don't make the mistake of underestimating the importance of being able to draw formal charges with confidence.

**Solutions****1.1.**

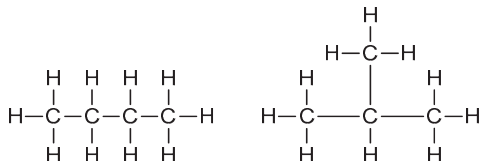
(a) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the chlorine atom and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the three carbon atoms) should be drawn in the center of the compound. Then, the chlorine atom can be placed in either of two locations: i) connected to the central carbon atom, or ii) connected to one of the other two (equivalent) carbon atoms. The hydrogen atoms are then placed at the periphery.



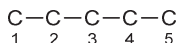
(b) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the four carbon atoms) should be drawn in the center of the compound. There are two different ways to connect four carbon atoms. They can either be arranged in a linear fashion or in a branched fashion:



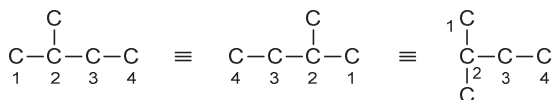
We then place the hydrogen atoms at the periphery, giving the following two constitutional isomers:



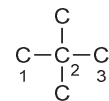
(c) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the five carbon atoms) should be drawn in the center of the compound. So we must explore all of the different ways to connect five carbon atoms. First, we can connect all five carbon atoms in a linear fashion:



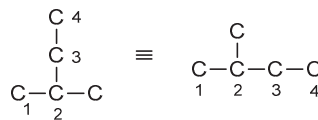
Alternatively, we can draw four carbon atoms in a linear fashion, and then draw the fifth carbon atom on a branch. There are many ways to draw this possibility:



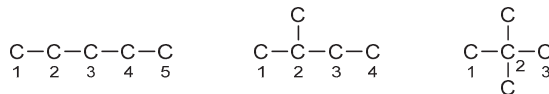
Finally, we can draw three carbon atoms in a linear fashion, and then draw the remaining two carbon atoms on separate branches.



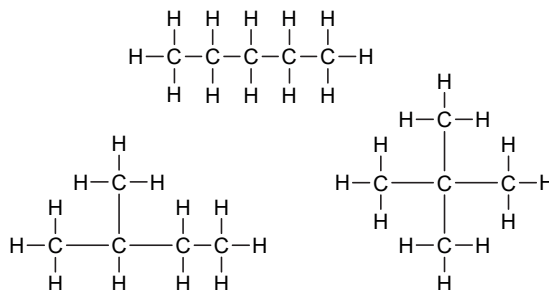
Note that we cannot place the last two carbon atoms together as one branch, because that possibility has already been drawn earlier (a linear chain of four carbon atoms with a single branch):



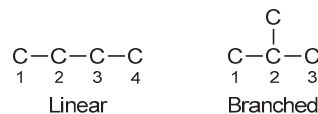
In summary, there are three different ways to connect five carbon atoms:



We then place the hydrogen atoms at the periphery, giving the following three constitutional isomers:



(d) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, the oxygen atom is divalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the four carbon atoms and the one oxygen atom) should be drawn in the center of the compound, with the hydrogen atoms at the periphery. There are several different ways to connect four carbon atoms and one oxygen atom. Let's begin with the four carbon atoms. There are two different ways to connect four carbon atoms. They can either be arranged in a linear fashion or in a branched fashion.

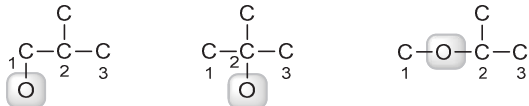


Next, the oxygen atom must be inserted. For each of the two skeletons above (linear or branched), there are

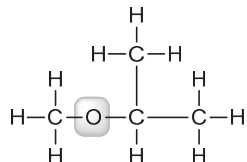
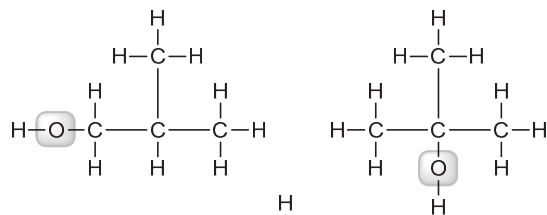
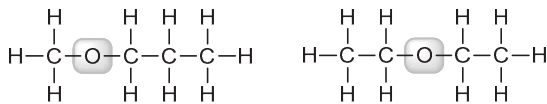
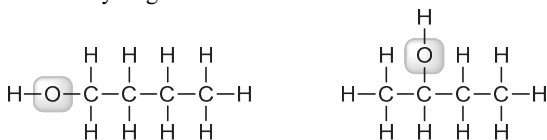
several different locations to insert the oxygen atom. The linear skeleton has four possibilities, shown here:



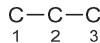
and the branched skeleton has three possibilities shown here:



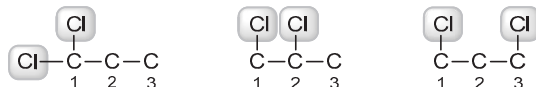
Finally, we complete all of the structures by drawing the bonds to hydrogen atoms.



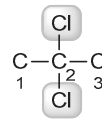
(e) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the chlorine atom and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the three carbon atoms) should be drawn in the center of the compound. There is only way to connect three carbon atoms:



Next, we must determine all of the different possible ways of connecting two chlorine atoms to the chain of three carbon atoms. If we place one chlorine atom at C1, then the second chlorine atom can be placed at C1, at C2 or at C3:



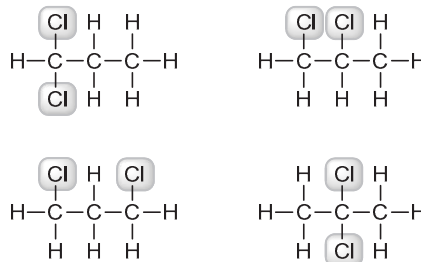
Furthermore, we can place both chlorine atoms at C2, giving a new possibility not shown above:



There are no other possibilities. For example, placing the two chlorine atoms at C2 and C3 is equivalent to placing them at C1 and C2:



Finally, the hydrogen atoms are placed at the periphery, giving the following four constitutional isomers:



1.2. The carbon atoms are tetravalent, while the chlorine atoms and fluorine atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The chlorine atoms and fluorine atoms are then placed at the periphery, as shown. There are only two possible constitutional isomers: one with the three chlorine atoms all connected to the same carbon, and one in which they are distributed over both carbon atoms. Any other representations that one may draw must be one of these structures drawn in a different orientation.



1.3.

(a) Carbon belongs to group 4A of the periodic table, and it therefore has four valence electrons. The periodic symbol for carbon (C) is drawn, and each valence electron is placed by itself (unpaired), around the C, like this:



(b) Oxygen belongs to group 6A of the periodic table, and it therefore has six valence electrons. The periodic symbol for oxygen (O) is drawn, and each valence electron is placed by itself (unpaired) on a side of the O, until all four sides are occupied. That takes care of four of the six electrons, leaving just two more electrons to

draw. Each of the two remaining electrons is then paired up with an electron already drawn, like this:



(c) Fluorine belongs to group 7A of the periodic table, and it therefore has seven valence electrons. The periodic symbol for fluorine (F) is drawn, and each valence electron is placed by itself (unpaired) on a side of the F, until all four sides are occupied. That takes care of four of the seven electrons, leaving three more electrons to draw. Each of the three remaining electrons is then paired up with an electron already drawn, like this:



(d) Hydrogen belongs to group 1A of the periodic table, and it therefore has one valence electron. The periodic symbol for hydrogen (H) is drawn, and the one and only valence electron is placed on a side of the H, like this:



(e) Bromine belongs to group 7A of the periodic table, and it therefore has seven valence electrons. The periodic symbol for bromine (Br) is drawn, and each valence electron is placed by itself (unpaired) on a side of the Br, until all four sides are occupied. That takes care of four of the seven electrons, leaving three more electrons to draw. Each of the three remaining electrons is then paired up with an electron already drawn, like this:



(f) Sulfur belongs to group 6A of the periodic table, and it therefore has six valence electrons. The periodic symbol for sulfur (S) is drawn, and each valence electron is placed by itself (unpaired) on a side of the S, until all four sides are occupied. That takes care of four of the six electrons, leaving just two more electrons to draw. Each of the two remaining electrons is then paired up with an electron already drawn, like this:



(g) Chlorine belongs to group 7A of the periodic table, and it therefore has seven valence electrons. The periodic symbol for chlorine (Cl) is drawn, and each valence electron is placed by itself (unpaired) on a side of the Cl, until all four sides are occupied. That takes care of four of the seven electrons, leaving three more electrons to draw. Each of the three remaining electrons is then paired up with an electron already drawn, like this:



(h) Iodine belongs to group 7A of the periodic table, and it therefore has seven valence electrons. The periodic symbol for iodine (I) is drawn, and each valence electron is placed by itself (unpaired) on a side of the I, until all four sides are occupied. That takes care of four of the seven electrons, leaving three more electrons to draw. Each of the three remaining electrons is then paired up with an electron already drawn, like this:



1.4. Both nitrogen and phosphorus belong to group 5A of the periodic table, and therefore, each of these atoms has five valence electrons. In order to achieve an octet, we expect each of these elements to form three bonds.

1.5. Aluminum is directly beneath boron on the periodic table (group 3A), and each of these elements has three valence electrons. Therefore, we expect the bonding properties to be similar.

1.6. The Lewis dot structure for a carbon atom is shown in the solution to Problem 1.3a. That drawing must be modified by removing one electron, resulting in a formal positive charge, as shown below. This resembles boron because it exhibits three valence electrons.



1.7.

(a) Lithium is in Group 1A of the periodic table, and therefore, it has just one valence electron.

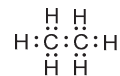


(b) If an electron is removed from a lithium atom, the resulting cation has zero valence electrons.

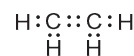


1.8.

(a) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, as shown.



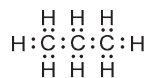
(b) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, and the unpaired electrons are shared to give a double bond. In this way, each of the carbon atoms achieves an octet.



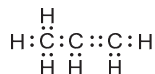
(c) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, and the unpaired electrons are shared to give a triple bond. In this way, each of the carbon atoms achieves an octet.



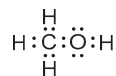
(d) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, as shown.



(e) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, and the unpaired electrons are shared to give a double bond. In this way, each of the carbon atoms achieves an octet.



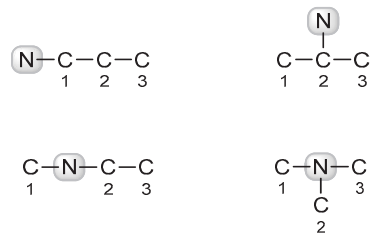
(f) The carbon atom has four valence electrons, the oxygen atom has six valence electrons, and each hydrogen atom has one valence electron. Only the carbon atom and the oxygen atom can form more than one bond, so we begin by connecting them to each other. Then, we connect all of the hydrogen atoms, as shown.



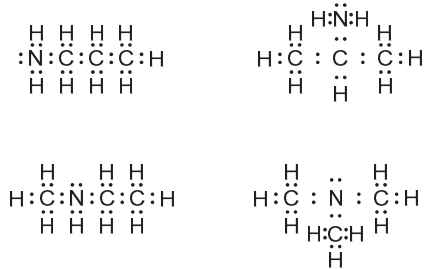
1.9. Boron has three valence electrons, each of which is shared with a hydrogen atom, shown below. The central boron atom lacks an octet of electrons, and it is therefore very unstable and reactive.



1.10. Each of the carbon atoms has four valence electrons; the nitrogen atom has five valence electrons; and each of the hydrogen atoms has one valence electron. We begin by connecting the atoms that have more than one bond (in this case, the three carbon atoms and the nitrogen atom). There are four different ways that these four atoms can be connected to each other, shown here.



For each of these possible arrangements, we connect the hydrogen atoms, giving the following four constitutional isomers.



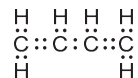
In each of these four structures, the nitrogen atom has one lone pair.

### 1.11.

(a) The carbon atom has four valence electrons, the nitrogen atom has five valence electrons and the hydrogen atom has one valence electron. Only the carbon atom and the nitrogen atom can form more than one bond, so we begin by connecting them to each other. Then, we connect the hydrogen atom to the carbon, as shown. The unpaired electrons are shared to give a triple bond. In this way, both the carbon atom and the nitrogen atom achieve an octet.

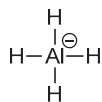


(b) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms as indicated in the given condensed formula ( $\text{CH}_2\text{CHCH}_2$ ), and the unpaired electrons are shared to give two double bonds on the outermost carbons. In this way, each of the carbon atoms achieves an octet.



### 1.12.

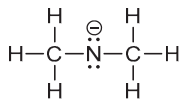
(a) Aluminum is in group 3A of the periodic table, and it should therefore have three valence electrons. In this case, the aluminum atom exhibits four valence electrons (one for each bond). With one extra electron, this aluminum atom will bear a negative charge.



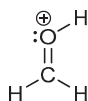
(b) Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. In this case, the oxygen atom exhibits only five valence electrons (one for each bond, and two for the lone pair). This oxygen atom is missing an electron, and it therefore bears a positive charge.



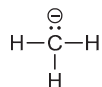
(c) Nitrogen is in group 5A of the periodic table, and it should therefore have five valence electrons. In this case, the nitrogen atom exhibits six valence electrons (one for each bond and two for each lone pair). With one extra electron, this nitrogen atom will bear a negative charge.



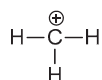
(d) Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. In this case, the oxygen atom exhibits only five valence electrons (one for each bond, and two for the lone pair). This oxygen atom is missing an electron, and it therefore bears a positive charge.



(e) Carbon is in group 4A of the periodic table, and it should therefore have four valence electrons. In this case, the carbon atom exhibits five valence electrons (one for each bond and two for the lone pair). With one extra electron, this carbon atom will bear a negative charge.

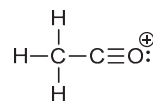


(f) Carbon is in group 4A of the periodic table, and it should therefore have four valence electrons. In this case, the carbon atom exhibits only three valence electrons (one for each bond). This carbon atom is missing an electron, and it therefore bears a positive charge.

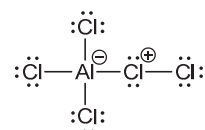


(g) Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. In this case,

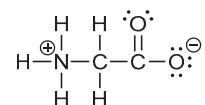
the oxygen atom exhibits only five valence electrons (one for each bond, and two for the lone pair). This oxygen atom is missing an electron, and it therefore bears a positive charge.



(h) Two of the atoms in this structure exhibit a formal charge because each of these atoms does not exhibit the appropriate number of valence electrons. The aluminum atom (group 3A) should have three valence electrons, but it exhibits four (one for each bond). With one extra electron, this aluminum atom will bear a negative charge. The neighboring chlorine atom (to the right) should have seven valence electrons, but it exhibits only six (one for each bond and two for each lone pair). It is missing one electron, so this chlorine atom will bear a positive charge.

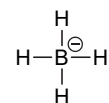


(i) Two of the atoms in this structure exhibit a formal charge because each of these atoms does not exhibit the appropriate number of valence electrons. The nitrogen atom (group 5A) should have five valence electrons, but it exhibits four (one for each bond). It is missing one electron, so this nitrogen atom will bear a positive charge. One of the two oxygen atoms (the one on the right) exhibits seven valence electrons (one for the bond, and two for each lone pair), although it should have only six. With one extra electron, this oxygen atom will bear a negative charge.

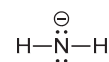


### 1.13.

(a) The boron atom in this case exhibits four valence electrons (one for each bond), although boron (group 3A) should only have three valence electrons. With one extra electron, this boron atom bears a negative charge.

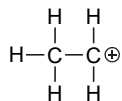


(b) Nitrogen is in group 5A of the periodic table, so a nitrogen atom should have five valence electrons. A negative charge indicates one extra electron, so this nitrogen atom must exhibit six valence electrons (one for each bond and two for each lone pair).

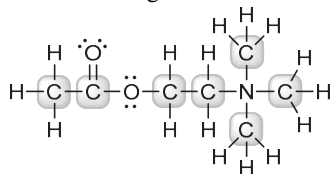




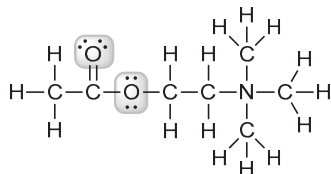
(c) One of the carbon atoms (below right) exhibits three valence electrons (one for each bond), but carbon (group 4A) is supposed to have four valence electrons. It is missing one electron, so this carbon atom therefore bears a positive charge.



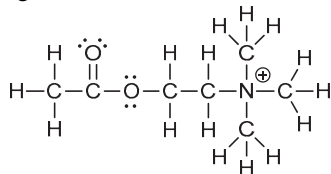
1.14. Carbon is in group 4A of the periodic table, and it should therefore have four valence electrons. Every carbon atom in acetylcholine has four bonds, thus exhibiting the correct number of valence electrons (four) and having no formal charge.



Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. Each oxygen atom in acetylcholine has two bonds and two lone pairs of electrons, so each oxygen atom exhibits six valence electrons (one for each bond, and two for each lone pair). With the correct number of valence electrons, each oxygen atom will lack a formal charge.

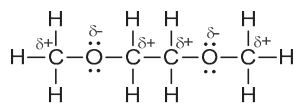


The nitrogen atom (group 5A) should have five valence electrons, but it exhibits four (one for each bond). It is missing one electron, so this nitrogen atom will bear a positive charge.

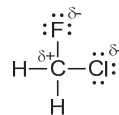


### 1.15.

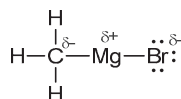
(a) Oxygen is more electronegative than carbon, and a C–O bond is polar covalent. For each C–O bond, the O will be electron rich ( $\delta^-$ ), and the C will be electron-poor ( $\delta^+$ ), as shown below.



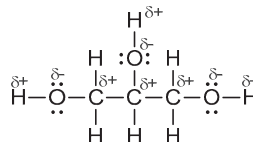
(b) Fluorine is more electronegative than carbon, and a C–F bond is polar covalent. For a C–F bond, the F will be electron-rich ( $\delta^-$ ), and the C will be electron-poor ( $\delta^+$ ). Chlorine is also more electronegative than carbon, so a C–Cl bond is also polar covalent. For a C–Cl bond, the Cl will be electron-rich ( $\delta^-$ ), and the C will be electron-poor ( $\delta^+$ ), as shown below.



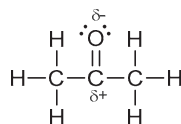
(c) Carbon is more electronegative than magnesium, so the C will be electron-rich ( $\delta^-$ ) in a C–Mg bond, and the Mg will be electron-poor ( $\delta^+$ ). Also, bromine is more electronegative than magnesium. So in a Mg–Br bond, the Br will be electron-rich ( $\delta^-$ ), and the Mg will be electron-poor ( $\delta^+$ ), as shown below.



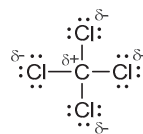
(d) Oxygen is more electronegative than carbon or hydrogen, so all C–O bonds and all O–H bond are polar covalent. For each C–O bond and each O–H bond, the O will be electron-rich ( $\delta^-$ ), and the C or H will be electron-poor ( $\delta^+$ ), as shown below.



(e) Oxygen is more electronegative than carbon. As such, the O will be electron-rich ( $\delta^-$ ) and the C will be electron-poor ( $\delta^+$ ) in a C=O bond, as shown below.

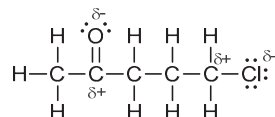


(f) Chlorine is more electronegative than carbon. As such, for each C–Cl bond, the Cl will be electron-rich ( $\delta^-$ ) and the C will be electron-poor ( $\delta^+$ ), as shown below.



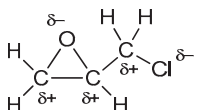
1.16. Oxygen is more electronegative than carbon. As such, the O will be electron-rich ( $\delta^-$ ) and the C will be electron-poor ( $\delta^+$ ) in a C=O bond. In addition, chlorine is more electronegative than carbon. So for a C–Cl

bond, the Cl will be electron-rich ( $\delta^-$ ) and the C will be electron-poor ( $\delta^+$ ), as shown below.



Notice that two carbon atoms are electron-poor ( $\delta^+$ ). These are the positions that are most likely to be attacked by an anion, such as hydroxide.

**1.17.** Oxygen is more electronegative than carbon. As such, the O will be electron-rich ( $\delta^-$ ) and the C will be electron-poor ( $\delta^+$ ) in a C–O bond. In addition, chlorine is more electronegative than carbon. So for a C–Cl bond, the Cl will be electron-rich ( $\delta^-$ ) and the C will be electron-poor ( $\delta^+$ ), as shown below. As you might imagine, epichlorohydrin is a very reactive molecule!



**1.18.**

(a) As indicated in Figure 1.10, carbon has two  $1s$  electrons, two  $2s$  electrons, and two  $2p$  electrons. This information is represented by the following electron configuration:  $1s^2 2s^2 2p^2$

(b) As indicated in Figure 1.10, oxygen has two  $1s$  electrons, two  $2s$  electrons, and four  $2p$  electrons. This information is represented by the following electron configuration:  $1s^2 2s^2 2p^4$

(c) As indicated in Figure 1.10, boron has two  $1s$  electrons, two  $2s$  electrons, and one  $2p$  electron. This information is represented by the following electron configuration:  $1s^2 2s^2 2p^1$

(d) As indicated in Figure 1.10, fluorine has two  $1s$  electrons, two  $2s$  electrons, and five  $2p$  electrons. This information is represented by the following electron configuration:  $1s^2 2s^2 2p^5$

(e) Sodium has two  $1s$  electrons, two  $2s$  electrons, six  $2p$  electrons, and one  $3s$  electron. This information is represented by the following electron configuration:  $1s^2 2s^2 2p^6 3s^1$

(f) Aluminum has two  $1s$  electrons, two  $2s$  electrons, six  $2p$  electrons, two  $3s$  electrons, and one  $3p$  electron. This information is represented by the following electron configuration:  $1s^2 2s^2 2p^6 3s^2 3p^1$

**1.19.**

(a) The electron configuration of a carbon atom is  $1s^2 2s^2 2p^2$  (see the solution to Problem 1.18a). However, if a carbon atom bears a negative charge, then it must have one extra electron, so the electron configuration should be as follows:  $1s^2 2s^2 2p^3$

(b) The electron configuration of a carbon atom is  $1s^2 2s^2 2p^2$  (see the solution to Problem 1.18a). However, if a carbon atom bears a positive charge, then it must be

missing an electron, so the electron configuration should be as follows:  $1s^2 2s^2 2p^1$

(c) As seen in Skillbuilder 1.6, the electron configuration of a nitrogen atom is  $1s^2 2s^2 2p^3$ . However, if a nitrogen atom bears a positive charge, then it must be missing an electron, so the electron configuration should be as follows:  $1s^2 2s^2 2p^2$

(d) The electron configuration of an oxygen atom is  $1s^2 2s^2 2p^4$  (see the solution to Problem 1.18b). However, if an oxygen atom bears a negative charge, then it must have one extra electron, so the electron configuration should be as follows:  $1s^2 2s^2 2p^5$

**1.20.** Silicon is in the third row, or period, of the periodic table. Therefore, it has a filled second shell, like neon, and then the additional electrons are added to the third shell. As indicated in Figure 1.10, neon has two  $1s$  electrons, two  $2s$  electrons, and six  $2p$  electrons. Silicon has an additional two  $3s$  electrons and two  $3p$  electrons to give a total of 14 electrons and an electron configuration of  $1s^2 2s^2 2p^6 3s^2 3p^2$ .

**1.21.** The bond angles of an equilateral triangle are  $60^\circ$ , but each bond angle of cyclopropane is supposed to be  $109.5^\circ$ . Therefore, each bond angle is severely strained, causing an increase in energy. This form of strain, called ring strain, will be discussed in Chapter 4. The ring strain associated with a three-membered ring is greater than the ring strain of larger rings, because larger rings do not require bond angles of  $60^\circ$ .

**1.22.**

(a) The C=O bond of formaldehyde is comprised of one  $\sigma$  bond and one  $\pi$  bond.

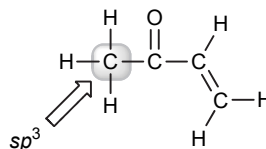
(b) Each C–H bond is formed from the interaction between an  $sp^2$  hybridized orbital from carbon and an  $s$  orbital from hydrogen.

(c) The oxygen atom is  $sp^2$  hybridized, so the lone pairs occupy  $sp^2$  hybridized orbitals.

**1.23.** Rotation of a single bond does not cause a reduction in the extent of orbital overlap, because the orbital overlap occurs on the bond axis. In contrast, rotation of a  $\pi$  bond results in a reduction in the extent of orbital overlap, because the orbital overlap is NOT on the bond axis.

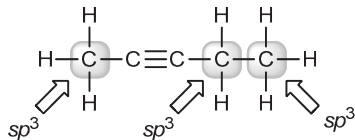
**1.24.**

(a) The highlighted carbon atom (below) has four  $\sigma$  bonds, and is therefore  $sp^3$  hybridized. The other carbon atoms in this structure are all  $sp^2$  hybridized, because each of them has three  $\sigma$  bonds and one  $\pi$  bond.

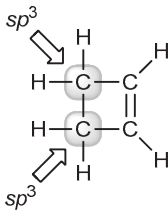


(b) Each of the highlighted carbon atoms has four  $\sigma$  bonds, and is therefore  $sp^3$  hybridized. Each of the

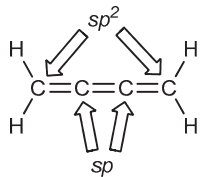
other two carbon atoms in this structure is  $sp$  hybridized, because each has two  $\sigma$  bonds and two  $\pi$  bonds.



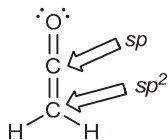
(b) Each of the highlighted carbon atoms (below) has four  $\sigma$  bonds, and is therefore  $sp^3$  hybridized. Each of the other two carbon atoms in this structure is  $sp^2$  hybridized, because each has three  $\sigma$  bonds and one  $\pi$  bond.



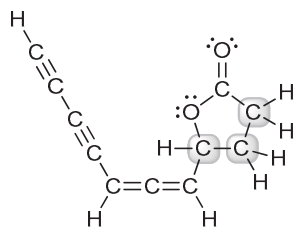
(d) Each of the two central carbon atoms has two  $\sigma$  bonds and two  $\pi$  bonds, and as such, each of these carbon atoms is  $sp$  hybridized. The other two carbon atoms (the outer ones) are  $sp^2$  hybridized because each has three  $\sigma$  bonds and one  $\pi$  bond.



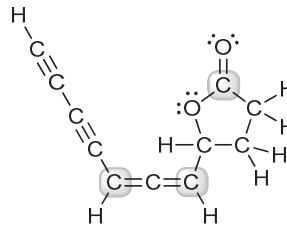
(e) One of the carbon atoms (the one connected to oxygen) has two  $\sigma$  bonds and two  $\pi$  bonds, and as such, it is  $sp$  hybridized. The other carbon atom is  $sp^2$  hybridized because it has three  $\sigma$  bonds and one  $\pi$  bond.



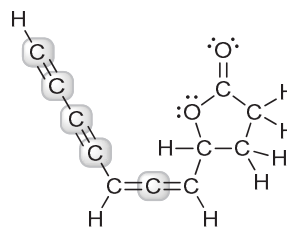
1.25. Each of the following three highlighted carbon atoms has four  $\sigma$  bonds, and is therefore  $sp^3$  hybridized:



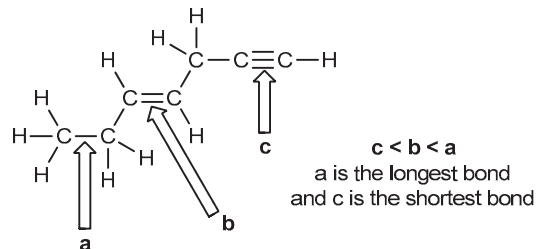
And each of the following three highlighted carbon atoms has three  $\sigma$  bonds and one  $\pi$  bond, and is therefore  $sp^2$  hybridized:



Finally, each of the following five highlighted carbon atoms has two  $\sigma$  bonds and two  $\pi$  bonds, and is therefore  $sp$  hybridized.



1.26. Carbon-carbon triple bonds generally have a shorter bond length than carbon-carbon double bonds, which are generally shorter than carbon-carbon single bonds (see Table 1.2).



### 1.27

(a) In this structure, the boron atom has four  $\sigma$  bonds and no lone pairs, giving a total of four electron pairs (steric number = 4). VSEPR theory therefore predicts a tetrahedral arrangement of electron pairs. Since all of the electron pairs are bonds, the structure is expected to have tetrahedral geometry.

(b) In this structure, the boron atom has three  $\sigma$  bonds and no lone pairs, giving a total of three electron pairs (steric number = 3). VSEPR theory therefore predicts a trigonal planar geometry.

(c) In this structure, the nitrogen atom has four  $\sigma$  sigma bonds and no lone pairs, giving a total of four electron pairs (steric number = 4). VSEPR theory therefore predicts a tetrahedral arrangement of electron pairs. Since all of the electron pairs are bonds, the structure is expected to have tetrahedral geometry.

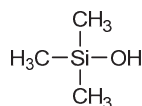
(d) The carbon atom has four  $\sigma$  bonds and no lone pairs, giving a total of four electron pairs (steric number = 4). VSEPR theory therefore predicts a tetrahedral

arrangement of electron pairs. Since all of the electron pairs are bonds, the structure is expected to have tetrahedral geometry.

**1.28.** In the carbocation, the carbon atom has three bonds and no lone pairs. Since there are a total of three electron pairs (steric number = 3), VSEPR theory predicts trigonal planar geometry, with bond angles of  $120^\circ$ . In contrast, the carbon atom of the carbanion has three bonds and one lone pair, giving a total of four electron pairs (steric number = 4). For this ion, VSEPR theory predicts a tetrahedral arrangement of electron pairs, with a lone pair positioned at one corner of the tetrahedron, giving rise to trigonal pyramidal geometry.

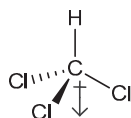
**1.29.** In ammonia, the nitrogen atom has three bonds and one lone pair. Therefore, VSEPR theory predicts trigonal pyramidal geometry, with bond angles of approximately  $107^\circ$ . In the ammonium ion, the nitrogen atom has four bonds and no lone pairs, so VSEPR theory predicts tetrahedral geometry, with bond angles of  $109.5^\circ$ . Therefore, we predict that the bond angles will increase (by approximately  $2.5^\circ$ ) as a result of the reaction.

**1.30.** The silicon atom has four  $\sigma$  bonds and no lone pairs, so the steric number is 4 ( $sp^3$  hybridization), which means that the arrangement of electron pairs will be tetrahedral. With no lone pairs, the arrangement of the atoms (geometry) is the same as the electronic arrangement. It is tetrahedral.

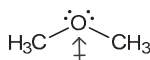


**1.31.**

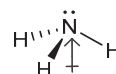
(a) This compound has three C–Cl bonds, each of which exhibits a dipole moment. To determine if these dipole moments cancel each other, we must identify the molecular geometry. The central carbon atom has four  $\sigma$  bonds so we expect tetrahedral geometry. As such, the three C–Cl bonds do not lie in the same plane, and they do not completely cancel each other out. There is a net molecular dipole moment, as shown:



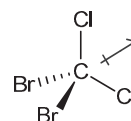
(b) The oxygen atom has two  $\sigma$  bonds and two lone pairs (steric number = 4), and VSEPR theory predicts bent geometry. As such, the dipole moments associated with the C–O bonds do not fully cancel each other. There is a net molecular dipole moment, as shown:



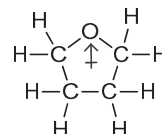
(c) The nitrogen atom has three  $\sigma$  bonds and one lone pair (steric number = 4), and VSEPR theory predicts trigonal pyramidal geometry (because one corner of the tetrahedron is occupied by a lone pair). As such, the dipole moments associated with the N–H bonds do not fully cancel each other. There is a net molecular dipole moment, as shown:



(d) The central carbon atom has four  $\sigma$  bonds (steric number = 4), and VSEPR theory predicts tetrahedral geometry. There are individual dipole moments associated with each of the C–Cl bonds and each of the C–Br bonds. If all four dipole moments had the same magnitude, then we would expect them to completely cancel each other to give no molecular dipole moment (as in the case of  $CCl_4$ ). However, the dipole moments for the C–Cl bonds are larger than the dipole moments of the C–Br bonds, and as such, there is a net molecular dipole moment, shown here:

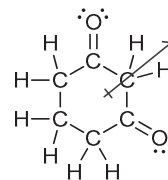


(e) The oxygen atom has two  $\sigma$  bonds and two lone pairs (steric number = 4), and VSEPR theory predicts bent geometry. As such, the dipole moments associated with the C–O bonds do not fully cancel each other. There is a net molecular dipole moment, as shown:



(f) There are individual dipole moments associated with each C–O bond (just as we saw in the solution to **1.31e**), but in this case, they fully cancel each other to give no net molecular dipole moment.

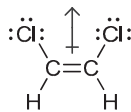
(g) Each C=O bond has a strong dipole moment, and they do not fully cancel each other because they are not pointing in opposite directions. As such, there will be a net molecular dipole moment, as shown here:



(h) Each C=O bond has a strong dipole moment, and in this case, they are pointing in opposite directions. As

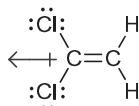
such, they fully cancel each other, giving no net molecular dipole moment.

(i) Each C–Cl bond has a dipole moment, and they do not fully cancel each other because they are not pointing in opposite directions. As such, there will be a net molecular dipole moment, as shown here:



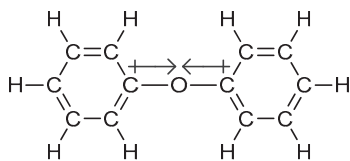
(j) Each C–Cl bond has a dipole moment, and in this case, they are pointing in opposite directions. As such, they fully cancel each other, giving no net molecular dipole moment.

(k) Each C–Cl bond has a dipole moment, and they do not fully cancel each other because they are not pointing in opposite directions. As such, there will be a net molecular dipole moment, as shown here:

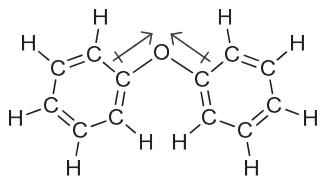


(l) Each C–Cl bond has a dipole moment, but in this case, they fully cancel each other to give no net molecular dipole moment.

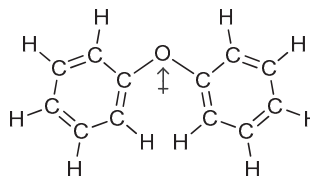
1.32. Each of the C–O bonds has an individual dipole moment, shown here.



To determine if these individual dipole moments fully cancel each other, we must determine the geometry around the oxygen atom. The oxygen atom has two  $\sigma$  bonds and two lone pairs, giving rise to a bent geometry. As such, the dipole moments associated with the C–O bonds do NOT fully cancel each other.



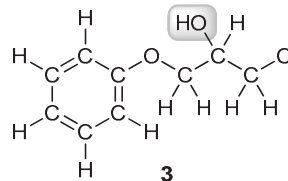
Therefore, there is a net molecular dipole moment, as shown:



1.33.

- (a) The latter compound is expected to have a higher boiling point, because it is less branched.
- (b) The latter compound is expected to have a higher boiling point, because it has more carbon atoms.
- (c) The latter compound is expected to have a higher boiling point, because it has an OH bond, which will lead to hydrogen bonding interactions.
- (d) The first compound is expected to have a higher boiling point, because it is less branched.

1.34. Compound 3 is expected to have a higher boiling point than compound 4, because the former has an O–H group and the latter does not. Compound 4 does not have the ability to form hydrogen-bonding interactions with itself, so it will have a lower boiling point. When this mixture is heated, the compound that boils first (4) can be collected, leaving behind compound 3.

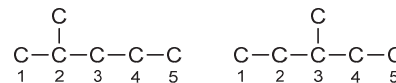


1.35.

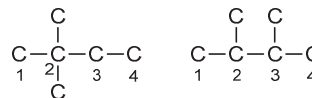
(a) The carbon atoms are tetravalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the six carbon atoms) should be drawn in the center of the compound, with the hydrogen atoms at the periphery. There are five different ways to connect six carbon atoms, which we will organize based on the length of the longest chain.



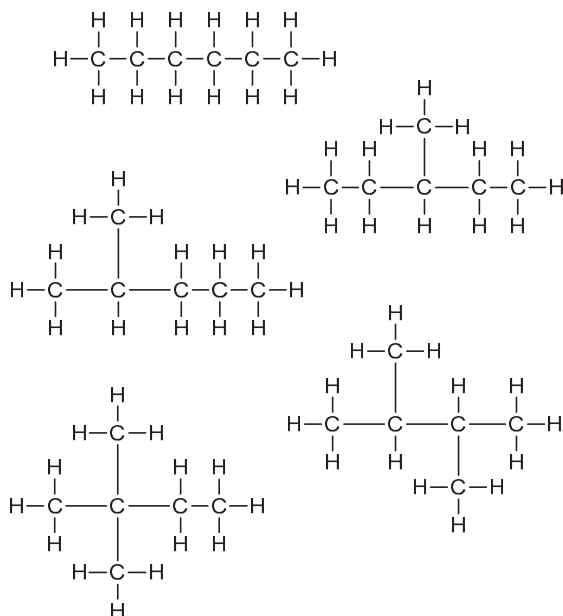
In a 5-carbon chain:



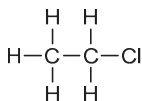
In a 4-carbon chain:



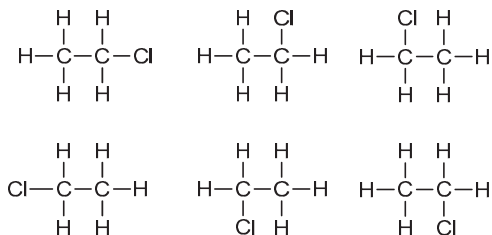
Finally, we complete all of the structures by drawing the bonds to hydrogen atoms.



(b) The carbon atoms are tetravalent, while the chlorine atom and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The chlorine atom and hydrogen atoms are then placed at the periphery, as shown.

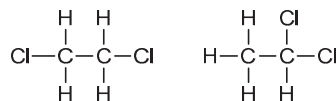


The chlorine atom can be placed in any one of the six available positions. The following six drawings all represent the same compound, in which the two carbon atoms are connected to each other, and the chlorine atom is connected to one of the carbon atoms.

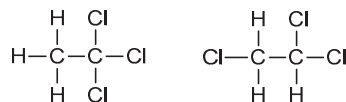


(c) The carbon atoms are tetravalent, while the chlorine atoms and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The chlorine atoms and hydrogen atoms are then placed at the periphery, and there are two different ways to do this. The two chlorine atoms can either be

connected to the same carbon atom or to different carbon atoms, as shown.

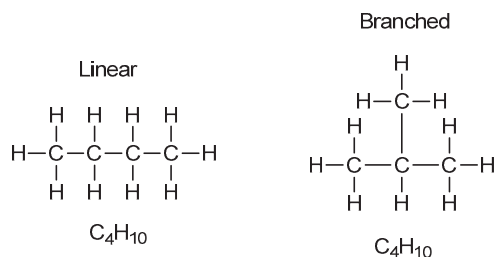


(d) The carbon atoms are tetravalent, while the chlorine atoms and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The chlorine atoms and hydrogen atoms are then placed at the periphery, and there are two different ways to do this. One way is to connect all three chlorine atoms to the same carbon atom. Alternatively, we can connect two chlorine atoms to one carbon atom, and then connect the third chlorine atom to the other carbon atom, as shown here:

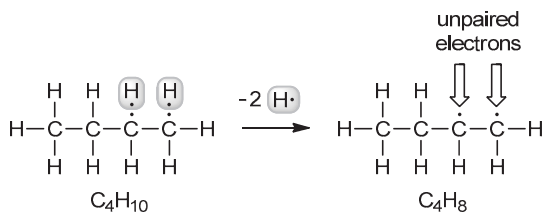


### 1.36.

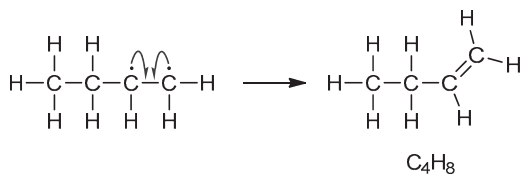
(a) The molecular formula ( $C_4H_8$ ) indicates that we must draw structures with four carbon atoms and eight hydrogen atoms. The carbon atoms are tetravalent, while the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the four carbon atoms) should be drawn in the center of the compound, with the hydrogen atoms at the periphery. When we connect four carbon atoms, either in a linear fashion or in a branched fashion (see solution to 1.1b), we find that ten hydrogen atoms are required in order for all four carbon atoms to achieve an octet (to have four bonds).



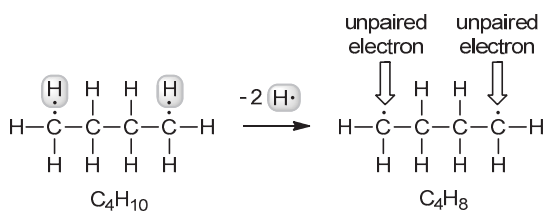
But the molecular formula ( $C_4H_8$ ) indicates only eight hydrogen atoms, so we must remove two hydrogen atoms. This gives two carbon atoms that lack an octet, because each of them has an unpaired electron.



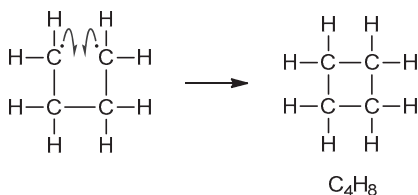
These electrons can be paired as a double bond:



but the problem statement directs us to draw only those constitutional isomers in which all of the bonds are single bonds. So we must think of another way to pair up the unpaired electrons. It is difficult to see how this can be accomplished if the unpaired electrons are on adjacent carbon atoms. But suppose the unpaired electrons are on distant carbon atoms:

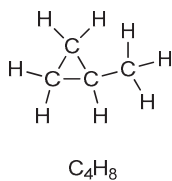


When drawn like this, it becomes apparent that we can pair the unpaired electrons by forming a C-C bond, giving a ring:

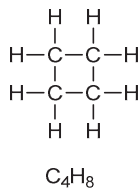


When the structure contains a ring, then eight hydrogen atoms are sufficient to provide all four carbon atoms with an octet of electrons. The ring can either be a 3-membered ring or a 4-membered ring, giving the following two constitutional isomers:

Three-membered ring



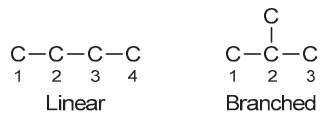
Four-membered ring



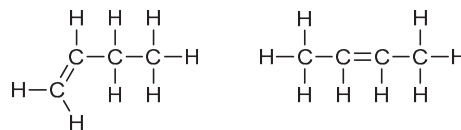
(b) See the solution to part (a) as an introduction to the following solution.

Since the unpaired electrons were paired as a double bond (rather than as a ring), we are looking for compounds that contain one double bond and do NOT have a ring. Since the structure does not contain a ring,

we can imagine arranging the carbon atoms either in a linear fashion or in a branched fashion:

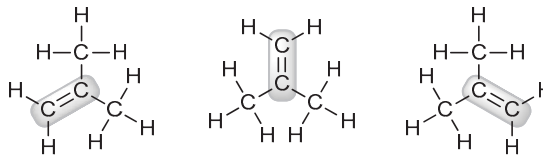


In the linear skeleton, there are two locations where we can place the double bond:

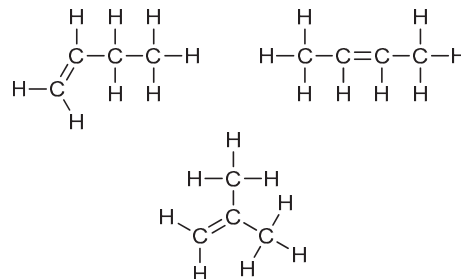


Notice that the double bond can be placed at C1-C2 or at C2-C3 (placing the double bond at C3-C4 is the same as placing it at C1-C2, because we can just assign numbers in the opposite direction).

Now let's explore the branched skeleton. There is only one location to place the double bond in a branched skeleton, because the following three drawings represent the same compound:



In summary, there are three constitutional isomers of  $C_4H_8$  that contain a double bond:



### 1.37.

(a) According to Table 1.1, the difference in electronegativity between Br and H is  $2.8 - 2.1 = 0.7$ , so an H-Br bond is expected to be polar covalent. Since bromine is more electronegative than hydrogen, the Br will be electron rich ( $\delta^-$ ), and the H will be electron-poor ( $\delta^+$ ), as shown below:

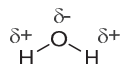


(b) According to Table 1.1, the difference in electronegativity between Cl and H is  $3.0 - 2.1 = 0.9$ , so an H-Cl bond is expected to be polar covalent. Since chlorine is more electronegative than hydrogen, the Cl

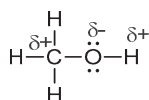
will be electron rich ( $\delta^-$ ), and the H will be electron-poor ( $\delta^+$ ), as shown below:



(c) According to Table 1.1, the difference in electronegativity between O and H is  $3.5 - 2.1 = 1.4$ , so an O–H bond is expected to be polar covalent. Oxygen is more electronegative than hydrogen, so for each O–H bond, the O will be electron rich ( $\delta^-$ ) and the H will be electron-poor ( $\delta^+$ ), as shown below:



(d) Oxygen (3.5) is more electronegative than carbon (2.5) or hydrogen (2.1), and a C–O or H–O bond is polar covalent. For each C–O or H–O bond, the O will be electron rich ( $\delta^-$ ), and the C or H will be electron-poor ( $\delta^+$ ), as shown below:



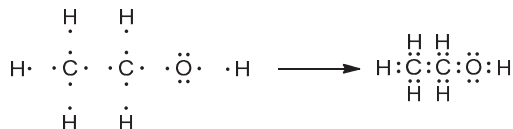
### 1.38.

(a) The difference in electronegativity between Na (0.9) and Br (2.8) is greater than the difference in electronegativity between H (2.1) and Br (2.8). Therefore, NaBr is expected to have more ionic character than HBr.

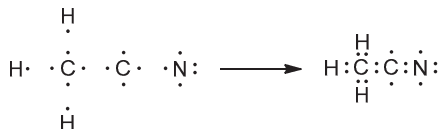
(b) The difference in electronegativity between F (4.0) and Cl (3.0) is greater than the difference in electronegativity between Br (2.8) and Cl (3.0). Therefore, FCl is expected to have more ionic character than BrCl.

### 1.39.

(a) Each carbon atom has four valence electrons, the oxygen atom has six valence electrons, and each hydrogen atom has one valence electron. In this case, the information provided in the problem statement ( $\text{CH}_3\text{CH}_2\text{OH}$ ) indicates how the atoms are connected to each other:



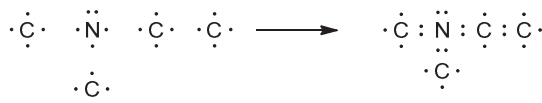
(b) Each carbon atom has four valence electrons, the nitrogen atom has five valence electrons, and each hydrogen atom has one valence electron. In this case, the information provided in the problem statement ( $\text{CH}_3\text{CN}$ ) indicates how the atoms are connected to each other:



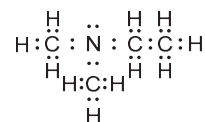
The unpaired electrons are then paired up to give a triple bond. In this way, each of the atoms achieves an octet.



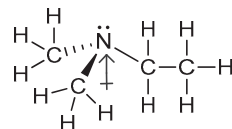
1.40. Each of the carbon atoms has four valence electrons; the nitrogen atom has five valence electrons; and each of the hydrogen atoms has one valence electron. We begin by connecting the atoms that have more than one bond (in this case, the four carbon atoms and the nitrogen atom). The problem statement indicates how we should connect them:



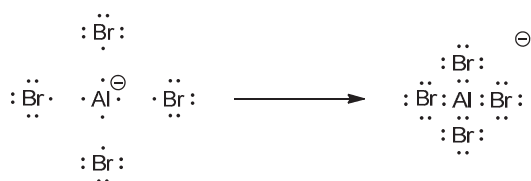
Then, we connect all of the hydrogen atoms, as shown.



The nitrogen atom has three  $\sigma$  bonds and one lone pair, so the steric number is 4, which means that the arrangement of electron pairs is expected to be tetrahedral. One corner of the tetrahedron is occupied by a lone pair, so the geometry of the nitrogen atom (the arrangement of atoms around that nitrogen atom) is trigonal pyramidal. As such, the individual dipole moments associated with the C–N bonds do not fully cancel each other. There is a net molecular dipole moment, as shown:



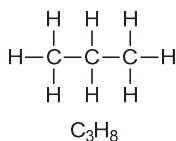
1.41. Bromine is in group 7A of the periodic table, so each bromine atom has seven valence electrons. Aluminum is in group 3A of the periodic table, so aluminum is supposed to have three valence electrons, but the structure bears a negative charge, which means that there is one extra electron. That is, the aluminum atom has four valence electrons, rather than three, which is why it has a formal negative charge. This gives the following Lewis structure:



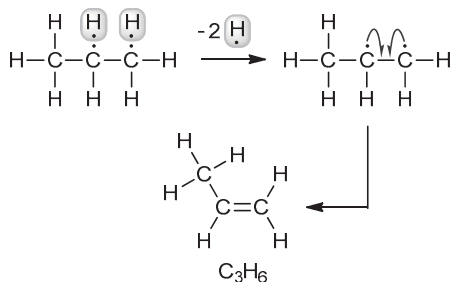


The aluminum atom has four bonds and no lone pairs, so the steric number is 4, which means that this aluminum atom will have tetrahedral geometry.

**1.42.** The molecular formula of cyclopropane is  $C_3H_6$ , so we are looking for a different compound that has the same molecular formula,  $C_3H_6$ . That is, we need to find another way to connect the carbon atoms, other than in a ring (there is only one way to connect three carbon atoms in a ring, so we must be looking for something other than a ring). If we connect the three carbon atoms in a linear fashion and then complete the drawing by placing hydrogen atoms at the periphery, we notice that the molecular formula ( $C_3H_8$ ) is not correct:



We are looking for a structure with the molecular formula  $C_3H_6$ . If we remove two hydrogen atoms from our drawing, we are left with two unpaired electrons, indicating that we should consider drawing a double bond:

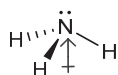


The structure of this compound (called propylene) is different from the structure of cyclopropane, but both compounds share the same molecular formula, so they are constitutional isomers.

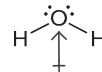
**1.43.**

(a) C–H bonds are considered to be covalent, although they do have a very small dipole moment, because there is a small difference in electronegativity between carbon (2.5) and hydrogen (2.1). Despite the very small dipole moments associated with the C–H bonds, the compound has no net dipole moment. The carbon atom has tetrahedral geometry (because it has four  $\sigma$  bonds), so the small effects from each C–H bond completely cancel each other.

(b) The nitrogen atom has trigonal pyramidal geometry. As such, the dipole moments associated with the N–H bonds do not fully cancel each other. There is a net molecular dipole moment, as shown:



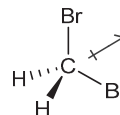
(c) The oxygen atom has two  $\sigma$  bonds and two lone pairs (steric number = 4), and VSEPR predicts bent geometry. As such, the dipole moments associated with the O–H bonds do not cancel each other. There is a net molecular dipole moment, as shown:



(d) The central carbon atom of carbon dioxide ( $CO_2$ ) has two  $\sigma$  bonds and no lone pairs, so it is  $sp$  hybridized and is expected to have linear geometry. Each C=O bond has a strong dipole moment, but in this case, they are pointing in opposite directions. As such, they fully cancel each other, giving no net molecular dipole moment.

(e) Carbon tetrachloride ( $CCl_4$ ) has four C–Cl bonds, each of which exhibits a dipole moment. However, the central carbon atom has four  $\sigma$  bonds so it is expected to have tetrahedral geometry. As such, the four dipole moments completely cancel each other out, and there is no net molecular dipole moment.

(f) This compound has two C–Br bonds, each of which exhibits a dipole moment. To determine if these dipole moments cancel each other, we must identify the molecular geometry. The central carbon atom has four  $\sigma$  bonds so it is expected to have tetrahedral geometry. As such, the C–Br bonds do not completely cancel each other out. There is a net molecular dipole moment, as shown:



**1.44.**

(a) As indicated in Figure 1.10, oxygen has two  $1s$  electrons, two  $2s$  electrons, and four  $2p$  electrons.

(b) As indicated in Figure 1.10, fluorine has two  $1s$  electrons, two  $2s$  electrons, and five  $2p$  electrons.

(c) As indicated in Figure 1.10, carbon has two  $1s$  electrons, two  $2s$  electrons, and two  $2p$  electrons.

(d) As seen in SkillBuilder 1.6, the electron configuration of a nitrogen atom is  $1s^2 2s^2 2p^3$

(e) This is the electron configuration of chlorine.

**1.45.**

(a) The difference in electronegativity between sodium (0.9) and bromine (2.8) is  $2.8 - 0.9 = 1.9$ . Since this difference is greater than 1.7, the bond is classified as ionic.

(b) The difference in electronegativity between sodium (0.9) and oxygen (3.5) is  $3.5 - 0.9 = 2.6$ . Since this difference is greater than 1.7, the Na–O bond is classified as ionic. In contrast, the O–H bond is polar covalent, because the difference in electronegativity

between oxygen (3.5) and hydrogen (2.1) is less than 1.7 but more than 0.5.

(c) Each C–H bond is considered to be covalent, because the difference in electronegativity between carbon (2.5) and hydrogen (2.1) is less than 0.5.

The C–O bond is polar covalent, because the difference in electronegativity between oxygen (3.5) and carbon (2.5) is less than 1.7 but more than 0.5. The Na–O bond is classified as ionic, because the difference in electronegativity between oxygen (3.5) and sodium (0.9) is greater than 1.7.

(d) Each C–H bond is considered to be covalent, because the difference in electronegativity between carbon (2.5) and hydrogen (2.1) is less than 0.5.

The C–O bond is polar covalent, because the difference in electronegativity between oxygen (3.5) and carbon (2.5) is less than 1.7 but more than 0.5. The O–H bond is polar covalent, because the difference in electronegativity between oxygen (3.5) and hydrogen (2.1) is less than 1.7 but more than 0.5.

(e) Each C–H bond is considered to be covalent, because the difference in electronegativity between carbon (2.5) and hydrogen (2.1) is less than 0.5.

The C=O bond is polar covalent, because the difference in electronegativity between oxygen (3.5) and carbon (2.5) is less than 1.7 but more than 0.5.

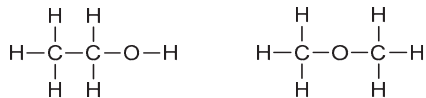


#### 1.46.

(a) Begin by determining the valency of each atom in the compound. The carbon atoms are tetravalent, the oxygen atom is divalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the two carbon atoms and the oxygen atom) should be drawn in the center of the compound, with the hydrogen atoms at the periphery. There are two different ways to connect two carbon atoms and an oxygen atom, shown here:

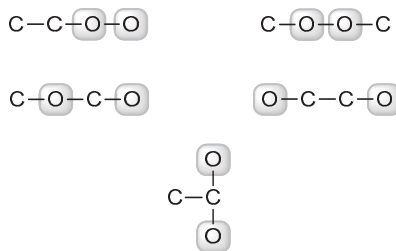


We then complete both structures by drawing the remaining bonds to hydrogen atoms:

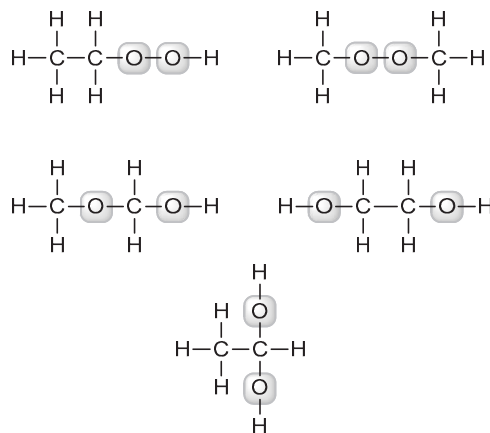


(b) Begin by determining the valency of each atom in the compound. The carbon atoms are tetravalent, the oxygen atoms are divalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the two carbon atoms and the two oxygen atoms) should be drawn in the center of the compound,

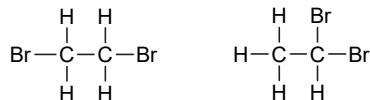
with the hydrogen atoms at the periphery. There are several different ways to connect two carbon atoms and two oxygen atoms (highlighted, for clarity of comparison), shown here:



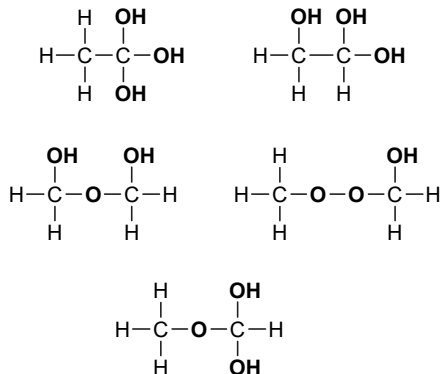
We then complete all of these structures by drawing the remaining bonds to hydrogen atoms:



(c) The carbon atoms are tetravalent, while the bromine atoms and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The bromine atoms and hydrogen atoms are then placed at the periphery, and there are two different ways to do this. The two bromine atoms can either be connected to the same carbon atom or to different carbon atoms, as shown.



1.47. Begin by determining the valency of each atom in the compound. The carbon atoms are tetravalent, the oxygen atoms are divalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the two carbon atoms and the three oxygen atoms) should be drawn in the center of the compound, with the hydrogen atoms at the periphery. There are many different ways to connect two carbon atoms and three oxygen atoms (see the solution to Problem 1.46b for comparison). Five such ways are shown, although there are certainly others:



## 1.48.

(a) Oxygen is more electronegative than carbon, and the withdrawal of electron density toward oxygen can be indicated with the following arrow:



(b) Carbon is more electronegative than magnesium, and the withdrawal of electron density toward carbon can be indicated with the following arrow:



(c) Nitrogen is more electronegative than carbon, and the withdrawal of electron density toward nitrogen can be indicated with the following arrow:



(d) Carbon is more electronegative than lithium, and the withdrawal of electron density toward carbon can be indicated with the following arrow:



(e) Chlorine is more electronegative than carbon, and the withdrawal of electron density toward chlorine can be indicated with the following arrow:



(f) Carbon is more electronegative than hydrogen, and the withdrawal of electron density toward carbon can be indicated with the following arrow:



(g) Oxygen is more electronegative than hydrogen, and the withdrawal of electron density toward oxygen can be indicated with the following arrow:



(h) Nitrogen is more electronegative than hydrogen, and the withdrawal of electron density toward nitrogen can be indicated with the following arrow:



## 1.49.

(a) The oxygen atom has two  $\sigma$  bonds and two lone pairs (steric number = 4), and VSEPR theory predicts bent geometry. The C-O-H bond angle is expected to be approximately  $105^\circ$ , and all other bonds angles are expected to be  $109.5^\circ$  (because each carbon atom has four  $\sigma$  bonds and tetrahedral geometry).

(b) The central carbon atom has three  $\sigma$  bonds and no lone pairs (steric number = 3), and VSEPR theory predicts trigonal planar geometry. As such, all bond angles are approximately  $120^\circ$ .



(c) Each of the carbon atoms has three  $\sigma$  bonds and no lone pairs (steric number = 3), and VSEPR theory predicts trigonal planar geometry. As such, all bond angles are approximately  $120^\circ$ .



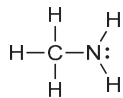
(d) Each of the carbon atoms has two  $\sigma$  bonds and no lone pairs (steric number = 2), and VSEPR theory predicts linear geometry. As such, all bond angles are approximately  $180^\circ$ .



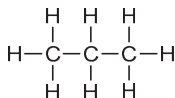
(e) The oxygen atom has two  $\sigma$  bonds and two lone pairs (steric number = 4), and VSEPR theory predicts bent geometry. Therefore, the C-O-C bond angle is expected to be around  $105^\circ$ . The remaining bond angles are all expected to be approximately  $109.5^\circ$  (because each carbon atom has four  $\sigma$  bonds and tetrahedral geometry).

(f) The nitrogen atom has three  $\sigma$  bonds and one lone pair (steric number = 4), and VSEPR theory predicts trigonal pyramidal geometry, with bond angles of  $107^\circ$ . The carbon atom is also tetrahedral (because it has four

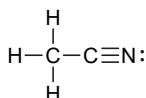
$\sigma$  bonds), although the bond angles around the carbon atom are expected to be approximately  $109.5^\circ$ .



(g) Each of the carbon atoms has four  $\sigma$  bonds (steric number = 4), so each of these carbon atoms has tetrahedral geometry. Therefore, all bond angles are expected to be approximately  $109.5^\circ$ .



(h) The structure of acetonitrile ( $\text{CH}_3\text{CN}$ ) is shown below (see the solution to Problem 1.39b).



One of the carbon atoms has four  $\sigma$  bonds (steric number = 4), and is expected to have tetrahedral geometry. The other carbon atom (connected to nitrogen) has two  $\sigma$  bonds and no lone pairs (steric number = 2), so we expect linear geometry.

As such, the  $\text{C}-\text{C}\equiv\text{N}$  bond angle is  $180^\circ$ , and all other bond angles are approximately  $109.5^\circ$ .

### 1.50.

(a) The nitrogen atom has three  $\sigma$  bonds and one lone pair (steric number = 4). It is  $sp^3$  hybridized (electronically tetrahedral), with trigonal pyramidal geometry (because one corner of the tetrahedron is occupied by a lone pair).

(b) The boron atom has three  $\sigma$  bonds and no lone pairs (steric number = 3). It is  $sp^2$  hybridized, with trigonal planar geometry.

(c) This carbon atom has three  $\sigma$  bonds and no lone pairs (steric number = 3). It is  $sp^2$  hybridized, with trigonal planar geometry.

(d) This carbon atom has three  $\sigma$  bonds and one lone pair (steric number = 4). It is  $sp^3$  hybridized (electronically tetrahedral), with trigonal pyramidal geometry (because one corner of the tetrahedron is occupied by a lone pair).

1.51. The double bond represents one  $\sigma$  bond and one  $\pi$  bond, while the triple bond represents one  $\sigma$  bond and two  $\pi$  bonds. All single bonds are  $\sigma$  bonds. Therefore, this compound has sixteen  $\sigma$  bonds and three  $\pi$  bonds.

### 1.52.

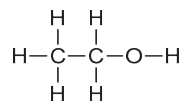
(a) The latter compound is expected to have a higher boiling point, because it has an  $\text{O}-\text{H}$  bond, which will lead to hydrogen bonding interactions.

(b) The latter compound is expected to have a higher boiling point, because it has more carbon atoms, and thus more opportunity for London interactions.

(c) Both compounds have the same number of carbon atoms, but the first compound has a  $\text{C}=\text{O}$  bond, which has a strong dipole moment. The first compound is therefore expected to exhibit strong dipole-dipole interactions and to have a higher boiling point than the second compound.

### 1.53.

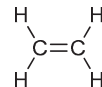
(a) This compound possesses an  $\text{O}-\text{H}$  bond, so it is expected to exhibit hydrogen bonding interactions.



(b) This compound lacks a hydrogen atom that is connected to an electronegative element. Therefore, this compound cannot serve as a hydrogen bond donor (although the lone pairs can serve as hydrogen bond acceptors). In the absence of another hydrogen bond donor, we do not expect there to be any hydrogen bonding interactions.



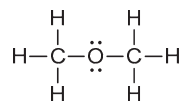
(c) This compound lacks a hydrogen atom that is connected to an electronegative element. Therefore, this compound will not exhibit hydrogen bonding interactions.



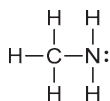
(d) This compound lacks a hydrogen atom that is connected to an electronegative element. Therefore, this compound will not exhibit hydrogen bonding interactions.



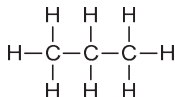
(e) This compound lacks a hydrogen atom that is connected to an electronegative element. Therefore, this compound cannot serve as a hydrogen bond donor (although lone pairs can serve as hydrogen bond acceptors). In the absence of another hydrogen bond donor, we do not expect there to be any hydrogen bonding interactions.



(f) This compound possesses an N–H bond, so it is expected to exhibit hydrogen bonding interactions.



(g) This compound lacks a hydrogen atom that is connected to an electronegative element. Therefore, this compound will not exhibit hydrogen bonding interactions.



(h) This compound possesses N–H bonds, so it is expected to exhibit hydrogen bonding interactions.



#### 1.54.

(a) Boron is in group 3A of the periodic table, and therefore has three valence electrons. It can use each of its valence electrons to form a bond, so we expect the molecular formula to be  $\text{BH}_3$ .

(b) Carbon is in group 4A of the periodic table, and therefore has four valence electrons. It can use each of its valence electrons to form a bond, so we expect the molecular formula to be  $\text{CH}_4$ .

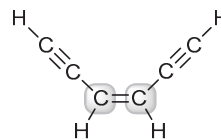
(c) Nitrogen is in group 5A of the periodic table, and therefore has five valence electrons. But it cannot form five bonds, because it only has four orbitals with which to form bonds. One of those orbitals must be occupied by a lone pair (two electrons), and each of the remaining three electrons is available to form a bond. Nitrogen is therefore trivalent, and we expect the molecular formula to be  $\text{NH}_3$ .

(d) Carbon is in group 4A of the periodic table, and therefore has four valence electrons. It can use each of its valence electrons to form a bond, and indeed, we expect the carbon atom to have four bonds. Two of the bonds are with hydrogen atoms, so the other two bonds must be with chlorine atoms. The molecular formula is  $\text{CH}_2\text{Cl}_2$ .

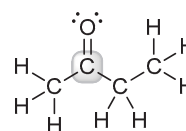
#### 1.55.

(a) Each of the highlighted carbon atoms has three  $\sigma$  bonds and no lone pairs (steric number = 3). Each of these carbon atoms is  $sp^2$  hybridized, with trigonal planar geometry. Each of the other four carbon atoms has two  $\sigma$  bonds and no lone pairs (steric number = 2). Those

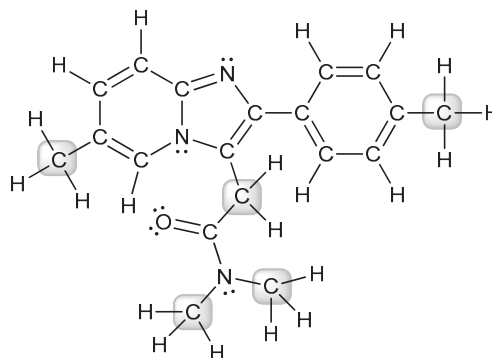
four carbon atoms are all  $sp$  hybridized, with linear geometry.



(b) The highlighted carbon atom has three  $\sigma$  bonds and no lone pairs (steric number = 3). This carbon atom is  $sp^2$  hybridized, with trigonal planar geometry. Each of the other three carbon atoms has four  $\sigma$  bonds (steric number = 4). Those three carbon atoms are all  $sp^3$  hybridized, with tetrahedral geometry.



1.56. Each of the highlighted carbon atoms has four  $\sigma$  bonds (steric number = 4), and is  $sp^3$  hybridized, with tetrahedral geometry. Each of the other fourteen carbon atoms in this structure has three  $\sigma$  bonds and no lone pairs (steric number = 3). Each of these fourteen carbon atoms is  $sp^2$  hybridized, with trigonal planar geometry.



#### 1.57.

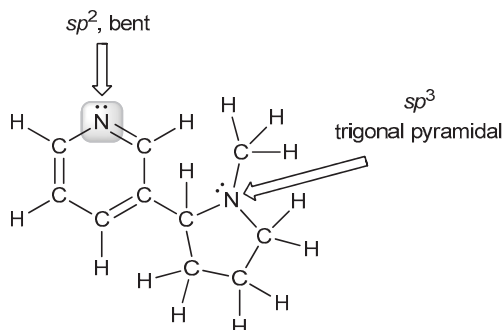
(a) Oxygen is the most electronegative atom in this compound. See Table 1.1 for electronegativity values.

(b) Fluorine is the most electronegative atom. See Table 1.1 for electronegativity values.

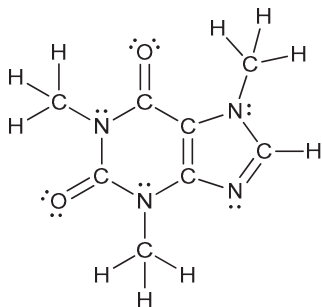
(c) Carbon is the most electronegative atom in this compound. See Table 1.1 for electronegativity values.

1.58. The highlighted nitrogen atom has two  $\sigma$  bonds and one lone pair (steric number = 3). This nitrogen atom is  $sp^2$  hybridized. It is electronically trigonal planar, but one of the  $sp^2$  hybridized orbitals is occupied by a lone pair, so the geometry (arrangement of atoms) is bent. The other nitrogen atom (not highlighted) has three  $\sigma$  bonds and a lone pair (steric number = 4). That nitrogen atom is  $sp^3$  hybridized and electronically

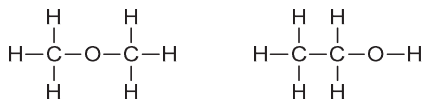
tetrahedral. One corner of the tetrahedron is occupied by a lone pair, so the geometry (arrangement of atoms) is trigonal pyramidal.



**1.59.** Each of the nitrogen atoms in this structure achieves an octet with three bonds and one lone pair, while each oxygen atom in this structure achieves an octet with two bonds and two lone pairs, as shown:



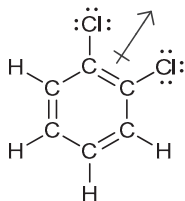
**1.60.** In the solution to Problem 1.46a, we saw that the following two compounds have the molecular formula  $C_2H_6O$ .



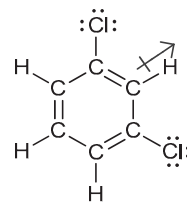
The second compound will have a higher boiling point because it possesses an OH group which can form hydrogen bonding interactions.

**1.61.**

(a) Each C–Cl bond has a dipole moment, and the two dipole moments do not fully cancel each other because they are not pointing in opposite directions. As such, there will be a net molecular dipole moment, as shown here:

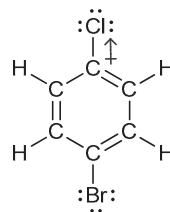


(b) Each C–Cl bond has a dipole moment, and the two dipole moments do not fully cancel each other because they are not pointing in opposite directions. As such, there will be a net molecular dipole moment, as shown here:



(c) Each C–Cl bond has a dipole moment, and in this case, the two dipole moments are pointing in opposite directions. As such, they fully cancel each other, giving no net molecular dipole moment.

(d) The C–Cl bond has a dipole moment, and the C–Br bond also has a dipole moment. These two dipole moments are in opposite directions, but they do not have the same magnitude. The C–Cl bond has a larger dipole moment than the C–Br bond, because chlorine is more electronegative than bromine. Therefore, there will be a net molecular dipole moment, as shown here:



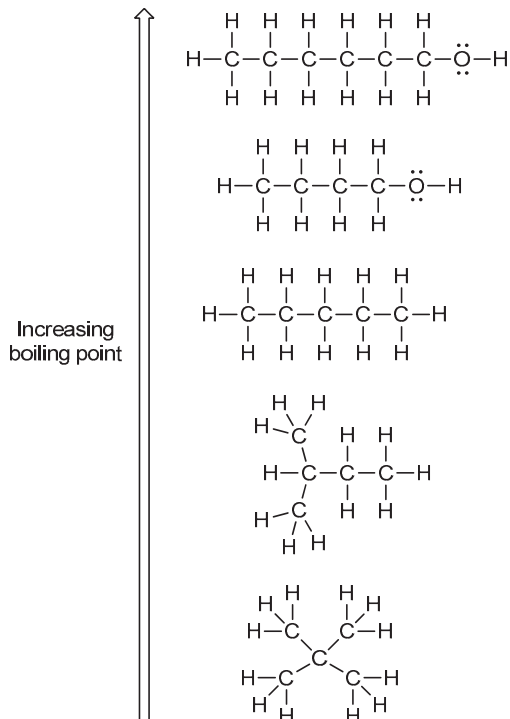
**1.62.** The third chlorine atom in chloroform partially cancels the effects of the other two chlorine atoms, thereby reducing the molecular dipole moment relative to methylene chloride.

**1.63.**  $CHCl_3$  is expected to have a larger molecular dipole moment than  $CBrCl_3$ , because the bromine atom in the latter compound serves to nearly cancel out the effects of the other three chlorine atoms (as is the case for  $CCl_4$ ).

**1.64.** The carbon atom of  $O=C=O$  has two  $\sigma$  bonds and no lone pairs (steric number = 2) and VSEPR theory predicts linear geometry. As a result, the individual dipole moments of each C=O bond cancel each other completely to give no overall molecular dipole moment. In contrast, the sulfur atom in  $SO_2$  has a steric number of three (because it also has a lone pair, in addition to the two S=O bonds), which means that it has bent geometry. As a result, the individual dipole moments of each S=O bond do NOT cancel each other completely, and the molecule does have a molecular dipole moment.

**1.65.** Two compounds possess OH groups, and these compounds will have the highest boiling points. Among these two compounds, the one with more carbon atoms (six) will be higher boiling than the one with fewer

carbon atoms (four). The remaining three compounds all have five carbon atoms and lack an OH group. The difference between these three compounds is the extent of branching. Among these three compounds, the compound with the greatest extent of branching has the lowest boiling point, and the one with the least branching has the highest boiling point.



## 1.66.

(a) Compounds A and B share the same molecular formula ( $C_4H_9N$ ) but differ in their constitution (connectivity of atoms), and they are therefore constitutional isomers.

(b) The nitrogen atom in compound B has three  $\sigma$  bonds and one lone pair (steric number = 4). It is  $sp^3$  hybridized (electronically tetrahedral), with trigonal pyramidal geometry (because one corner of the tetrahedron is occupied by a lone pair).

(c) A double bond represents one  $\sigma$  bond and one  $\pi$  bond, while a triple bond represents one  $\sigma$  bond and two  $\pi$  bonds. A single bond represents a  $\sigma$  bond. With this in mind, compound B has 14  $\sigma$  bonds, as compared with compounds A and C, which have 13 and 11  $\sigma$  bonds, respectively.

(d) As explained in the solution to part (c), compound C has the fewest  $\sigma$  bonds.

(e) A double bond represents one  $\sigma$  bond and one  $\pi$  bond, while a triple bond represents one  $\sigma$  bond and two  $\pi$  bonds. As such, compound C exhibits two  $\pi$  bonds.

(f) Compound A has a  $C=N$  bond, in which the carbon atom has three  $\sigma$  bonds and no lone pairs (steric number = 3). It is  $sp^2$  hybridized.

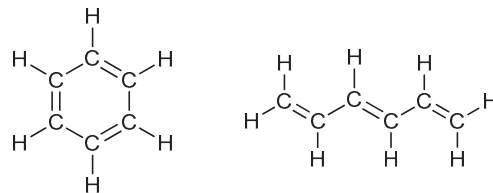
(g) Each of the carbon atoms in compound B is  $sp^3$  hybridized with four  $\sigma$  bonds (steric number = 4).

Similarly, the nitrogen atom in compound B has three  $\sigma$  bonds and one lone pair (steric number = 4). This nitrogen atom is also  $sp^3$  hybridized.

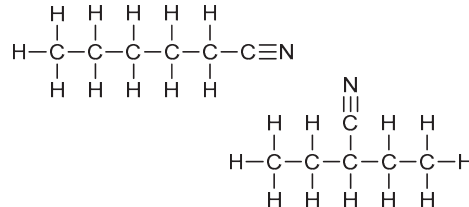
(h) Compound A has an N-H bond, and is therefore expected to form hydrogen bonding interactions. Compounds B and C do not contain an N-H bond, so compound A is expected to have the highest boiling point.

## 1.67.

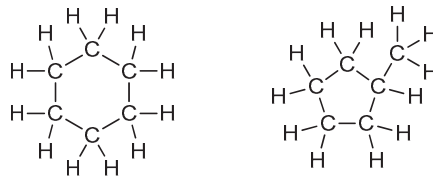
(a) In each of the following two compounds, all of the carbon atoms are  $sp^2$  hybridized (each carbon atom has three  $\sigma$  bonds and one  $\pi$  bond). There are certainly many other possible compounds for which all of the carbon atoms are  $sp^2$  hybridized.



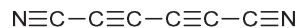
(b) In each of the following two compounds, all of the carbon atoms are  $sp^3$  hybridized (because each carbon atom has four  $\sigma$  bonds) with the exception of the carbon atom connected to the nitrogen atom. That carbon atom has two  $\sigma$  bonds and is therefore  $sp$  hybridized. There are certainly many other acceptable answers.



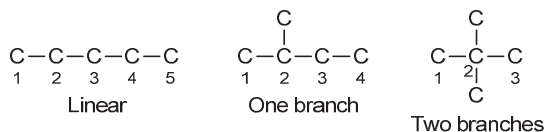
(c) In each of the following two compounds, there is a ring, and all of the carbon atoms are  $sp^3$  hybridized (because each carbon atom has four  $\sigma$  bonds). There are certainly many other acceptable answers.



(d) In each of the following two compounds, all of the carbon atoms are  $sp$  hybridized (because each carbon atom has two  $\sigma$  bonds). There are certainly many other acceptable answers.



**1.68.** In the solution to Problem 1.1c, we saw that there are three ways to arrange five carbon atoms:

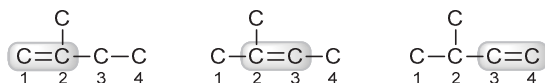


For each of these three skeletons, we must consider each possible location where a double bond can be placed. The skeleton with two branches cannot support a double bond, because the central carbon atom already has four bonds to carbon atoms, and it cannot accommodate a fifth bond (it cannot form another bond with any one of the four carbon atoms to which it is already connected). So we only have to consider the other two skeletons above (the linear skeleton and the skeleton with one branch). In the linear skeleton, the double bond can be placed at C1-C2 or at C2-C3.

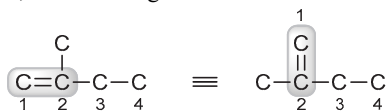


Placing the double bond at C3-C4 is the same as placing the double bond at C2-C3. Similarly, placing the double bond at C4-C5 is the same as placing the double bond at C1-C2.

For the skeleton with one branch, there are three different locations where the double bond can be placed, shown here:

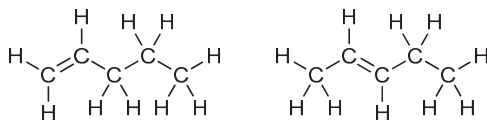


Be careful, the following two locations are the same:

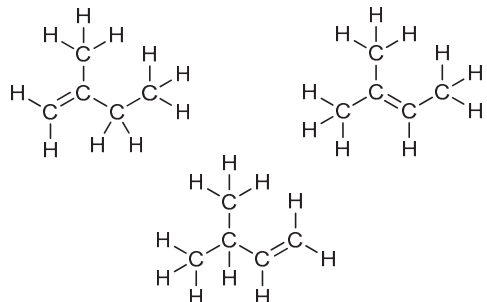


Finally, we complete all five possible structures by drawing the remaining bonds to the hydrogen atoms (see next page):

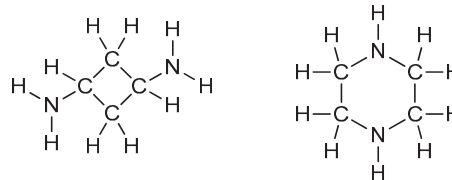
Linear skeleton



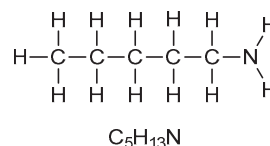
Branched skeleton



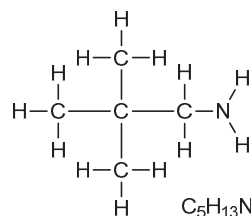
**1.69.** In each of the following two compounds, the molecular formula is  $C_4H_{10}N_2$ , there is a ring (as suggested in the hint given in the problem statement), there are no  $\pi$  bonds, there is no net dipole moment, and there is an N-H bond, which enables hydrogen bonding interactions.



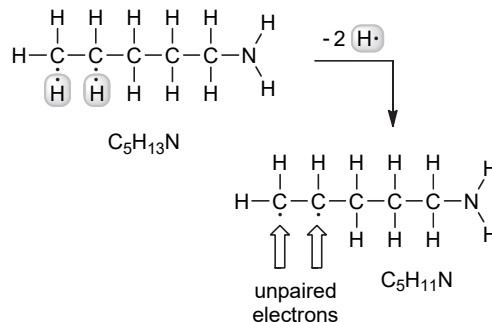
**1.70.** If we try to draw a linear skeleton with five carbon atoms and one nitrogen atom, we find that the number of hydrogen atoms is not correct (there are thirteen, rather than eleven):



This will be the case even if try to draw a branched skeleton:



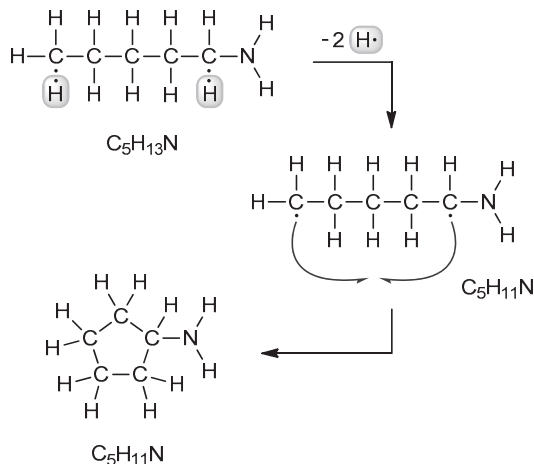
In fact, regardless of how the skeleton is branched, it will still have 13 hydrogen atoms. But we need to draw a structure with only 11 hydrogen atoms ( $C_5H_{11}N$ ). So we must remove two hydrogen atoms, which gives two unpaired electrons:



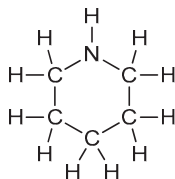
This indicates that we should consider pairing these electrons as a double bond. However, the problem statement specifically indicates that the structure cannot contain a double bond. So, we must find another way to pair the unpaired electrons. We encountered a similar issue in the solution to problem 1.36a, in which we



paired the electrons by forming a ring. We can do something similar here:



Now we have the correct number of hydrogen atoms (eleven), which means that our structure must indeed contain a ring. But this particular cyclic structure (cyclic = containing a ring) does not meet all of the criteria described in the problem statement. Specifically, each carbon atom must be connected to exactly two hydrogen atoms. This is not the case in the structure above. This issue can be remedied in the following structure, which has a ring, and each of the carbon atoms is connected to exactly two hydrogen atoms, as required by the problem statement.



### 1.71.

(a) In compound **A**, the nitrogen atom has two  $\sigma$  bonds and no lone pairs (steric number = 2). It is  $sp$  hybridized. The highlighted carbon atom has one  $\sigma$  bond and one lone pair (steric number = 2), so that carbon atom is  $sp$  hybridized.

(b) The highlighted carbon atom is  $sp$  hybridized, so the lone pair occupies an  $sp$  hybridized orbital.

(c) The nitrogen atom is  $sp$  hybridized and therefore has linear geometry. As such, the C-N-C bond angle in **A** is expected to be  $180^\circ$ .

(d) The nitrogen atom in **B** has two  $\sigma$  bonds and one lone pair (steric number = 3). It is  $sp^2$  hybridized. The highlighted carbon atom has three  $\sigma$  bonds and no lone pairs (steric number = 3), and that carbon atom is  $sp^2$  hybridized. Each of the chlorine atoms has three lone pairs and one bond (steric number = 4), and the chlorine atoms are  $sp^3$  hybridized.

(e) The nitrogen atom is  $sp^2$  hybridized, so the lone pair occupies an  $sp^2$  hybridized orbital.

(f) The nitrogen atom is  $sp^2$  hybridized so the C-N-C bond angle in **B** is expected to be approximately  $120^\circ$ .

1.72. By analyzing the data, we can see that  $C(sp^2)\text{-Cl}$  must be shorter than  $1.79\text{\AA}$  [compare with  $C(sp^3)\text{-Cl}$ ], while  $C(sp)\text{-I}$  must be longer than  $1.79\text{\AA}$  [compare with  $C(sp)\text{-Br}$ ]. Therefore,  $C(sp)\text{-I}$  must be longer than  $C(sp^2)\text{-Cl}$ .

### 1.73.

(a) In the first compound, the fluorine isotope ( $^{18}\text{F}$ ) has no formal charge. Therefore, it must have three lone pairs (see Section 1.4 for a review of how formal charges are calculated). Since it has one  $\sigma$  bond and three lone pairs, it must have a steric number of 4, and is  $sp^3$  hybridized. The bromine atom also has no formal charge. So, it too, like the fluorine isotope, must have three lone pairs. Once again, one  $\sigma$  bond and three lone pairs give a steric number of 4, so the bromine atom is  $sp^3$  hybridized.

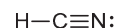
In the second compound, the nitrogen atom has no formal charge. Therefore, it must have one lone pair. Since the nitrogen atom has three  $\sigma$  bonds and one lone pair, it must have a steric number of 4, and is  $sp^3$  hybridized.

In the product, the fluorine isotope ( $^{18}\text{F}$ ) has no formal charge. Therefore, it must have three lone pairs. Since it has one  $\sigma$  bond and three lone pairs, it must have a steric number of 4, and is  $sp^3$  hybridized. The nitrogen atom does have a positive formal charge. Therefore, it must have no lone pairs. Since it has four  $\sigma$  bonds and no lone pairs, it must have a steric number of 4, and is  $sp^3$  hybridized. Finally, the bromine atom has a negative charge and no bonds. So it must have four lone pairs. With four lone pairs and no bonds, it will have a steric number of 4, and is expected to be  $sp^3$  hybridized.

In summary, all of the atoms that we analyzed are  $sp^3$  hybridized.

(b) The nitrogen atom is  $sp^3$  hybridized. With four bonds, we expect the geometry around the nitrogen atom to be tetrahedral. So, the bond angle for each C-N-C bond is expected to be approximately  $109.5^\circ$ .

1.74. We must first draw the structure of HCN. To draw a Lewis structure, we begin by counting the valence electrons (H has 1, C has 4, and N has 5, for a total of 10). The structure must have 10 valence electrons (no more and no less). Carbon should have four bonds, and it can only form a single bond with the hydrogen atom, so there must be a triple bond between carbon and nitrogen:



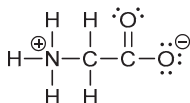
The single bond accounts for two electrons, and the triple bonds accounts for another six electrons. The remaining two electrons must be a lone pair on nitrogen. This accounts for all 10 valence electrons, and it gives all atoms an octet.

Since the carbon atom has a triple bond, it must be  $sp$  hybridized, with linear geometry.

1.75. The molecular formula of cyclobutane is  $C_4H_8$ . Of the four structures shown, only structure c has the same molecular formula ( $C_4H_8$ ).

1.76. Each of the structures has two carbon atoms and one oxygen atom. However, only the second structure has an OH group. This compound will have an elevated boiling point, relative to the other three structures, because of hydrogen bonding.

1.77. The first statement (a) is the correct answer, because an oxygen atom has a negative charge, and the nitrogen atom has a positive charge, as shown here:

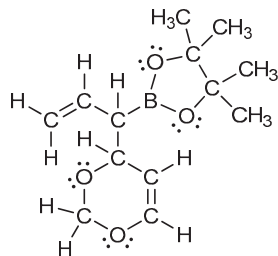


1.78.

(a) Boron is in group 3A of the periodic table and is therefore expected to be trivalent. That is, it has three valence electrons, and it uses each one of those valence electrons to form a bond, giving rise to three bonds. It does not have any electrons left over for a lone pair (as in the case of nitrogen). With three  $\sigma$  bonds and no lone pairs, the boron atom has a steric number of three, and is  $sp^2$  hybridized.

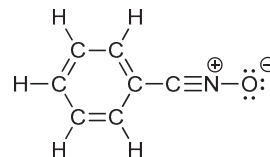
(b) Since the boron atom is  $sp^2$  hybridized, we expect the bond angle to be approximately  $120^\circ$ . However, in this case, the O-B-O system is part of a five-membered ring. That is, there are five different bond angles (of which the O-B-O angle is one of them) that together must form a closed loop. That requirement could conceivably force some of the bond angles (including the O-B-O bond angle) to deviate from the predicted value. In fact, we will explore this very phenomenon, called ring strain, in Chapter 4, and we will see that five-membered rings actually possess very little ring strain compared with smaller rings.

(c) Each of the oxygen atoms has no formal charge, and must therefore have two bonds and two lone pairs. The boron atom has no lone pairs, as explained in the solution to part (a) of this problem.



1.79.

(a) If we analyze each atom (in both **1** and **2**) using the procedure outlined in Section 1.4, we find that none of the atoms in compound **1** have a formal charge, while compound **2** possesses two formal charges:



The nitrogen atom has a positive charge (it is supposed to be using five valence electrons, but it is actually using four), and the oxygen atom has a negative charge (it is supposed to be using six valence electrons, but it is actually using seven).

(b) Compound **1** possesses polar bonds, as a result of the presence of partial charges ( $\delta^+$  and  $\delta^-$ ). The associated dipole moments can form favorable interactions with the dipole moments present in the polar solvent molecules (dipole-dipole interactions). However, compound **2** has formal charges (negative on O and positive on N), so the dipole moment of the N-O bond is expected to be much more significant than the dipole moments in compound **1**. The dipole moment of the N-O bond in compound **2** is the result of full charges, rather than partial charges. As such, compound **2** is expected to experience much stronger interactions with the solvent molecules, and therefore, **2** should be more soluble than **1** in a polar solvent.

(c) In compound **1**, the carbon atom (attached to nitrogen) has three  $\sigma$  bonds and no lone pairs (steric number = 3). That carbon atom is  $sp^2$  hybridized, with trigonal planar geometry. As such, the C-C-N bond angle in compound **1** is expected to be approximately  $120^\circ$ . However, in compound **2**, the same carbon atom has two  $\sigma$  bonds and no lone pairs (steric number = 2). This carbon atom is  $sp$  hybridized, with linear geometry. As such, the C-C-N bond angle in **2** is expected to be  $180^\circ$ . The conversion of **1** to **2** therefore involves an increase in the C-C-N bond angle of approximately  $60^\circ$ .

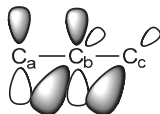
1.80.

(a)  $C_a$  has three  $\sigma$  bonds and no lone pairs, so it has a steric number of 3, and is  $sp^2$  hybridized. The same is true for  $C_c$ . In contrast,  $C_b$  has two  $\sigma$  bonds and no lone pairs, so it has a steric number of 2, and is therefore  $sp$  hybridized.

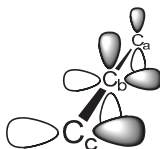
(b) Since  $C_a$  is  $sp^2$  hybridized, we expect its geometry to be trigonal planar, so the bond angle should be approximately  $120^\circ$ .

(c) Since  $C_b$  is  $sp$  hybridized, we expect its geometry to be linear, so the bond angle should be approximately  $180^\circ$ .

(d) The central carbon atom ( $C_b$ ) is  $sp$  hybridized, so it is using two  $sp$  hybridized orbitals to form its two  $\sigma$  bonds, which will be arranged in a linear fashion. The remaining two  $p$  orbitals of  $C_b$  used for  $\pi$  bonding will be  $90^\circ$  apart from one another (just as we saw for the carbon atoms of a triple bond; see Figure 1.33).

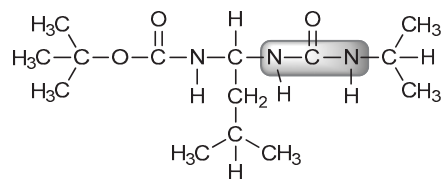
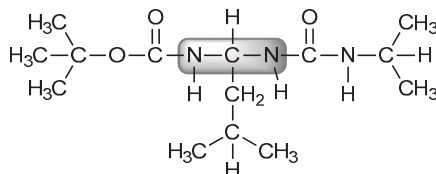


As a result, the two  $\pi$  systems are orthogonal (or  $90^\circ$ ) to each other. Therefore, the  $p$  orbitals on  $C_a$  and  $C_c$  are orthogonal. The following is another drawing from a different perspective (looking down the axis of the linear  $C_a-C_b-C_c$  system).



## 1.81.

(a) The following highlighted regions represent the two different N-C-N units in the structure:



The first N-C-N unit (shown above) exhibits a central carbon atom that is  $sp^3$  hybridized and is therefore expected to have tetrahedral geometry. Accordingly, the bond angles about that carbon atom are expected to be approximately  $109.5^\circ$ .

The other N-C-N unit exhibits a central carbon atom that is  $sp^2$  hybridized and is therefore expected to have trigonal planar geometry. Accordingly, the bond angles about that carbon atom are expected to be approximately  $120^\circ$ .

(b) The non-covalent interaction is an intramolecular, hydrogen bonding interaction between the H (connected to the highlighted nitrogen atom) and the lone pair of the oxygen atom:

