Student Study Guide
and Solutions Manual

# Organic Chemistry

SECOND EDITION

# DAVID KLEIN

**WILEY**

# Student Study Guide and Solutions Manual, 2e

for

Organic Chemistry, 2e

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WILEY

This book is printed on acid free paper. ∞

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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!


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# 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   Determining the Constitution of Small Molecules**

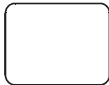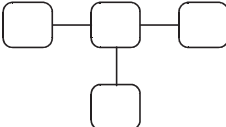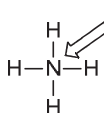| STEP 1 - DETERMINE THE VALENCY (NUMBER OF EXPECTED BONDS) FOR EACH ATOM IN $C_2H_5Cl$ | STEP 2 - DRAW THE STRUCTURE OF $C_2H_5Cl$ BY PLACING ATOMS WITH THE HIGHEST VALENCY AT THE CENTER, AND PLACING MONOVALENT ATOMS AT THE PERIPHERY |
|---|---|
| Each carbon atom is expected to form ___ bonds. <br><br> Each hydrogen atom is expected to form ___ bonds. <br><br> The chlorine atom is expected to form ___ bonds. | |

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

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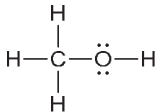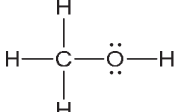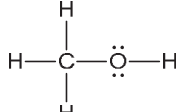
## SkillBuilder 1.3  Drawing the Lewis Structure of a Small Molecule

| STEP 1 - DRAW THE LEWIS DOT STRUCTURE OF EACH ATOM IN CH$_2$O | STEP 2 - FIRST CONNECT ATOMS THAT FORM MORE THAN ONE BOND | STEP 3 - CONNECT THE HYDROGEN ATOMS | STEP 4 - PAIR ANY UNPAIRED ELECTRONS, SO THAT EACH ATOM ACHIEVES AN OCTET |
|---|---|---|---|
| | | | |
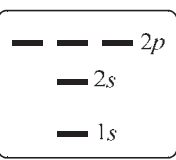
## SkillBuilder 1.4  Calculating Formal Charge

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

## SkillBuilder 1.5  Locating Partial Charges Resulting from Induction

| STEP 1 - CIRCLE THE BONDS BELOW THAT ARE POLAR COVALENT | STEP 2 - FOR EACH POLAR COVALENT BOND, DRAW AN ARROW THAT SHOWS THE DIRECTION OF THE DIPOLE MOMENT | STEP 3 - INDICATE THE LOCATION OF ALL PARTIAL CHARGES ($\delta$+ and $\delta$-) |
|---|---|---|
| | | |

## SkillBuilder 1.6  Identifying Electron Configurations

| STEP 1 - IN THE ENERGY DIAGRAM SHOWN HERE, DRAW THE ELECTRON CONFIGURATION OF NITROGEN (USING ARROWS TO REPRESENT ELECTRONS). | STEP 2 - FILL IN THE BOXES BELOW WITH THE NUMBERS THAT CORRECTLY DESCRIBE THE ELECTRON CONFIGURATION OF NITROGEN |
|---|---|
| Nitrogen  2p 2s 1s | 1s 2s 2p |

## SkillBuilder 1.7  Identifying Hybridization States

| A CARBON ATOM WITH FOUR SINGLE BONDS WILL BE _____ HYBRIDIZED | A CARBON ATOM WITH ONE DOUBLE BOND WILL BE _____ HYBRIDIZED | A CARBON ATOM WITH A TRIPLE BOND WILL BE _____ HYBRIDIZED |
|---|---|---|
| | | |

**SkillBuilder 1.8   Predicting Geometry**

| STEP 1 - DETERMINE THE STERIC NUMBER OF THE NITROGEN ATOM BELOW BY ADDING THE NUMBER OF SINGLE BONDS AND LONE PAIRS | STEP 2 - THE STERIC NUMBER DETERMINES THE HYBRIDIZATION STATE AND ELECTRONIC GEOMETRY. FILL IN THE CHART BELOW: | | | STEP 3 - IDENTIFY THE GEOMETRY IN EACH CASE BELOW: |
|---|---|---|---|---|

H—N̈—H
|
H

# of single bonds = ☐

# of lone pairs = ☐

**Steric Number = ☐**

| Steric # | Hybridization State | Electronic Geometry |
|---|---|---|
| 4 | | |
| 3 | | |
| 2 | | |

*tetrahedral* arrangement of electron pairs

NO LONE PAIRS        ONE LONE PAIR        TWO LONE PAIRS

☐        ☐        ☐

**SkillBuilder 1.9   Identifying the Presence of Molecular Dipole Moments**

| STEP 1 - IDENTIFY THE GEOMETRY OF THE OXYGEN ATOM BELOW | STEP 2 - REDRAW THE COMPOUND. DRAW AN ARROW FOR EACH DIPOLE MOMENT (SHOWING ITS DIRECTION). | STEP 3 - REDRAW THE COMPOUND, AND DRAW THE NET DIPOLE MOMENT |
|---|---|---|

$H_3C$—C—Ö—C—$CH_3$ (with H's)

Geometry = ☐

**SkillBuilder 1.10   Predicting Physical Properties**

| Dipole-Dipole Interactions | H-Bonding Interactions | Carbon Skeleton |
|---|---|---|
| CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT | CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT | CIRCLE THE COMPOUND BELOW THAT IS EXPECTED TO HAVE THE HIGHER BOILING POINT |

# 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 though 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 in the compound. The carbon atom is tetravalent, the oxygen atom is divalent, and the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, C and O) should be drawn in the center of the compound. The hydrogen atoms are then placed at the periphery, as shown.
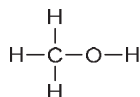


**(b)** Begin by determining the valency of each atom in the compound. The carbon atom is tetravalent, while the chlorine and hydrogen atoms are all monovalent. The carbon atom is the only atom with more than one bond, so it must be drawn in the center of the compound. The chlorine atom and the hydrogen atoms are then placed at the periphery, as shown.
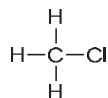


The chlorine atom can be placed in any one of the four available positions. The following four drawings all represent the same compound, in which the central carbon atom is connected to the Cl.
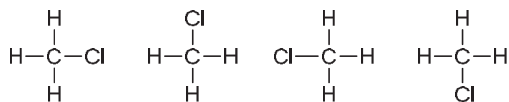


**(c)** The carbon atoms are tetravalent, while the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The hydrogen atoms are then placed at the periphery, as shown.
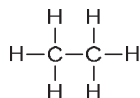


**(d)** The carbon atom is tetravalent, the nitrogen atom is trivalent, and the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, C and N) should be drawn in the center of the compound. The hydrogen atoms are then placed at the periphery, as shown.
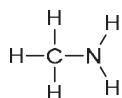


**(e)** The carbon atoms are tetravalent, while the fluorine atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The fluorine atoms are then placed at the periphery, as shown.
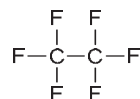


**(f)** The carbon atoms are tetravalent, while the bromine atom and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The bromine atom and hydrogen atoms are then placed at the periphery, as shown.
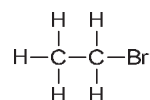


The bromine atom can be placed in any one of the six available positions. The following six drawings all represent the same compound, in which the two carbon atoms are connected to each other, and the bromine atom is connected to one of the carbon atoms.
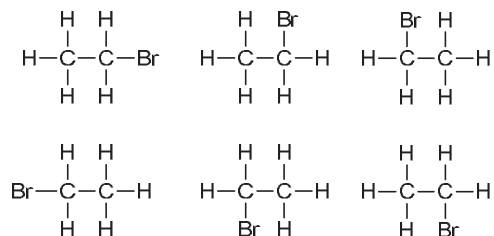


**(g)** The carbon atoms are tetravalent, while the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the three carbon atoms) should be drawn in the center of the compound. The hydrogen atoms are then placed at the periphery, as shown.
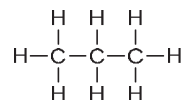


**1.2.** Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the chlorine atom and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the three carbon atoms) should be drawn in the center of the compound. Then, as indicated in the problem statement, 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

electron is placed by itself (unpaired), around the C, like this:

$$\cdot \overset{\cdot}{\underset{\cdot}{C}} \cdot$$

**(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:

$$: \overset{\cdot\cdot}{\underset{\cdot}{O}} :$$

**(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:

$$: \overset{\cdot\cdot}{\underset{\cdot\cdot}{F}} \cdot$$

**(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:

$$H \cdot$$

**(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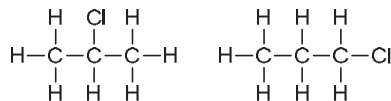, and each valence electron is placed by itself (unpaired) on a side of the Br, until all four sides are occupied. That takes care of four of the seven electrons, leaving three more electrons to draw. Each of the three remaining electrons is then paired up with an electron already drawn, like this:

$$: \overset{\cdot\cdot}{\underset{\cdot\cdot}{Br}} \cdot$$

**(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:

$$: \overset{\cdot\cdot}{\underset{\cdot}{S}} :$$

**(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:

$$: \overset{\cdot\cdot}{\underset{\cdot\cdot}{Cl}} \cdot$$

**(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:

$$: \overset{\cdot\cdot}{\underset{\cdot\cdot}{I}} \cdot$$

**1.6.** 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.

**1.7.** Aluminum is directly beneath boron on the periodic table (group **3A**), and therefore both elements exhibit three valence electrons.

**1.8.** The Lewis dot structure for a carbon atom is shown in the solution to Problem **1.5a**. 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.

$$\cdot \overset{\cdot}{\underset{\cdot}{C}} \oplus$$

**1.9.** The Lewis dot structure for a carbon atom is shown in the solution to Problem **1.5a**. That drawing must be modified by drawing one additional electron, resulting in a formal negative charge, as shown below. This resembles nitrogen because it exhibits five valence electrons.

$$\cdot \overset{\cdot}{\underset{\cdot}{C}} \overset{\ominus}{:}$$

**1.10.**
**(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.

$$H : \overset{H}{\underset{H}{C}} : \overset{H}{\underset{H}{C}} : H$$

**(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.

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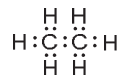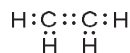
**(c)** Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, and the unpaired electrons are shared to give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

$$H:C:::C:H$$

**(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.

$$H\ H\ H$$
$$H:C:C:C:H$$
$$H\ H\ H$$

**(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.

$$H$$
$$H:C:C::C:H$$
$$H\ H\ \ H$$

**(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.

$$H$$
$$H:C:\ddot{O}:H$$
$$H$$
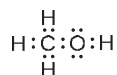
**1.11.** Boron has three valence electrons, each of which is shared with a hydrogen atom, shown below. The central boron atom lacks an octet of electrons, and it is therefore very unstable and reactive.

$$H$$
$$H:B$$
$$H$$

**1.12.** 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 below.
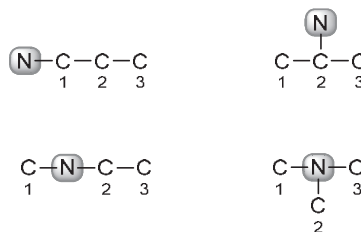


For each of these possible arrangements, we connect the hydrogen atoms, giving the following four constitutional isomers.
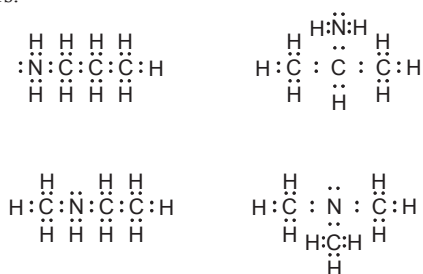


In each of these four structures, the nitrogen atom has one lone pair.

**1.13.**
**(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.

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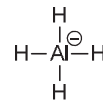
**(b)** Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. In this case, the oxygen atom exhibits only five valence electrons (one for each bond, and two for the lone pair). This oxygen atom is missing an electron, and it therefore bears a positive charge.

$$H$$
$$\overset{\oplus}{O}$$
$$H\ \ \ H$$

**(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.
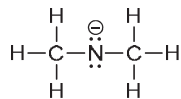


**(d)** Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. In this case, the oxygen atom exhibits only five valence electrons (one for each bond, and two for the lone pair). This oxygen atom is missing an electron, and it therefore bears a positive charge.
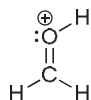


**(e)** Carbon is in group 4A of the periodic table, and it should therefore have four valence electrons. In this case, the carbon atom exhibits five valence electrons (one for each bond and two for the lone pair). With one extra electron, this carbon atom will bear a negative charge.



**(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.
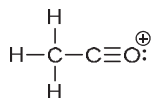


**(h)** Two of the atoms in this structure exhibit a formal charge because each of these atoms does not exhibit the appropriate number of valence electrons. The aluminum atom (group 3A) should have three valence electrons, but it exhibits four (one for each bond). With one extra electron, this aluminum 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.
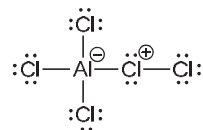


**(i)** Two of the atoms in this structure exhibit a formal charge because each of these atoms does not exhibit the appropriate number of valence electrons. The nitrogen atom (group 5A) should have five valence electrons, but it exhibits four (one for each bond). It is missing one electron, so this nitrogen 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.
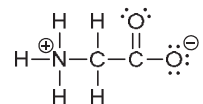


**1.14.**
**(a)** The boron atom in this case exhibits four valence electrons (one for each bond), although boron (group 3A) should only have three valence electrons. With one extra electron, this boron atom bears a negative charge.
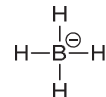


**(b)** The nitrogen atom in this case exhibits six valence electrons (one for each bond and two for each lone pair). But nitrogen (group 5A) should only have five valence electrons. With one extra electron, this nitrogen atom bears a negative charge.
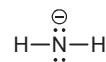


**(c)** One of the carbon atoms (below right) exhibits three valence electrons (one for each bond), but carbon (group 4A) is supposed to have four valence electrons. It is missing one electron, so this carbon atom therefore bears a positive charge.
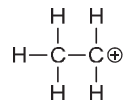


**1.15.**
**(a)** Oxygen is more electronegative than carbon, and a C–O bond is polar covalent. For each C–O bond, the O will be electron rich (δ–), and the C will be electron-poor (δ+), as shown below.
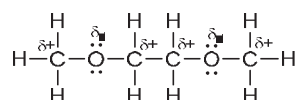
**(b)** Fluorine is more electronegative than carbon, and a C–F bond is polar covalent. For a C–F bond, the F will be electron-rich (δ–), and the C will be electron-poor (δ+). Chlorine is also more electronegative than carbon, so a C–Cl bond is also polar covalent. For a C–Cl bond, the Cl will be electron-rich (δ–), and the C will be electron-poor (δ+), as shown below.
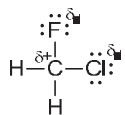


**(c)** Carbon is more electronegative than magnesium, so the C will be electron-rich (δ–) in a C–Mg bond, and the Mg will be electron-poor (δ+). Also, bromine is more electronegative than magnesium. So in a Mg–Br bond, the Br will be electron-rich (δ–), and the Mg will be electron-poor (δ+), as shown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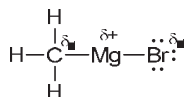


**(d)** Oxygen is more electronegative than carbon or hydrogen, so all C–O bonds and all O–H bond are polar covalent. For each C–O bond and each O–H bond, the O will be electron-rich (δ–), and the C or H will be electron-poor (δ+), as shown below.
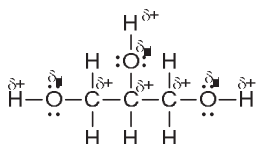


**(e)** Oxygen is more electronegative than carbon. As such, the O will be electron-rich (δ–) and the C will be electron-poor (δ+) in a C=O bond, as shown below.
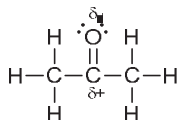


**(f)** Chlorine is more electronegative than carbon. As such, for each C–Cl bond, the Cl will be electron-rich (δ–) and the C will be electron-poor (δ+), as shown below.
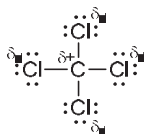


**1.16.** Oxygen is more electronegative than carbon. As such, the O will be electron-rich (δ–) and the C will be electron-poor (δ+) in a C=O bond. In addition, chlorine is more electronegative than carbon. So for a C–Cl

bond, the Cl will be electron-rich (δ–) and the C will be electron-poor (δ+), as shown below.
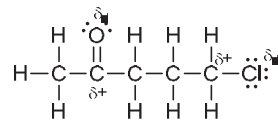


Notice that two carbon atoms are electron-poor (δ+). These are the positions that are most likely to be attacked by an anion, such as hydroxide.

**1.17.**
**(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: $1s^2 2s^2 2p^6 3s^2 3p^1$

**1.18.**
**(a)** The electron configuration of a carbon atom is $1s^2 2s^2 2p^2$ (see the solution to Problem 1.17a). 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 1.17a). 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 1.17b). However, if an oxygen atom bears a negative charge, then it must have one extra electron, so the electron configuration should be as follows: $1s^2 2s^2 2p^5$

**1.19.**   The bond angles of an equilateral triangle are 60º, but each bond angle of cyclopropane is supposed to be 109.5º.  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 60º.

**1.20.**
**(a)** The C=O bond of formaldehyde is comprised of one σ bond and one π 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.

**1.21.**   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 π bond results in a reduction in the extent of orbital overlap, because the orbital overlap is NOT on the bond axis.

**1.22.**
**(a)** The highlighted carbon atom (below) has four σ 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 σ bonds and one π bond.
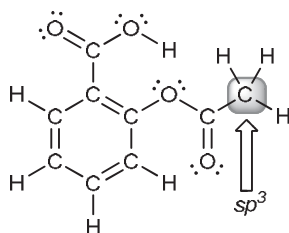


**(b)** Each of the highlighted carbon atoms (below) has four σ bonds, and is therefore $sp^3$ hybridized.  The other carbon atoms in this structure are all $sp^2$ hybridized, because each of them has three σ bonds and one π bond.
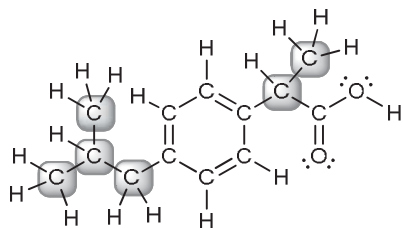


**1.23.**
**(a)** Each of the two central carbon atoms has two σ bonds and two π bonds, and as such, each of these carbon atoms is $sp$ hybridized.  The other two carbon

atoms (the outer ones) are $sp^2$ hybridized because each has three σ bonds and one π bond.
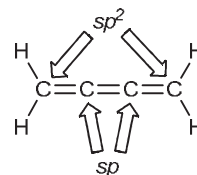


**(b)** One of the carbon atoms (the one connected to oxygen) has two σ bonds and two π bonds, and as such, it is $sp$ hybridized.   The other carbon atom is $sp^2$ hybridized because it has three σ bonds and one π bond.
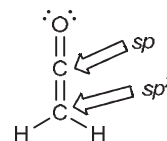


**1.24.**   Carbon-carbon triple bonds generally have a shorter bond length than carbon-carbon double bonds, which are generally shorter than carbon-carbon single bonds (see Table 1.2).



c < b < a
a is the longest bond
and c is the shortest bond
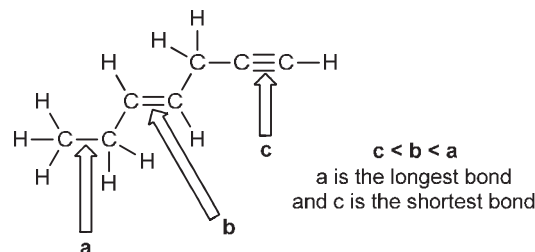
**1.25.**
**(a)** The nitrogen atom has three σ bonds and one lone pair, so the steric number is 4 ($sp^3$ hybridization), which means that the electronic arrangement will be tetrahedral. One corner of the tetrahedron is occupied by a lone pair, so the arrangement of atoms is trigonal pyramidal.



**(b)** The oxygen atom has three σ bonds and one lone pair, so the steric number is 4 ($sp^3$ hybridization), which means that the electronic arrangement will be tetrahedral. One corner of the tetrahedron is occupied by a lone pair, so the arrangement of atoms is trigonal pyramidal.



**(c)** The boron atom has four σ bonds and no lone pairs, so the steric number is 4 ($sp^3$ hybridization), which means that the electronic arrangement will be tetrahedral. With no lone pairs, the arrangement of atoms (geometry)

is the same as the electronic arrangement.    It is tetrahedral.
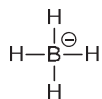


**(d)** The boron atom has three σ bonds and no lone pairs, so the steric number is 3 ($sp^2$ hybridization), which means that the electronic arrangement will be trigonal planar.  With no lone pairs, the arrangement of atoms (geometry) is the same as the electronic arrangement.  It is trigonal planar.
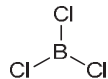


**(e)** The boron atom has four σ bonds and no lone pairs, so the steric number is 4 ($sp^3$ hybridization), which means that the electronic arrangement will be tetrahedral. With no lone pairs, the arrangement of atoms (geometry) is the same as the electronic arrangement.    It is tetrahedral.
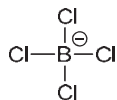


**(f)**  The carbon atom has four σ bonds and no lone pairs, so the steric number is 4 ($sp^3$ hybridization), which means that the electronic arrangement will be tetrahedral. With no lone pairs, the arrangement of atoms (geometry) is the same as the electronic arrangement.    It is tetrahedral.
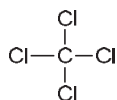


**(g)** The carbon atom has four σ bonds and no lone pairs, so the steric number is 4 ($sp^3$ hybridization), which means that the electronic arrangement will be tetrahedral. With no lone pairs, the arrangement of atoms (geometry) is the same as the electronic arrangement.    It is tetrahedral.
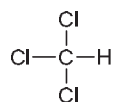


**(h)** The carbon atom has four σ bonds and no lone pairs, so the steric number is 4 ($sp^3$ hybridization), which means that the electronic arrangement will be tetrahedral. With no lone pairs, the arrangement of atoms (geometry) is the same as the electronic arrangement.    It is tetrahedral.
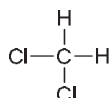


**1.26.**
**(a)**   The carbon atom highlighted (below) has three σ bonds and no lone pairs (steric number = 3) and is therefore $sp^2$ hybridized and trigonal planar.
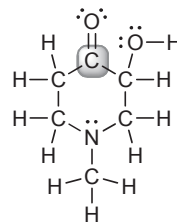


Each of the other carbon atoms has four σ bonds (steric number = 4) and is therefore tetrahedral.    The nitrogen atom has three σ bonds and one lone pair (steric number = 4), so the electronic arrangement is tetrahedral.  But one corner of the tetrahedron is occupied by a lone pair, so the arrangement of atoms is trigonal pyramidal.  The oxygen atom (of the OH group) has two σ bonds and two lone pairs (steric number = 4), so the electronic arrangement is tetrahedral.  But two corners of the tetrahedron are occupied by lone pairs, so the arrangement of atoms is bent.  The oxygen atom of the C=O group has one σ bond and two lone pairs (steric number = 3), so it is $sp^2$ hybridized.

**(b)**   Each of the highlighted carbon atoms has three σ bonds and no lone pairs (steric number = 3) and is therefore trigonal planar.  Each of the other carbon atoms (not highlighted) has four σ bonds (steric number = 4), with tetrahedral geometry.   The highlighted nitrogen atom has two σ bonds and one lone pair (steric number = 3), so the electronic arrangement is trigonal planar.  But there is one lone pair, so the arrangement of atoms is bent.  The other nitrogen atom (not highlighted) has three σ bonds and one lone pair (steric number = 4), so the electronic arrangement will be tetrahedral.  One corner of the tetrahedron is occupied by a lone pair, so the arrangement of atoms is trigonal pyramidal.  The oxygen atom has two σ bonds and two lone pairs (steric number = 4), so the electronic arrangement will be tetrahedral. Two corners of the tetrahedron are occupied by lone pairs, so the arrangement of atoms is bent.
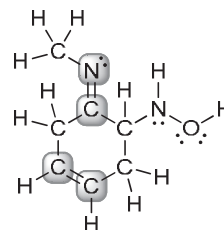
**(c)** Each of the carbon atoms has three σ bonds and no lone pairs (steric number = 3) and is therefore trigonal planar:
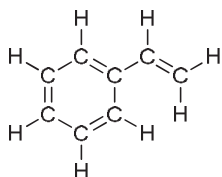


**1.27.** The carbon atom of the carbocation has three σ bonds and no lone pairs (steric number = 3), and is therefore trigonal planar. The carbon atom of the carbanion has three σ bonds and one lone pair (steric number = 4), and is therefore trigonal pyramidal (the electronic arrangement is tetrahedral, but one corner of the tetrahedron is occupied by a lone pair, giving a trigonal pyramidal arrangement of atoms).

**1.28.** Every carbon atom in benzene has three σ bonds and no lone pairs. With a steric number of 3, each of these carbon atoms is $sp^2$ hybridized and trigonal planar. Therefore, the entire molecule is planar (all of the atoms in this molecule occupy the same plane).

**1.29.**
**(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 σ bonds so it is $sp^3$ hybridized, with 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:
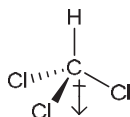


**(b)** The oxygen atom has two σ bonds and two lone pairs (steric number = 4), so it is $sp^3$ hybridized (electronically tetrahedral), with bent geometry (because two corners of the tetrahedron are occupied by lone pairs). As such, the dipole moments associated with the C–O bonds do not fully cancel each other. There is a net molecular dipole moment, as shown:
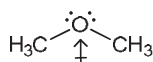


**(c)** The nitrogen atom has three σ bonds and one lone pair (steric number = 4), so it is $sp^3$ hybridized (electronically tetrahedral), with trigonal pyramidal geometry (because one corner of the tetrahedron is occupied by a lone pair). As such, the dipole moments associated with the N–H bonds do not fully cancel each

other. There is a net molecular dipole moment, as shown:
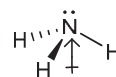


**(d)** The central carbon atom has four σ bonds (steric number = 4) and is therefore $sp^3$ hybridized, with tetrahedral geometry. There are individual dipole moments associated with each of the C–Cl bonds and each of the C–Br bonds. If all four dipole moments had the same magnitude, then we would expect 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:
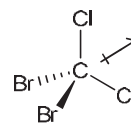


**(e)** The oxygen atom has two σ bonds and two lone pairs (steric number = 4), so it is $sp^3$ hybridized (electronically tetrahedral), with bent geometry (because two corners of the tetrahedron are occupied by lone pairs). As such, the dipole moments associated with the C–O bonds do not fully cancel each other. There is a net molecular dipole moment, as shown:
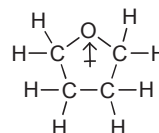


**(f)** There are individual dipole moments associated with each C–O bond (just as we saw in the solution to **1.29e**), but in this case, they fully cancel each other to give no net molecular dipole moment.

**(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:
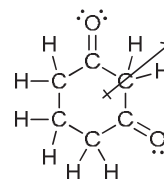


**(h)** Each C=O bond has a strong dipole moment, and in this case, they are pointing in opposite directions. As such, they fully cancel each other, giving no net molecular dipole moment.

**(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:
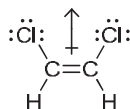


**(j)** Each C–Cl bond has a dipole moment, and in this case, they are pointing in opposite directions. As such, they fully cancel each other, giving no net molecular dipole moment.

**(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:
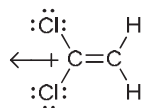


**(l)** Each C–Cl bond has a dipole moment, but in this case, they fully cancel each other to give no net molecular dipole moment.

**1.30.** CHCl₃ is expected to have a larger molecular dipole moment than CBrCl₃, 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 CCl₄).

**1.31.** The carbon atom of O=C=O has two σ bonds and no lone pairs (steric number = 2) and is therefore *sp* hybridized, with 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 SO₂ 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.

**1.32.**
**(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.

**1.33.** 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.
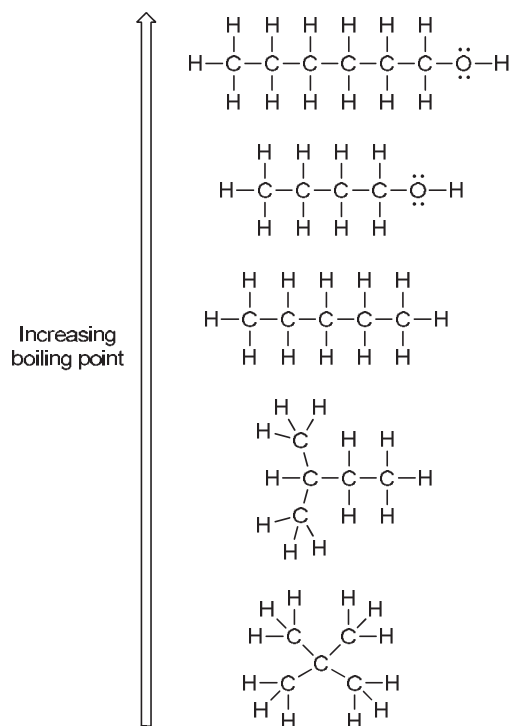


**1.34.**
**(a)** Begin by determining the valency of each atom in the compound. The carbon atoms are tetravalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the four carbon atoms) should be drawn in the center of the compound, with the hydrogen atoms at the periphery. There are two different ways to connect four carbon atoms. They can either be arranged in a linear fashion or in a branched fashion.
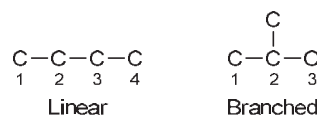


Finally, we complete both of the structures by drawing the bonds to hydrogen atoms.
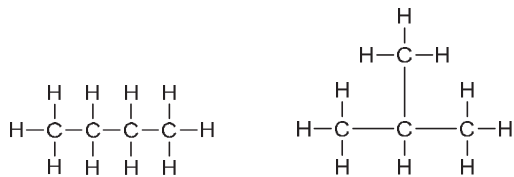
**(b)** The carbon atoms are tetravalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the five carbon atoms) should be drawn in the center of the compound, with the hydrogen atoms at the periphery. There are three different ways to connect five carbon atoms, as shown here:
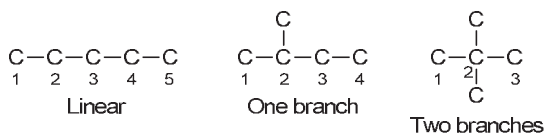
C—C—C—C—C
1  2  3  4  5
Linear

C—C—C—C
1  2  3  4
One branch

C—C—C
1  2  3
Two branches

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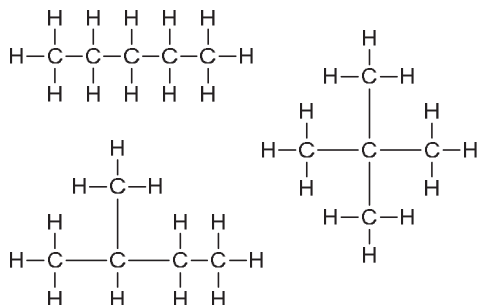
**(c)** The carbon atoms are tetravalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the six carbon atoms) should be drawn in the center of the compound, with the hydrogen atoms at the periphery. There are five different ways to connect six carbon atoms,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

In a 6-carbon chain:
C—C—C—C—C—C
1  2  3  4  5  6
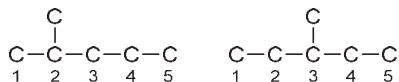
In a 5-carbon chain:
C—C—C—C—C
1  2  3  4  5

C—C—C—C—C
1  2  3  4  5

In a 4-carbon chain:
C—C—C—C
1  2  3  4

C—C—C—C
1  2  3  4
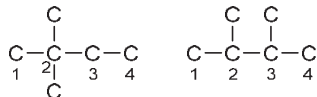
Finally, we complete all of the structures by drawing the bonds to hydrogen atoms.

**(d)** 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.

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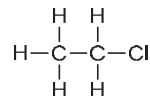
The chlorine atom can be placed in any one of the six available positions. The following six drawings all represent the same compound, in which the two carbon atoms are connected to each other, and the chlorine atom is connected to one of the carbon atoms.

**(e)** 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.



**(f)** 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:



**1.35.**
**(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 1.34a), we find that ten hydrogen atoms are required in order for all four carbons atom 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:



**(b)** See the solution to **1.35a** 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:
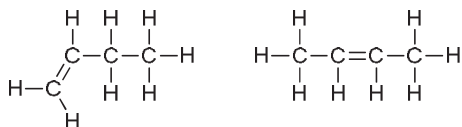


Notice that the double bond can be placed at C1-C2 or at C2-C3 (placing the double bond at C3-C4 is the same as placing it at C1-C2, because we can just assign numbers in the opposite direction).

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:
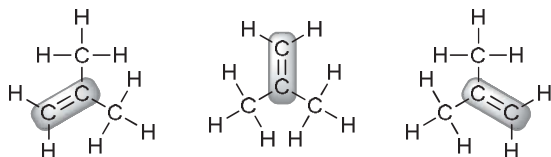


In summary, there are three constitutional isomers of $C_4H_8$ that contain a double bond:
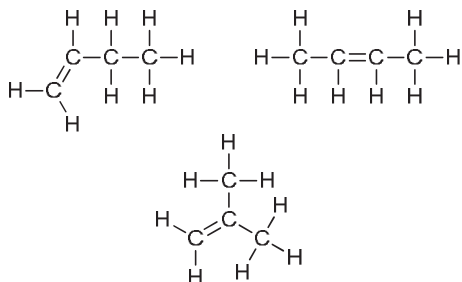


**1.36.**
**(a)** According to Table 1.1, the difference in electronegativity between Br and H is $2.8 - 2.1 = 0.7$, so an H–Br bond is expected to be polar covalent. Since bromine is more electronegative than hydrogen, the Br will be electron rich ($\delta-$), and the H will be electron-poor ($\delta+$), 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:
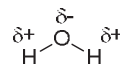


**(d)** Oxygen (3.5) is more electronegative than carbon (2.5) or hydrogen (2.1), and a C–O or H–O bond is polar covalent. For each C–O or H–O bond, the O will be electron rich ($\delta-$), and the C or H will be electron-poor ($\delta+$), as shown below:
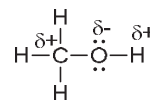


**1.37.**
**(a)** The difference in electronegativity between Na and Br is greater than the difference in electronegativity between H and Br. Therefore, NaBr is expected to have more ionic character than HBr.
**(b)** The difference in electronegativity between F (4.0) and Cl (3.0) is greater than the difference in electronegativity between Br (2.8) and Cl (3.0). Therefore, FCl is expected to have more ionic character than BrCl.

**1.38.**
**(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 ($CH_3CH_2OH$) 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 ($CH_3CN$) 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.

geometry. The oxygen atom is only connected to one group so its geometry is not relevant.

**1.39.**
**(a)** The carbon atom bearing a negative charge (highlighted) has three σ bonds and one lone pair, so the steric number is 4 (*sp³* hybridization), which means that the electronic arrangement will be tetrahedral. One corner of the tetrahedron is occupied by a lone pair, so the geometry of that carbon atom (the arrangement of atoms around that carbon atom) is trigonal pyramidal. The structure has three other carbon atoms. Each of them has four σ bonds (steric number = 4) and is therefore tetrahedral.

**(b)** The highlighted carbon atom has four σ bonds, so the steric number is 4 (*sp³* hybridization), which means that this carbon atom will be tetrahedral. Each of the other two carbon atoms has three σ bonds and no lone pairs, so the steric number is 3 (*sp²* hybridization), which means that these carbon atoms will be trigonal planar. The oxygen atom has three σ bonds and one lone pair, so the steric number is 4 (*sp³* hybridization), which means that the electronic arrangement will be tetrahedral. One corner of the tetrahedron is occupied by a lone pair, so the geometry of that oxygen atom (the arrangement of atoms around that oxygen atom) is trigonal pyramidal.

**(c)** The nitrogen atom and each of the two carbon atoms has four σ bonds, so the steric number is 4 (*sp³* hybridization), which means that each of these atoms will have tetrahedral geometry. The oxygen atom has two σ bonds and two lone pairs (steric number = 4), so the electronic arrangement is tetrahedral. But two corners of the tetrahedron are occupied by lone pairs, so the geometry of the oxygen atom (the arrangement of atoms around the oxygen atom) is bent.

**(d)** Each of the three carbon atoms has four σ bonds, so the steric number is 4 (*sp³* hybridization), which means that each of these carbon atoms will have tetrahedral

**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 σ bonds and one lone pair, so the steric number is 4 (*sp³* hybridization), which means that the electronic arrangement will 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:

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The aluminum atom has four bonds and no lone pairs, so the steric number is 4 ($sp^3$ hybridization), 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 draw four bonds for each carbon atom, we notice that the molecular formula ($C_3H_8$) is not correct:



C₃H₈
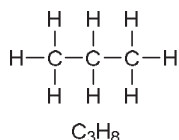
We are looking for a structure with molecular formula $C_3H_6$. If we remove two hydrogen atoms from our drawing, we are left with two unpaired electrons, indicating that we should consider drawing a double bond:



C₃H₆
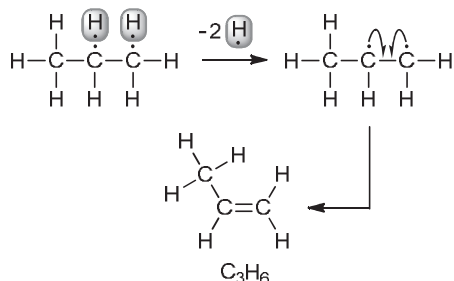
The structure of this compound (called propylene) is different from the structure of cyclopropane, but both compounds share the same molecular formula, so they are constitutional isomers.

**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 σ bonds), so the small effects from each C-H bond completely cancel each other.

**(b)** The nitrogen atom has trigonal pyramidal geometry (see the solution to Problem **1.25a**). 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:



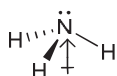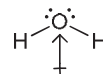**(c)** The oxygen atom has two σ bonds and two lone pairs (steric number = 4), so it is $sp^3$ hybridized (electronically tetrahedral), with bent geometry (because two corners of the tetrahedron are occupied by lone pairs). As such, the dipole moments associated with the O–H bonds do not cancel each other. There is a net molecular dipole moment, as shown:



**(d)** The central carbon atom of carbon dioxide ($CO_2$) has two σ bonds and no lone pairs, so it is $sp$ hybridized and has 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 σ bonds so it is $sp^3$ hybridized, with 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 σ bonds so it is $sp^3$ hybridized, with tetrahedral geometry. As such, the C–Br bonds are separated by a bond angle of approximately 109.5°, and they do not completely cancel each other out. There is a net molecular dipole moment, as shown:
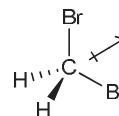


**1.44.**
**(a)** As indicated in Figure 1.10, oxygen has two $1s$ electrons, two $2s$ electrons, and four $2p$ electrons.
**(b)** As indicated in Figure 1.10, fluorine has two $1s$ electrons, two $2s$ electrons, and five $2p$ electrons.
**(c)** As indicated in Figure 1.10, carbon has two $1s$ electrons, 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.
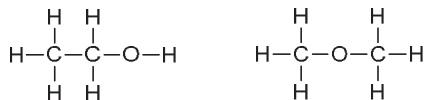


**1.46.**
**(a)** Begin by determining the valency of each atom in the compound. The carbon atoms are tetravalent, the oxygen atom is divalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the two carbon atoms and the oxygen atom) should be drawn in the 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:
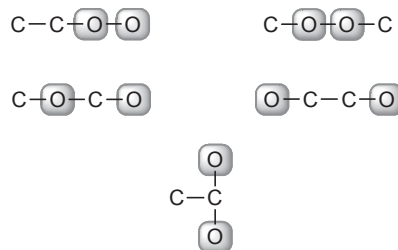


We then complete all of these structures by drawing the remaining bonds to hydrogen atoms:
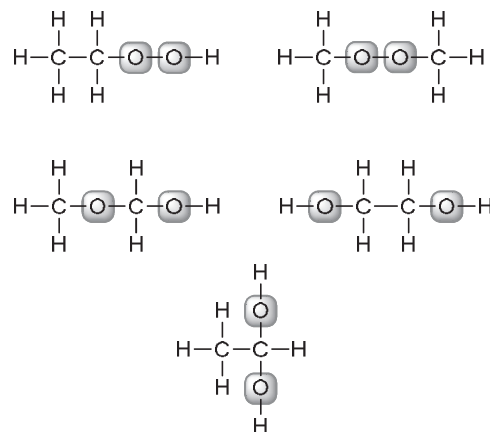


**(c)** The carbon atoms are tetravalent, while the bromine atoms and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The bromine atoms and hydrogen atoms are then placed at the periphery, and there 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 below, although there are certainly others:

H—C—C—OH (with H, OH above; H, OH below)

H—C—C—OH (with OH, OH above; H, H below)

H—C—O—C—H (with OH, OH above; H, H below)

H—C—O—O—C—H (with H, OH above; H, H below)

H—C—O—C—H (with H, OH above; H, OH below)
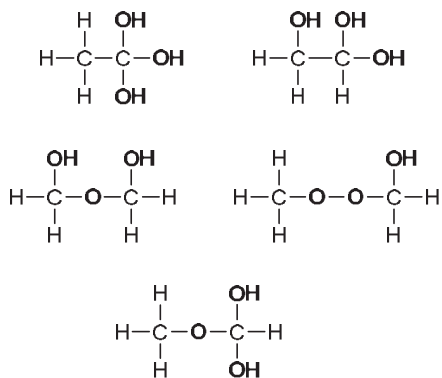
**1.48.**
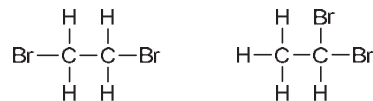**(a)** Oxygen is more electronegative than carbon, and the withdrawal of electron density toward oxygen can be indicated with the following arrow:

$$\longmapsto$$
C—O

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

$$\longleftarrow\!\!\!+$$
C—Mg

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

$$\longmapsto$$
C—N

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

$$\longleftarrow\!\!\!+$$
C—Li

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

$$\longmapsto$$
C—Cl

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

$$\longleftarrow\!\!\!+$$
C—H

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

$$\longleftarrow\!\!\!+$$
O—H

**(h)** Nitrogen is more electronegative than hydrogen, and the withdrawal of electron density toward nitrogen can be indicated with the following arrow:
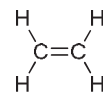
$$\longleftarrow\!\!\!+$$
N—H

**1.49.**
**(a)** The oxygen atom has two σ bonds and two lone pairs (steric number = 4), so it is $sp^3$ hybridized. Each of the carbon atoms is also $sp^3$ hybridized (because each has four σ bonds). Therefore, all bond angles are expected to be approximately 109.5º.

**(b)** The central carbon atom has three σ bonds and no lone pairs (steric number = 3), so it is $sp^2$ hybridized, with trigonal planar geometry. As such, all bond angles are approximately 120º.

(O double-bonded to C, with H and H)

**(c)** Each of the carbon atoms has three σ bonds and no lone pairs (steric number = 3), so each carbon atom is $sp^2$ hybridized, with trigonal planar geometry. As such, all bond angles are approximately 120º.

(H₂C=CH₂ structure)

**(d)** Each of the carbon atoms has two σ bonds and no lone pairs (steric number = 2), so each carbon atom is $sp$ hybridized, with linear geometry. As such, all bond angles are approximately 180º.

$$H-C\equiv C-H$$

**(e)** The oxygen atom has two σ bonds and two lone pairs (steric number = 4), so it is $sp^3$ hybridized. Each of the carbon atoms is also $sp^3$ hybridized (because each has four σ bonds). Therefore, all bond angles are expected to be approximately 109.5º.

**(f)** The nitrogen atom has three σ bonds and one lone pair (steric number = 4), so it is $sp^3$ hybridized. The carbon atom is also $sp^3$ hybridized (because it has four σ bonds). Therefore, all bond angles are expected to be approximately 109.5º.

(H—C—N: structure with H atoms)
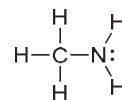
**(g)** Each of the carbon atoms has four σ bonds (steric number = 4), so each of these carbon atoms is $sp^3$ hybridized and has tetrahedral geometry. Therefore, all bond angles are expected to be approximately 109.5º.

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

**(h)** The structure of acetonitrile (CH₃CN) is shown below (see the solution to Problem **1.38b**).

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C\equiv N:$$

One of the carbon atoms has four σ bonds (steric number = 4), so it is $sp^3$ hybridized and has tetrahedral geometry. The other carbon atom (connected to nitrogen) has two σ bonds and no lone pairs (steric number = 2), so it is $sp$ hybridized with linear geometry.
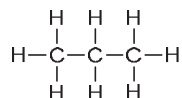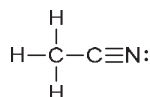As such, the C–C≡N bond angle is 180º, and all other bond angles are approximately 109.5º.

**1.50.**
**(a)** The nitrogen atom has three σ bonds and one lone pair (steric number = 4), so 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 σ bonds and no lone pairs (steric number = 3), so it is $sp^2$ hybridized, with trigonal planar geometry.

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

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

**(e)** This oxygen atom has three σ bonds and one lone pair (steric number = 4), so 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 σ bond and one π bond, while the triple bond represents one σ bond and two π bonds. All single bonds are σ bonds. Therefore, this compound has sixteen σ bonds and three π bonds.

**1.52.**
**(a)** The latter compound is expected to have a higher boiling point, because it has an O–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 C=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.
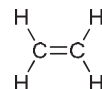
**1.53.**
**(a)** This compound possesses an O–H bond, so it is expected to exhibit hydrogen bonding interactions.

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O-H$$
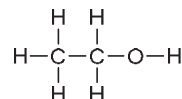
**(b)** This compound lacks a hydrogen atom that is connected to an electronegative element. Therefore, this compound cannot serve as a hydrogen bond donor (although the lone pairs can serve as hydrogen bond acceptors). In the absence of another hydrogen bond donor, we do not expect there to be any hydrogen bonding interactions.

$$\underset{H}{\overset{\overset{\displaystyle :\!\ddot O\!:}{\|}}{C}}{\phantom{x}}_{H}$$

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

$$\overset{H}{\underset{H}{}}C=C\overset{H}{\underset{H}{}}$$

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

$$H-C\equiv C-H$$

**(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.
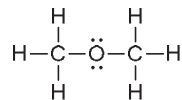
$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\ddot O-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-H$$

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

$$H-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}:$$

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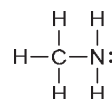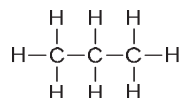


**(h)** This compound possesses an N–H bond, so it is expected to exhibit hydrogen bonding interactions.
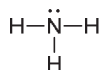


**1.54.**
**(a)** Boron is in group 3A of the periodic table, and therefore has three valence electrons. It can use each of its valence electrons to form a bond, so we expect the molecular formula to be $BH_3$.
**(b)** Carbon is in group 4A of the periodic table, and therefore has four valence electrons. It can use each of its valence electrons to form a bond, so we expect the molecular formula to be $CH_4$.

**(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 $NH_3$.

**(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 $CH_2Cl_2$.
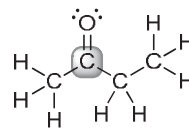
**1.55.**
**(a)** Each of the highlighted carbon atoms has three σ bonds and no lone pairs (steric number = 3), so each of these carbon atoms is $sp^2$ hybridized, with trigonal planar geometry. Each of the other four carbon atoms has two σ bonds and no lone pairs (steric number = 2), and therefore, those four carbon atoms are all $sp$ hybridized, with linear geometry.
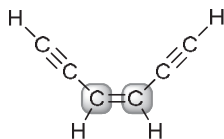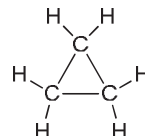


**(b)** The highlighted carbon atom has three σ bonds and no lone pairs (steric number = 3), so this carbon atom is $sp^2$ hybridized, with trigonal planar geometry. Each of the other three carbon atoms has four σ bonds (steric

number = 4), and therefore, those three carbon atoms are all $sp^3$ hybridized, with tetrahedral geometry.



**(c)** Each of the carbon atoms in this compound has four σ bonds (steric number = 4). Therefore, all of these carbon atoms are $sp^3$ hybridized, with tetrahedral geometry, or as close to it as this "triangle" will allow. We will discuss the geometry of this three-membered ring in more detail in Chapter 4.



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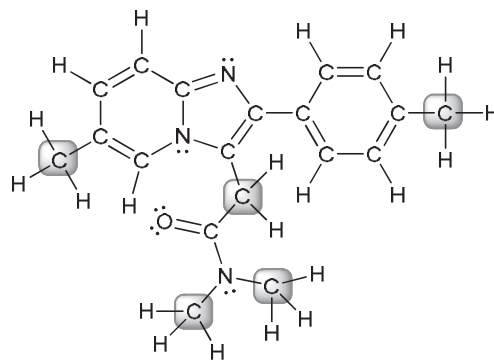


**1.57.**
**(a)** Oxygen is the most electronegative atom in this compound. See Table 1.1 for electronegativity values.

**(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 (below) has two σ bonds and one lone pair (steric number = 3), so 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 σ bonds and a lone pair (steric number = 4), so 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.



$sp^2$, bent

$sp^3$
trigonal pyramidal
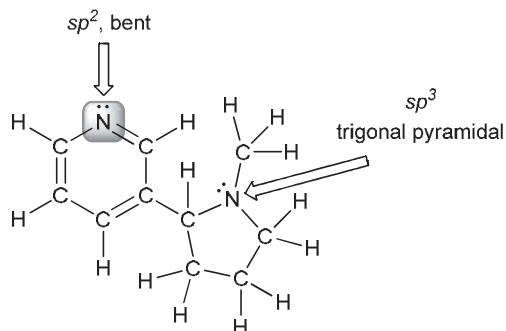
**1.59.** Each of the nitrogen atoms in this structure achieves an octet with three bonds and one lone pair, while each oxygen atom in this structure achieves an octet with two bonds and two lone pairs, as shown:
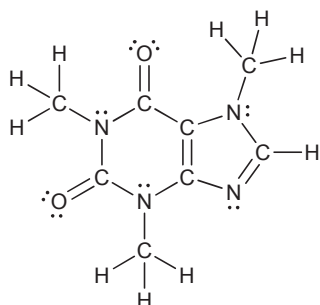


**1.60.** In the solution to Problem 1.46a, we saw that the following two compounds have the molecular formula $C_2H_6O$.
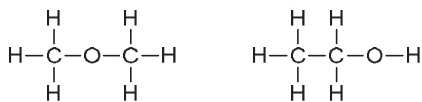


The second compound will have a higher boiling point because it possesses an OH group which can form hydrogen bonding interactions.

**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:
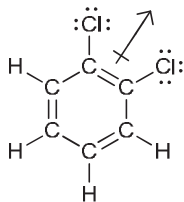


**(b)** Each C–Cl bond has a dipole moment, and the two dipole moments do not fully cancel each other because they are not pointing in opposite directions. As such, there will be a net molecular dipole moment, as shown here:
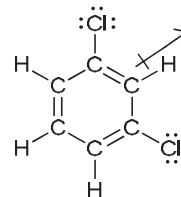


**(c)** Each C–Cl bond has a dipole moment, and in this case, the two dipole moments are pointing in opposite directions. As such, they fully cancel each other, giving no net molecular dipole moment.

**(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:
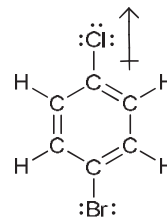


**1.62.** The third chlorine atom in chloroform partially cancels the effects of the other two chlorine atoms, thereby reducing the molecular dipole moment relative to methylene chloride.

**1.63.**
**(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 σ bonds and one lone pair (steric number = 4), so 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 σ bond and one π bond, while a triple bond represents one σ bond and two π bonds. A single bond represents a σ bond. With this in mind, compound B has 14 σ bonds, as compared with compounds A and C, which have 13 and 11 σ bonds, respectively.
**(d)** As explained in the solution to Problem **1.63c**, compound C has the fewest σ bonds.
**(e)** A double bond represents one σ bond and one π bond, while a triple bond represents one σ bond and two π bonds. As such, compound C exhibits two π bonds.

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

**(g)** Each of the carbon atoms in compound B is $sp^3$ hybridized, because each has four σ bonds (steric number = 4). Similarly, the nitrogen atom in compound B has three σ bonds and one lone pair (steric number = 4), so 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.
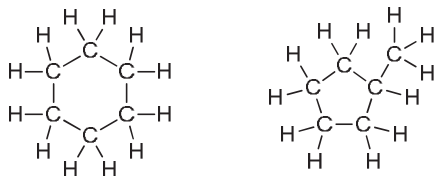
**1.64.**

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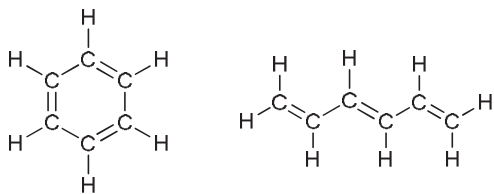


**(b)** In each of the following two compounds, all of the carbon atoms are $sp^3$ hybridized (because each carbon atom has four σ bonds) with the exception of the carbon atom connected to the nitrogen atom. That carbon atom has two σ bonds and is therefore $sp$ hybridized. There are certainly many other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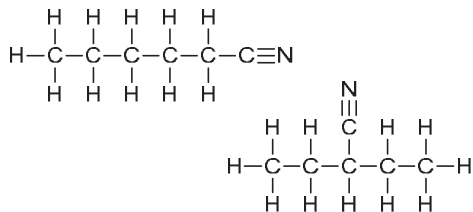


**(c)** In each of the following two compounds, there is a ring, and all of the carbon atoms are $sp^3$ hybridized (because each carbon atom has four σ bonds). There are certainly many other acceptable answers.
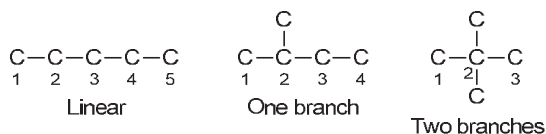


**(d)** In each of the following two compounds, all of the carbon atoms are $sp$ hybridized (because each carbon

atom has two σ bonds). There are certainly many other acceptable answers.
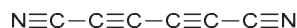


**1.65.** In the solution to Problem **1.34b**, we saw that there are three ways to arrange five carbon atoms:



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:
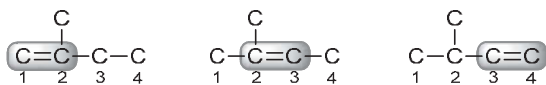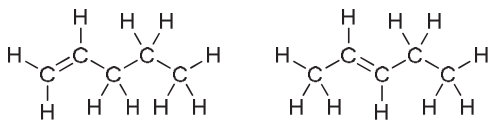


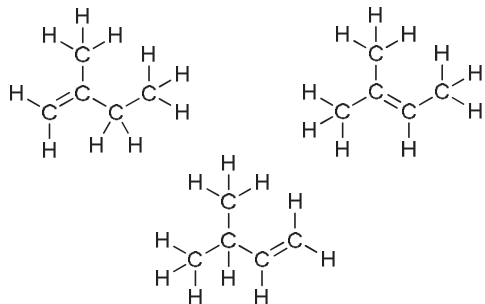Be careful, the following two locations are the same:
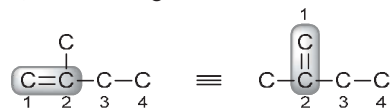


Finally, we complete all five possible structures by drawing the remaining bonds to the hydrogen atoms (see next page):
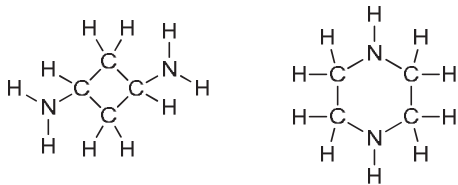
Linear skeleton



Branched skeleton



**1.66.** 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 π bonds, there is no net dipole moment, and there is an N-H bond, which enables hydrogen bonding interactions.    There are certainly other acceptable answers.



**1.67.**    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):



$C_5H_{13}N$
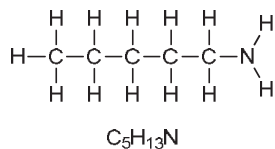
This will be the case even if try to draw a branched skeleton:



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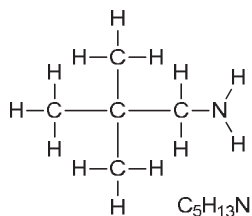
In fact, regardless of how the skeleton is branched, it will still have 13 hydrogen atoms.  But we need to draw a structure with only 11 hydrogen atoms ($C_5H_{11}N$).  So we must remove two hydrogen atoms, which gives two unpaired electrons:



$C_5H_{13}N$    -2 (H·)

$C_5H_{11}N$

unpaired electrons
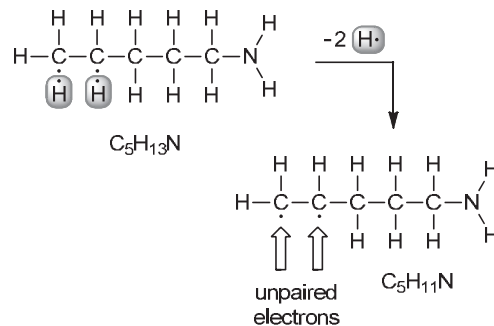
This indicates that we should consider pairing these electrons as a double bond.  However, the problem statement specifically indicates that the structure cannot contain a double bond.  So, we must find another way to pair the unpaired electrons.  We encountered a similar issue in the solution to problem **1.35a**, in which we paired the electrons by forming a ring.   We can do something similar here:



$C_5H_{13}N$    -2 (H·)

$C_5H_{11}N$

$C_5H_{11}N$
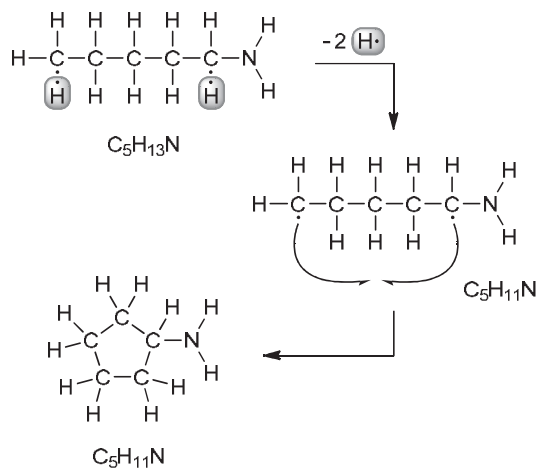
Now we have the correct number of hydrogen atoms (eleven), which means that our structure must indeed contain a ring.  But this particular cyclic structure (cyclic = containing a ring) does not meet all of the criteria described in the problem statement.  Specifically, each carbon atom must be connected 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.
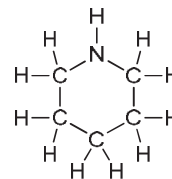
**1.68.**
**(a)** In compound **A**, the nitrogen atom has two σ bonds and no lone pairs (steric number = 2), so it is *sp* hybridized. The highlighted carbon atom has one σ bond and one lone pair (steric number = 2), so that carbon atom is *sp* hybridized.
**(b)** The highlighted carbon atom is *sp* 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°.

**(d)** The nitrogen atom in **B** has two σ bonds and one lone pair (steric number = 3); therefore, it is *sp²* hybridized. The highlighted carbon atom has three σ bonds and no lone pairs (steric number = 3), so that carbon atom is *sp²* hybridized. Each of the chlorine atoms has three lone pairs and one bond (steric number = 4), so the chlorine atoms are *sp³* hybridized.
**(e)** The nitrogen atom is *sp²* hybridized, so the lone pair occupies an *sp²* hybridized orbital.
**(f)** The nitrogen atom is *sp²* hybridized so the C-N-C bond angle in **B** is expected to be approximately 120°.

**1.69.**  The molecule has two different C=C π bonds, both highlighted in grey. Bond **A** is surrounded by four groups: two $CH_3$ groups, one (small) hydrogen atom, and one large carbon chain. Bond **B** is also surrounded by four groups, but they are different: three (small) hydrogen atoms, and one large carbon chain. Based on size, a $CH_3$ group and/or a carbon chain are much larger than a single hydrogen atom, and would occupy more space surrounding the π bond. Since there is more branching on bond **A** (and as a result more space surrounding it is occupied by groups that are larger than H), we would say that bond **A** is more sterically crowded than bond **B**.

Steric Crowding of π-bond A          Steric Crowding of π-bond B
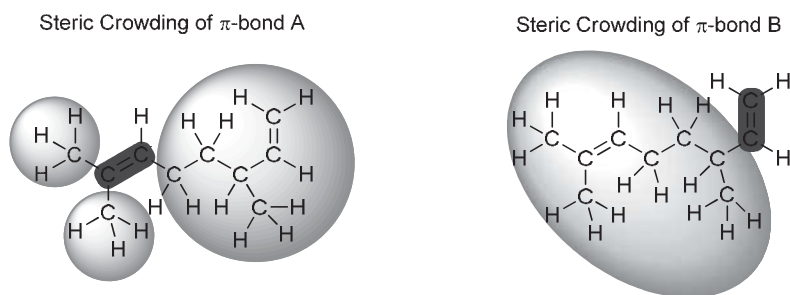


**1.70.**  The first observation is that compounds **3** and **4** are difficult to separate at room temperature, which means that compound **3** must be soluble in compound **4**, and vice versa; compound **4** is soluble in compound **3**. In Section 1.13 we discussed the principle of solubility known as, "like dissolves like". Compound **3** and compound **4** are comprised mainly of carbon and hydrogen atoms, and because of the oxygen atoms present in each, both will have molecular dipole moments. Also of note, compound **3** possesses an O-H group; it has the ability to form hydrogen-bonding interactions with itself, *or with* the oxygen atoms of compound **4**.
When a mixture of compound **3** and **4** is heated, they can be separated from each other based on a difference in their boiling points.  Compound **3** will have a much 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**.
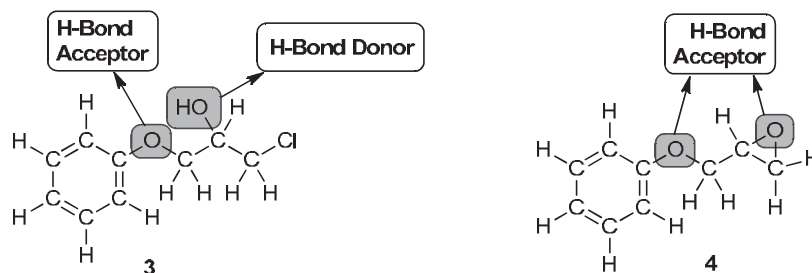


**1.71.**
**(a)** We compare the following bonds: C(*sp³*)–F (1.40Å), C(*sp³*)–Cl (1.79Å), C(*sp³*)–Br (1.97Å), and C(*sp³*)–I (2.16Å).  Notice that the bond length increases as the size of the halogen increases.  This should make sense, since the valence electrons in iodine are farther away from the nucleus than the valence electrons in Br, so we

expect a C-I bond to be longer than a C-Br bond.  For the same reason, we expect a C-Br bond to be longer than a C-Cl bond, which in turn is longer than a C-F bond.

**(b)** We compare the following bonds: $C_{sp}3$–F (1.40Å), C(*sp²*)–F (1.34Å), and C(*sp*)–F (1.27Å).  Notice that the bond length decreases as the hybridization state goes

from $sp^3$ to $sp^2$ to $sp$. This should make sense, because $sp$ hybridized atoms hold their valence electrons closer to the nucleus (see Table 1.2 in the textbook), and therefore form shorter bonds.

**(c)** According to the trend that we discovered in part (a), we would expect C($sp^2$)–Cl to be shorter than C($sp$)–I, because the Cl atom holds its valence electrons closer to the nucleus (when compared with iodine). However, according to the trend that we discovered in part (b), we would expect C($sp^2$)–Cl to be longer than C($sp$)–I, because the carbon atom is $sp^2$ hybridized, so its valence electrons are farther from the nucleus than in the case of an $sp$ hybridized carbon atom. These two trends are in conflict, and we would not be able to determine which factor dominates without the data that is provided. By analyzing the data, we can see that C($sp^2$)–Cl must be shorter than 1.79Å [compare with C($sp^3$)–Cl], while C($sp$)–I must be longer than 1.79Å [compare with C($sp$)–Br]. Therefore, C($sp$)–I must be longer than C($sp^2$)–Cl.

**1.72.**
**(a)** In the first compound, the fluorine isotope ($^{18}$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 σ bond and three lone pairs, it must have a steric number of 4, so it 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 σ 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 σ bonds and one lone pair, it must have a steric number of 4, so it is $sp^3$ hybridized. The oxygen atom also has no formal charge. Therefore, it must have two lone pairs. Since the oxygen atom has two σ bonds and two lone pairs, it must have a steric number of 4, so it is $sp^3$ hybridized.
In the product, the fluorine isotope ($^{18}$F) has no formal charge. Therefore, it must have three lone pairs. Since it has one σ bond and three lone pairs, it must have a steric number of 4, so it is $sp^3$ hybridized. The nitrogen atom does have a positive formal charge. Therefore, it must have no lone pairs. Since it has four σ bonds and no lone pairs, it must have a steric number of 4, so it is $sp^3$ hybridized. The oxygen atom also has no formal charge. Therefore, it must have two lone pairs. Since the oxygen atom has two σ bonds and two lone pairs, it must have a steric number of 4, so it 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, so it is $sp^3$ hybridized.
In summary, all of the heteroatoms (in all of the structures) 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°.

**(c)** The oxygen atom is $sp^3$ hybridized, so each of the lone pairs occupies an $sp^3$ hybridized orbital.

**1.73.**
**(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 σ bonds and no lone pairs, the boron atom has a steric number of three, so it is $sp^2$ hybridized.

**(b)** Since the boron atom is $sp^2$ hybridized, we expect the bond angle to be approximately 120°. 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.

**(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 Problem **1.73a**.
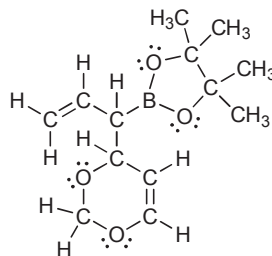


**1.74.**
**(a)** If we analyze each atom (in both **1** and **2**) using the procedure outlined in Section 1.4, we find that none of the atoms in compound **1** have a formal charge, while compound **2** possesses two formal charges:
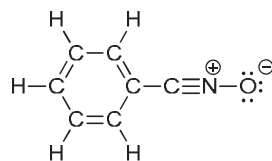


The nitrogen atom has a positive charge (it is supposed to be using five valence electrons, but it is actually using four), and the oxygen atom has a negative charge (it is supposed to be using six valence electrons, but it is actually using seven).

**(b)** Compound **1** possesses polar bonds, as a result of the presence of partial charges (δ+ and δ-). 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 σ bonds and no lone pairs (steric number = 3), so 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°. However, in compound **2**, the same carbon atom has two σ bonds and no lone pairs (steric number = 2), so now this carbon atom is $sp$ hybridized, with linear geometry. As such, the C-C-N bond angle in **2** is expected to be 180°. The conversion of **1** to **2** therefore involves an increase in the C-C-N bond angle of approximately 60°.

**1.75.**
**(a)** $C_a$ has three σ bonds and no lone pairs, so it has a steric number of 3, and is therefore $sp^2$ hybridized. The same is true for $C_c$. In contrast, $C_b$ has two σ 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°.

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

**(d)** The central carbon atom ($C_b$) is $sp$ hybridized, so it is using two $sp$ hybridized orbitals to form its two σ bonds, which will be arranged in a linear fashion. The remaining two $p$ orbitals of $C_b$ (used for π bonding) need to be as far apart from each other as possible, so they will be 90° apart from one another (just as we saw for the carbon atoms of a triple bond; see Figure 1.33).
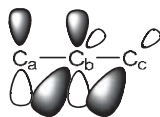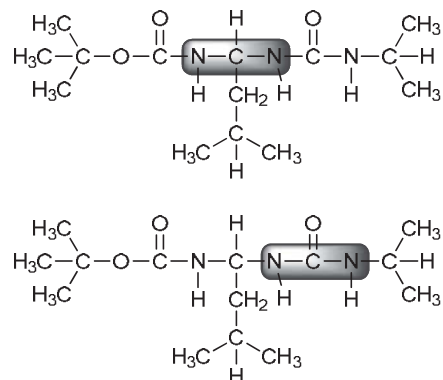


As a result, the two π systems are orthogonal (or 90°) to each other. Therefore, the $p$ orbitals on $C_a$ and $C_c$ are orthogonal. The following is another drawing from a

different perspective (looking down the axis of the linear $C_a$-$C_b$-$C_c$ system.



**1.76.**
**(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°.
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°.

**(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:
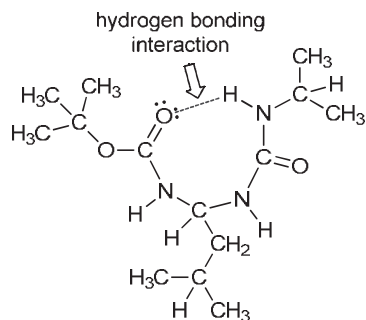
**1.77.** First, let's compare the functional groups at the peripheries of the binding sites in each of the two polymers. Each carboxylic acid group (COOH) in polymer **A** can serve as both a hydrogen-bond *donor* and *acceptor*, while each of the nitrogen atoms in polymer **B** can only serve as a hydrogen-bond *acceptor*.
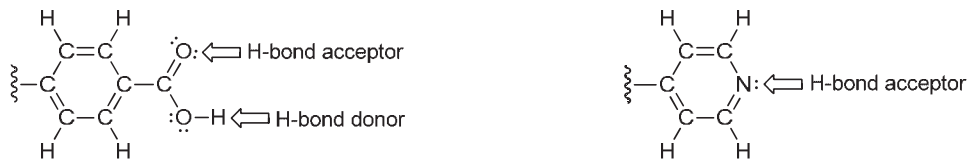
Now, let's compare the functional groups at the termini of the two guest molecules. The OH and $NH_2$ groups can each serve as a donor or an acceptor. The OH group is a stronger hydrogen-bond donor than the $NH_2$ group, because oxygen is more electronegative than nitrogen, thus resulting in a greater partial positive charge on the hydrogen atom attached to oxygen.
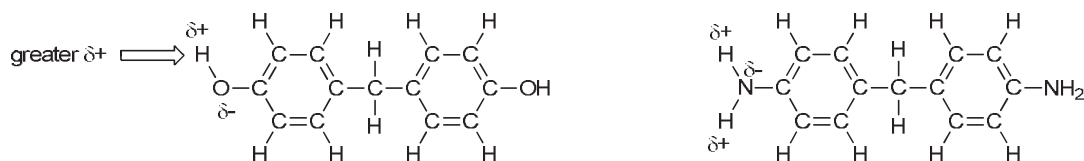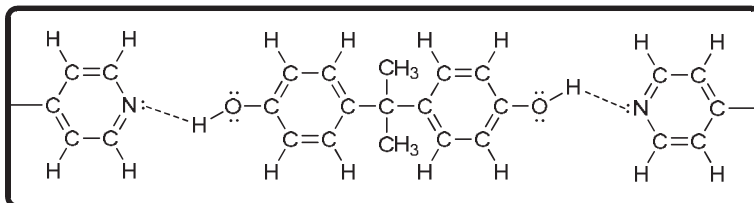
On the other hand, the $NH_2$ group is a better hydrogen-bond acceptor. Nitrogen is less electronegative than oxygen, so the lone pair on nitrogen is held less strongly to the nitrogen, and thus it is more available to form a hydrogen bond.

With this in mind, we can draw pictures proposing the mode of binding of each guest within each polymer. Each carboxylic acid group (COOH) in the binding site of polymer **A** can form two H-bonds to the functional group on each side of the guest molecule (OH in guest **1**, $NH_2$ in guest **2**), as shown below.

Polymer **A** with guest **1**

Polymer **A** with guest **2**
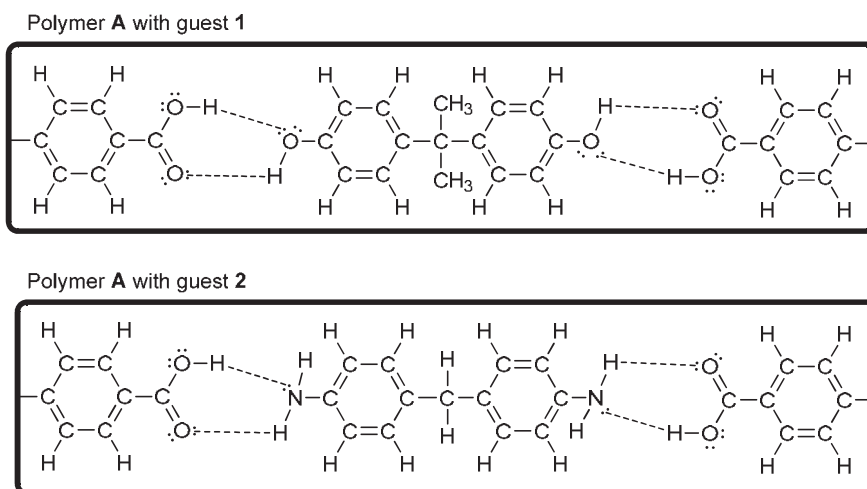
Each guest molecule binds similarly because: (a) the two guest molecules have similar size and shape, so they can both fit into the binding site, and (b) the increased H-bond *donating* ability of the OH group (which leads to stronger binding of guest **1**) is balanced by the increased H-bond *accepting* ability of the $NH_2$ group (which leads to stronger binding of guest **2**).

In contrast, the groups on the periphery of polymer **B** can only accept (but not donate) hydrogen bonds as explained above. Guest **1** binds strongly with polymer **B** (due to the formation of strong hydrogen-bonds). The binding of guest **2** is significantly weaker (due to the formation of relatively weaker hydrogen-bonds).

Polymer **B** with guest **1**



Polymer **B** with guest **2**