Student Study Guide and Solutions Manual

ORGANIC CHEMISTRY

DAVID KLEIN

FOURTH EDITION

WILEY

Student Study Guide and Solutions Manual, 4e

for

Organic Chemistry, 4e

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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.
- ***Review of Mechanisms***. These exercises are designed to help you practice drawing the mechanisms. To verify that you have drawn the mechanism correctly, you can open your textbook to the corresponding chapter, where you will find the mechanisms appearing in numbered boxes throughout the chapter. In those numbered boxes, you will find the answers to each of these exercises.
- ***Common Mistakes to Avoid***. This is a new feature to this edition. The most common student mistakes are described, so that you can avoid them when solving problems.
- ***A List of Useful Reagents***. This is a new feature to this edition. This list provides a review of the reagents that appear in each chapter, as well as a description of how each reagent is used.
- ***Solutions***. At the end of each chapter, you'll find detailed solutions to all problems in the textbook, including all SkillBuilders, conceptual checkpoints, additional problems, integrated problems, and challenge problems.

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

David Klein
Johns Hopkins University

Chapter 1
A Review of General Chemistry: Electrons, Bonds and Molecular Properties

Review of Concepts

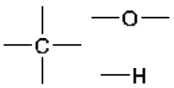
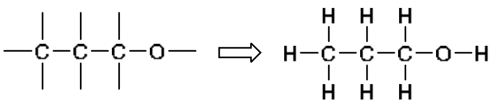
Fill in the blanks below. To verify that your answers are correct, look in your textbook at the end of Chapter 1. Each of the sentences below appears verbatim in the section entitled *Review of Concepts and Vocabulary*.

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

Review of Skills

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

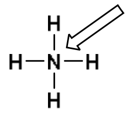
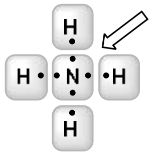
SkillBuilder 1.1 Drawing Constitutional Isomers of Small Molecules

Step 1 Determine the valency of each atom in C_3H_8O.	**Step 2** Connect the atoms of highest valency, and place the monovalent atoms at the periphery.	**Step 3** Consider other ways to connect the atoms.
		

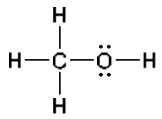
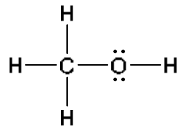
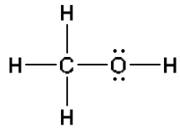
SkillBuilder 1.2 Drawing the Lewis Structure of a Small Molecule

Step 1 Draw the Lewis dot structure of each atom in CH_2O.	**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.

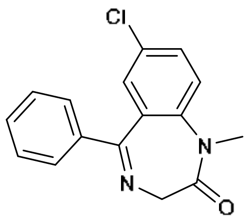
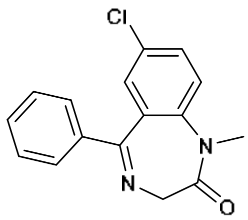
SkillBuilder 1.3 Calculating Formal Charge

Step 1 Determine the appropriate number of valence electrons.  Nitrogen is in Group _____ of the periodic table, and is expected to have _____ valence electrons.	**Step 2** Determine the number of valence electrons in this case.  In this case, the nitrogen atom exhibits only _____ valence electrons.	**Step 3** Assign a formal charge to the nitrogen atom.

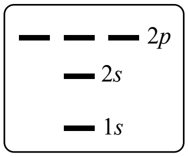
SkillBuilder 1.4 Locating Partial Charges Resulting from Induction

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 (δ+ and δ–). 

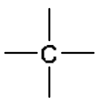
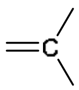
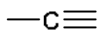
SkillBuilder 1.5 Reading Bond-Line Structures

Circle all carbon atoms in the compound below 	Draw all hydrogen atoms in the compound below 

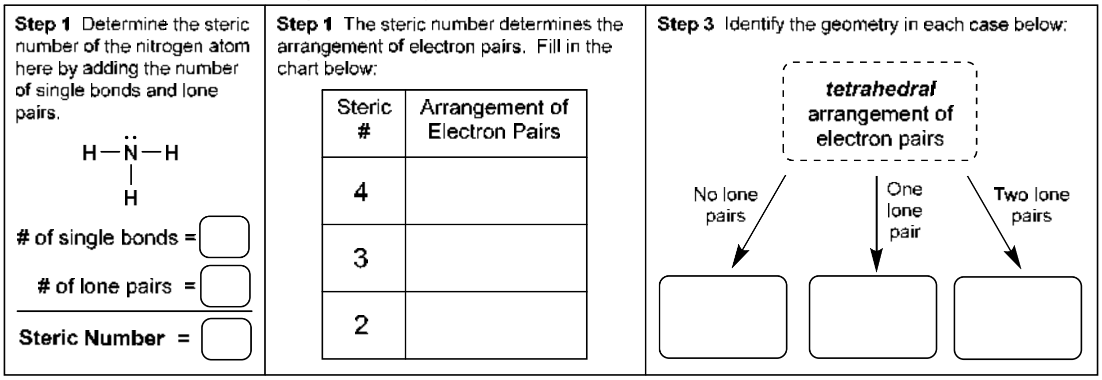
SkillBuilder 1.6 Identifying Electron Configurations

Step 1 In the energy diagram shown here, draw the electron configuration of nitrogen (using arrows to represent electrons).  Nitrogen	**Step 2** Fill in the boxes below with the numbers that correctly describe the electron configuration of nitrogen. $1s^{\square}\ 2s^{\square}\ 2p^{\square}$

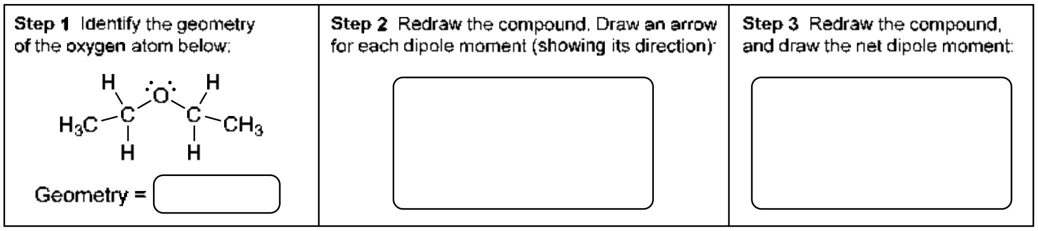
SkillBuilder 1.7 Identifying Hybridization States

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. 

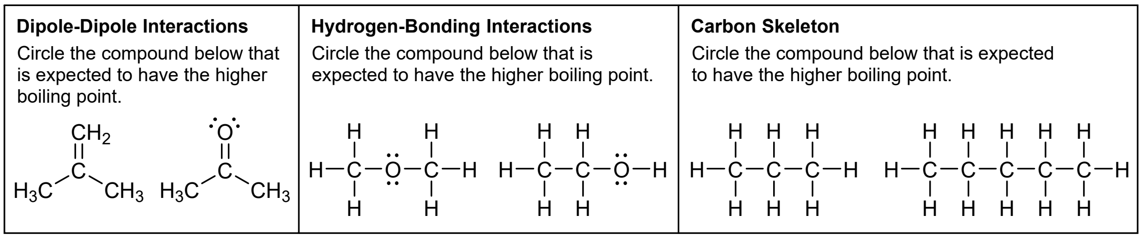
SkillBuilder 1.8 Predicting Geometry



SkillBuilder 1.9 Identifying the Presence of Molecular Dipole Moments

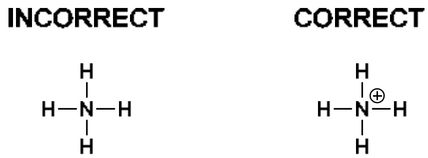


SkillBuilder 1.10 Predicting Physical Properties



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:

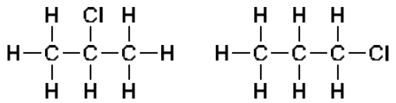


As we progress though the course, we will see structures of increasing complexity. If formal charges are present, failure to draw them constitutes an error, and must be scrupulously avoided. If you have trouble drawing formal charges, go back and master that skill. You can't go on without it. Don't make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

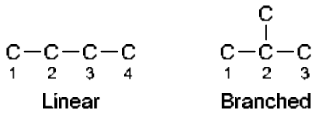
Solutions

1.1.

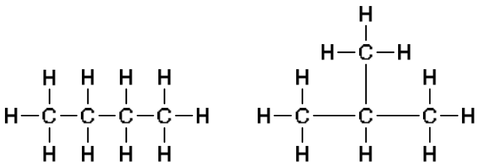
(a) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the chlorine atom and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the three carbon atoms) should be drawn in the center of the compound. Then, the chlorine atom can be placed in either of two locations: i) connected to the central carbon atom, or ii) connected to one of the other two (equivalent) carbon atoms. The hydrogen atoms are then placed at the periphery (ensuring that each carbon atom has a total of four bonds). The formula C_3H_7Cl has two constitutional isomers.



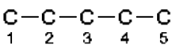
(b) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the four carbon atoms) should be drawn in the center of the compound. There are two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



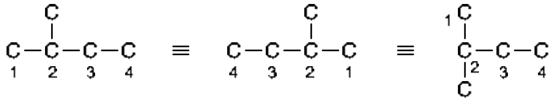
We then place the hydrogen atoms at the periphery (ensuring that each carbon atom has a total of four bonds). The formula C_4H_{10} has two constitutional isomers:



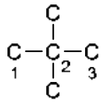
(c) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the five carbon atoms) should be drawn in the center of the compound. So we must explore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



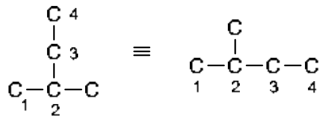
Alternatively, we can draw four carbon atoms in a linear fashion, and then draw the fifth carbon atom on a branch. There are many ways to draw this possibility:



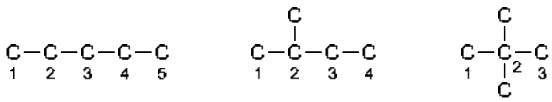
Finally, we can draw three carbon atoms in a linear fashion, and then draw the remaining two carbon atoms on separate branches.



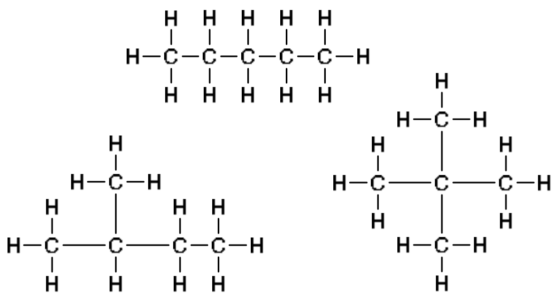
Note that we cannot draw a unique carbon skeleton (a unique arrangement of carbon atoms) simply by placing the last two carbon atoms together as one branch, because that possibility has already been drawn earlier (a linear chain of four carbon atoms with a single branch):



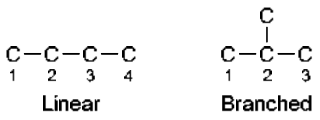
In summary, there are three different ways to connect five carbon atoms:



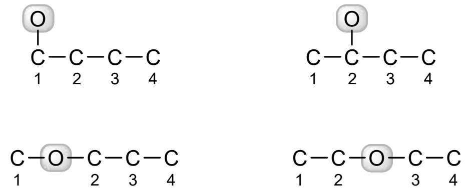
We then place the hydrogen atoms at the periphery (ensuring that each carbon atom has a total of four bonds). The formula C_5H_{12} has three constitutional isomers:



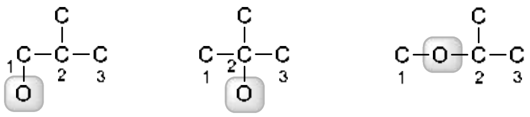
(d) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, the oxygen atom is divalent, and the hydrogen atoms are all monovalent. Any atoms with more than one bond (in this case, the four carbon atoms and the one oxygen atom) should be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



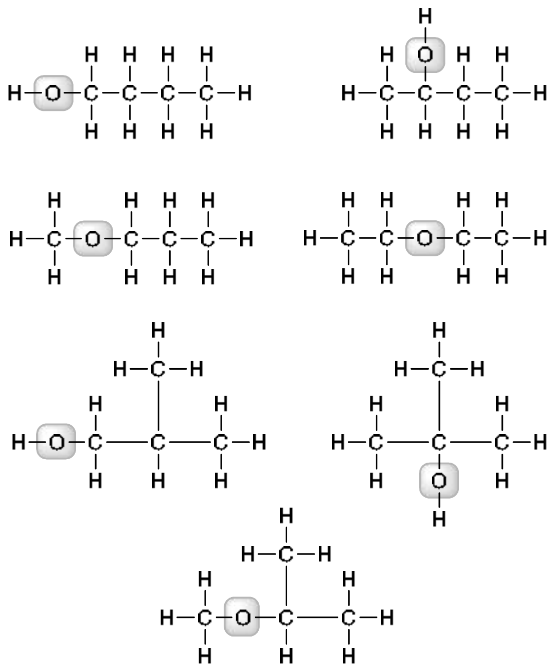
Next, the oxygen atom must be inserted. For each of the two skeletons above (linear or branched), there are several different locations to insert the oxygen atom. The linear skeleton has four possibilities, shown here:



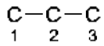
and the branched skeleton has three possibilities shown here:



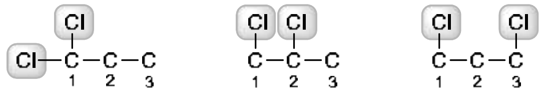
Finally, we complete all of the structures by drawing the bonds to hydrogen atoms (ensuring that each carbon atom has four bonds, and each oxygen atoms has two bonds). The formula $C_4H_{10}O$ has seven constitutional isomers:



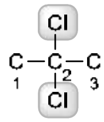
(e) Begin by determining the valency of each atom that appears in the molecular formula. The carbon atoms are tetravalent, while the chlorine atom and hydrogen atoms are all monovalent. The atoms with more than one bond (in this case, the three carbon atoms) should be drawn in the center of the compound.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



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

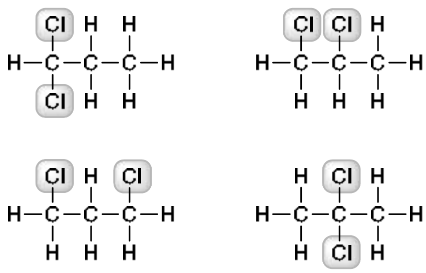


Furthermore, we can place both chlorine atoms at C2, giving a new possibility not shown above:

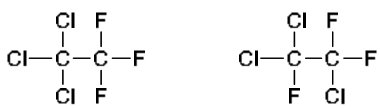


There are no other possibilities. For example, placing the two chlorine atoms at C2 and C3 is equivalent to placing them at C1 and C2:

Finally, the hydrogen atoms are placed at the periphery (ensuring that each carbon atom has a total of four bonds). The formula $C_3H_6Cl_2$ has four constitutional isomers:

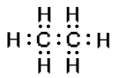


1.2. The carbon atoms are tetravalent, while the chlorine atoms and fluorine atoms are all monovalent. The atoms with more than one bond (in this case, the two carbon atoms) should be drawn in the center of the compound. The chlorine atoms and fluorine atoms are then placed at the periphery, as shown.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

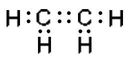


1.3.

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

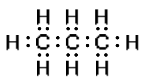


(b) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, and the unpaired electrons are shared to give a double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

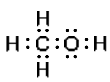


(c) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, and the unpaired electrons are shared to give a triple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

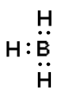
(d) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms, as shown.



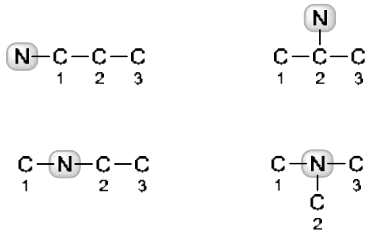
(e) The carbon atom has four valence electrons, the oxygen atom has six valence electrons, and each hydrogen atom has one valence electron. Only the carbon atom and the oxygen atom can form more than one bond, so we begin by connecting them to each other. Then, we connect all of the hydrogen atoms, as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



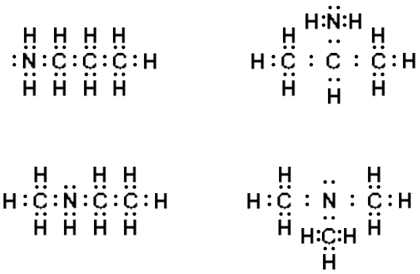
1.4. Boron is in column 3A of the periodic table, so it has three valence electrons. Each of these valence electrons is shared with a hydrogen atom, shown below. The central boron atom lacks an octet of electrons, and it is therefore very unstable and reactive.



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



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

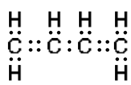


In each of these four structures, the nitrogen atom has one lone pair.

1.6.

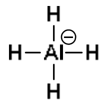
(a) The carbon atom has four valence electrons, the nitrogen atom has five valence electrons and the hydrogen atom has one valence electron. Only the carbon atom and the nitrogen atom can form more than one bond, so we begin by connecting them to each other. Then, we connect the hydrogen atom to the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

(b) Each carbon atom has four valence electrons, and each hydrogen atom has one valence electron. Only the carbon atoms can form more than one bond, so we begin by connecting the carbon atoms to each other. Then, we connect all of the hydrogen atoms as indicated in the given condensed formula ($CH_2CHCHCH_2$), and the unpaired electrons are shared to give two double bonds on the outermost carbons. In this way, each of the carbon atoms achieves an octet.

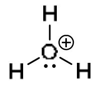


1.7.

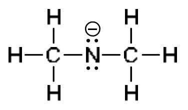
(a) Aluminum is in group 3A of the periodic table, and it should therefore have three valence electrons. In this case, the aluminum atom exhibits four valence electrons (one for each bond). With one extra electron, this aluminum atom will bear a negative charge.



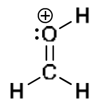
(b) Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. In this case, the oxygen atom exhibits only five valence electrons (one for each bond, and two for the lone pair). This oxygen atom is missing an electron, and it therefore bears a positive charge.



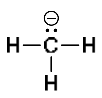
(c) Nitrogen is in group 5A of the periodic table, and it should therefore have five valence electrons. In this case, the nitrogen atom exhibits six valence electrons (one for each bond and two for each lone pair). With one extra electron, this nitrogen atom will bear a negative charge.



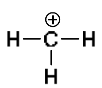
(d) Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. In this case, the oxygen atom exhibits only five valence electrons (one for each bond, and two for the lone pair). This oxygen atom is missing an electron, and it therefore bears a positive charge.



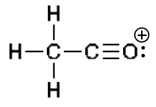
(e) Carbon is in group 4A of the periodic table, and it should therefore have four valence electrons. In this case, the carbon atom exhibits five valence electrons (one for each bond and two for the lone pair). With one extra electron, this carbon atom will bear a negative charge.



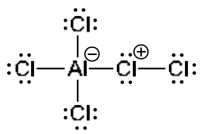
(f) Carbon is in group 4A of the periodic table, and it should therefore have four valence electrons. In this case, the carbon atom exhibits only three valence electrons (one for each bond). This carbon atom is missing an electron, and it therefore bears a positive charge.



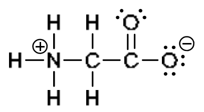
(g) Oxygen is in group 6A of the periodic table, and it should therefore have six valence electrons. In this case, the oxygen atom exhibits only five valence electrons (one for each bond, and two for the lone pair). This oxygen atom is missing an electron, and it therefore bears a positive charge.



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

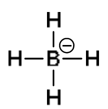


(i) Two of the atoms in this structure exhibit a formal charge because each of these atoms does not exhibit the appropriate number of valence electrons. The nitrogen atom (group 5A) should have five valence electrons, but it exhibits four (one for each bond). It is missing one electron, so this nitrogen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

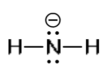


1.8.

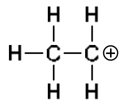
(a) The boron atom in this case exhibits four valence electrons (one for each bond), although boron (group 3A) should only have three valence electrons. With one extra electron, this boron atom bears a negative charge.



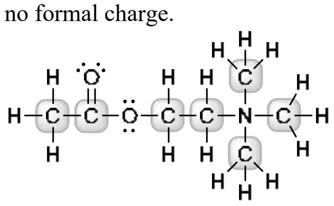
(b) Nitrogen is in group 5A of the periodic table, so a nitrogen atom should have five valence electrons. A negative charge indicates one extra electron, so this nitrogen atom must exhibit six valence electrons (one for each bond and two for each lone pair).



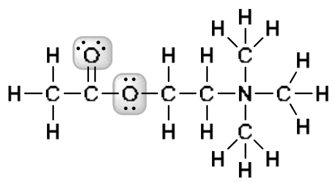
(c) One of the carbon atoms (below right) exhibits three valence electrons (one for each bond), but carbon (group 4A) is supposed to have four valence electrons. It is missing one electron, so this carbon atom therefore bears a positive charge.



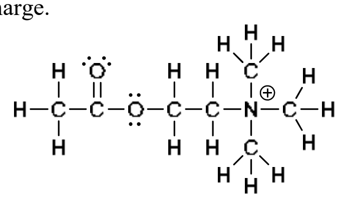
1.9. Carbon is in group 4A of the periodic table, and it should therefore have four valence electrons. Every carbon atom in acetylcholine has four bonds, thus exhibiting the correct number of valence electrons (four) and having no formal charge.



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

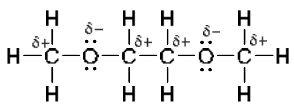


The nitrogen atom (group 5A) should have five valence electrons, but it exhibits four (one for each bond). It is missing one electron, so this nitrogen atom will bear a positive charge.

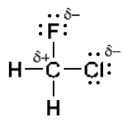


1.10.

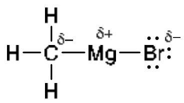
(a) Oxygen is more electronegative than carbon, and a C–O bond is polar covalent. For each C–O bond, the O will be electron-rich (δ–), and the C will be electron-poor (δ+), as shown below.



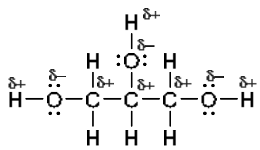
(b) Fluorine is more electronegative than carbon, and a C–F bond is polar covalent. For a C–F bond, the F will be electron-rich (δ–), and the C will be electron-poor (δ+). Chlorine is also more electronegative than carbon, so a C–Cl bond is also polar covalent. For a C–Cl bond, the Cl will be electron-rich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



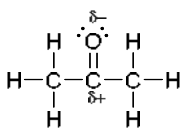
(c) Carbon is more electronegative than magnesium, so the C will be electron-rich (δ–) in a C–Mg bond, and the Mg will be electron-poor (δ+). Also, bromine is more electronegative than magnesium. So in a Mg–Br bond, the Br will be electron-rich (δ–), and the Mg will be electron-poor (δ+), as shown below.



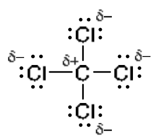
(d) Oxygen is more electronegative than carbon or hydrogen, so all C–O bonds and all O–H bond are polar covalent. For each C–O bond and each O–H bond, the O will be electron-rich (δ–), and the C or H will be electron-poor (δ+), as shown below.



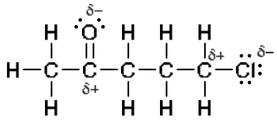
(e) Oxygen is more electronegative than carbon. As such, the O will be electron-rich (δ–) and the C will be electron-poor (δ+) in a C=O bond, as shown below.



(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.

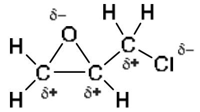


1.11. Oxygen is more electronegative than carbon. As such, the O will be electron-rich (δ–) and the C will be electron-poor (δ+) in a C=O bond. In addition, chlorine is more electronegative than carbon. So for a C–Cl bond, the Cl will be electron-rich (δ–) and the C will be electron-poor (δ+), as shown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



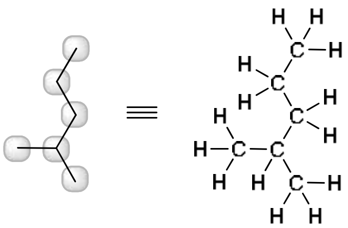
Notice that two carbon atoms are electron-poor (δ+). These are the positions that are most likely to be attacked by an electron-rich anion, such as hydroxide.

1.12. 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. As you might imagine, epichlorohydrin is a very reactive molecule!

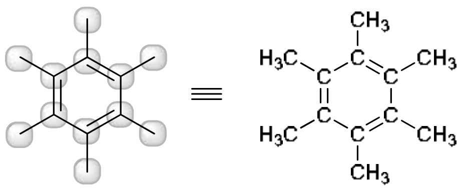


1.13.

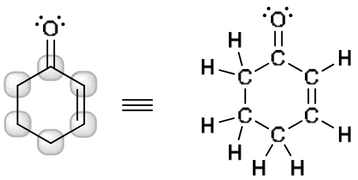
(a) Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has six carbon atoms. Each carbon atom has enough attached hydrogen atoms to have exactly four bonds, as shown:



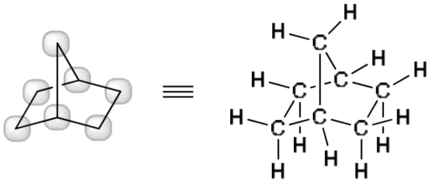
(b) Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has twelve carbon atoms. Each carbon atom has enough attached hydrogen atoms to have exactly four bonds, as shown:



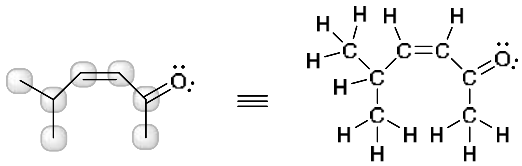
(c) Each corner represents a carbon atom (highlighted below), so this compound has six carbon atoms. Each carbon atom has enough attached hydrogen atoms to have exactly four bonds, as shown:



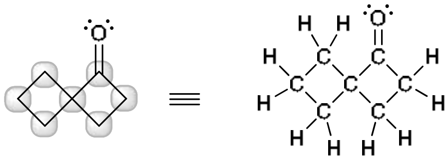
(d) Each corner represents a carbon atom (highlighted below), so this compound has seven carbon atoms. Each carbon atom has enough attached hydrogen atoms to have exactly four bonds, as shown:



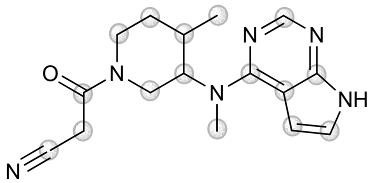
(e) Each corner and each endpoint represents a carbon atom (highlighted below), so this compound has seven carbon atoms. Each carbon atom has enough attached hydrogen atoms to have exactly four bonds, as shown:



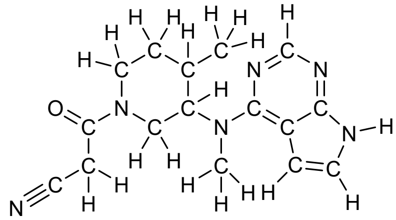
(f) Each corner represents a carbon atom (highlighted below), so this compound has seven carbon atoms. Each carbon atom has enough attached hydrogen atoms to have exactly four bonds, as shown:



1.14. Remember that each corner and each endpoint represents a carbon atom. This compound therefore has 16 carbon atoms, highlighted below:



Each carbon atom should have four bonds. We therefore draw enough hydrogen atoms in order to give each carbon atom a total of four bonds. Any carbon atoms that already have four bonds will not have any hydrogen atoms:



1.15.

(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: $1s^22s^22p^2$

(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: $1s^22s^22p^4$

(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: $1s^22s^22p^1$

(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: $1s^22s^22p^5$

(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: $1s^22s^22p^63s^1$

(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: $1s^22s^22p^63s^23p^1$

1.16.

(a) The electron configuration of a carbon atom is $1s^22s^22p^2$ (see the solution to Problem 1.15a). However, if a carbon atom bears a negative charge, then it must have one extra electron, so the electron configuration should be as follows: $1s^22s^22p^3$

(b) The electron configuration of a carbon atom is $1s^22s^22p^2$ (see the solution to Problem 1.15a). However, if a carbon atom bears a positive charge, then it must be missing an electron, so the electron configuration should be as follows: $1s^22s^22p^1$

(c) As seen in SkillBuilder 1.6, the electron configuration of a nitrogen atom is $1s^22s^22p^3$. However, if a nitrogen atom bears a positive charge, then it must be missing an electron, so the electron configuration should be as follows: $1s^22s^22p^2$

(d) The electron configuration of an oxygen atom is $1s^22s^22p^4$ (see the solution to Problem 1.15b). However, if an oxygen atom bears a negative charge, then it must have one extra electron, so the electron configuration should be as follows: $1s^22s^22p^5$

1.17. Silicon is in the third row, or period, of the periodic table. Therefore, it has a filled second shell, like neon, and then the additional electrons are added to the third shell. As indicated in Figure 1.10, neon has two 1*s* electrons, two 2*s* electrons, and six 2*p* electrons. Silicon has an additional two 3*s* electrons and two 3*p* electrons to give a total of 14 electrons and an electron configuration of $1s^22s^22p^63s^23p^2$.

1.18. The 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.

1.19.

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

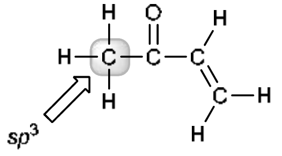
(b) Each C–H bond is formed from the interaction between an *sp*²-hybridized orbital from carbon and an *s* orbital from hydrogen.

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

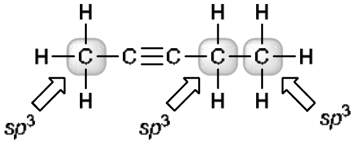
1.20. Rotation of a single bond does not cause a reduction in the extent of orbital overlap, because the orbital overlap occurs on the bond axis. In contrast, rotation of a π bond results in a reduction in the extent of orbital overlap between the two *p* orbitals, because the orbital overlap is NOT on the bond axis.

1.21.

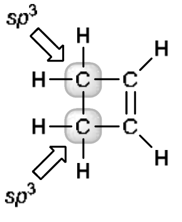
(a) The highlighted carbon atom (below) has four σ bonds, and is therefore *sp*³ hybridized. The other carbon atoms in this structure are all *sp*² hybridized, because each of them has three σ bonds and one π bond.



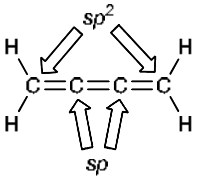
(b) Each of the highlighted carbon atoms has four σ bonds, and is therefore *sp*³ hybridized. The other two carbon atoms in this structure are *sp* hybridized, because each has two σ bonds and two π bonds.



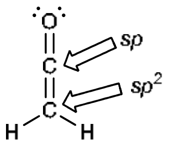
(c) Each of the highlighted carbon atoms (below) has four σ bonds, and is therefore *sp*³ hybridized. The other two carbon atoms in this structure are *sp*² hybridized, because each has three σ bonds and one π bond.



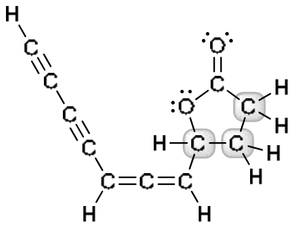
(d) Each of the two central carbon atoms has two σ bonds and two π bonds, and as such, each of these carbon atoms is *sp* hybridized. The other two carbon atoms (the outer ones) are sp^2 hybridized because each has three σ bonds and one π bond.



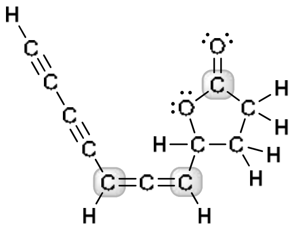
(e) One of the carbon atoms (the one connected to oxygen) has two σ bonds and two π bonds, and as such, it is *sp* hybridized. The other carbon atom is sp^2 hybridized because it has three σ bonds and one π bond.



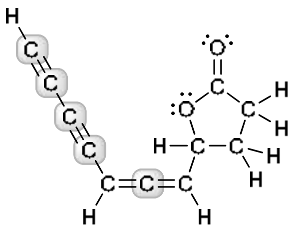
1.22. Each of the following three highlighted carbon atoms has four σ bonds, and is therefore sp^3 hybridized:



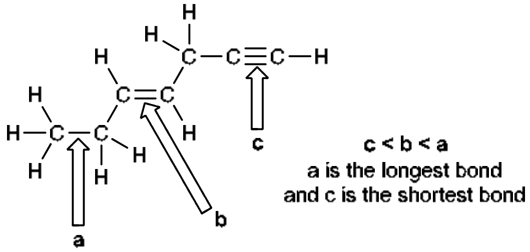
And each of the following three highlighted carbon atoms has three σ bonds and one π bond, and is therefore sp^2 hybridized:



Finally, each of the following five highlighted carbon atoms has two σ bonds and two π bonds, and is therefore *sp* hybridized.



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

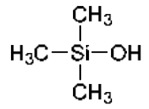


1.24.
(a) In this structure, the boron atom has four σ bonds and no lone pairs, giving a total of four electron pairs (steric number = 4). VSEPR theory therefore predicts a tetrahedral arrangement of electron pairs. Since all of the electron pairs are bonds, the structure is expected to have tetrahedral geometry.
(b) In this structure, the boron atom has three σ bonds and no lone pairs, giving a total of three electron pairs (steric number = 3). VSEPR theory therefore predicts a trigonal planar geometry.
(c) In this structure, the nitrogen atom has four σ sigma bonds and no lone pairs, giving a total of four electron pairs (steric number = 4). VSEPR theory therefore predicts a tetrahedral arrangement of electron pairs. Since all of the electron pairs are bonds, the structure is expected to have tetrahedral geometry.
(d) The carbon atom has four σ bonds and no lone pairs, giving a total of four electron pairs (steric number = 4). VSEPR theory therefore predicts a tetrahedral arrangement of electron pairs. Since all of the electron pairs are bonds, the structure is expected to have tetrahedral geometry.

1.25. In the carbocation, the carbon atom has three bonds and no lone pairs. Since there are a total of three electron pairs (steric number = 3), and all three are bonds, VSEPR theory predicts trigonal planar geometry, with bond angles of 120°. In contrast, the carbon atom of the carbanion has three bonds and one lone pair, giving a total of four electron pairs (steric number = 4). For this ion, VSEPR theory predicts a tetrahedral arrangement of electron pairs, with a lone pair positioned at one corner of the tetrahedron, giving rise to trigonal pyramidal geometry with bond angles approximately 107°.

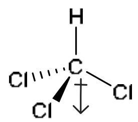
1.26. In ammonia, the nitrogen atom has three bonds and one lone pair. Therefore, VSEPR theory predicts trigonal pyramidal geometry, with bond angles of approximately 107°. In the ammonium ion, the nitrogen atom has four bonds and no lone pairs, so VSEPR theory predicts tetrahedral geometry, with bond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

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

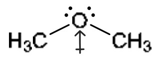


1.28.

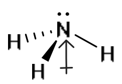
(a) This compound has three C–Cl bonds, each of which exhibits a dipole moment. To determine if these dipole moments cancel each other, we must identify the molecular geometry. The central carbon atom has four σ bonds so we expect tetrahedral geometry. As such, the three polar C–Cl bonds do not lie in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



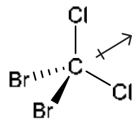
(b) The oxygen atom has two σ bonds and two lone pairs (steric number = 4), and VSEPR theory predicts bent geometry. As such, the dipole moments associated with the polar C–O bonds do not fully cancel each other, and the dipole moments associated with the lone pairs also do not fully cancel each other.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



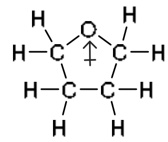
(c) The nitrogen atom has three σ bonds and one lone pair (steric number = 4), and VSEPR theory predicts trigonal pyramidal geometry (because one corner of the tetrahedron is occupied by a lone pair). As such, the dipole moments associated with the polar N–H bonds do not fully cancel each other, and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



(d) The central carbon atom has four σ bonds (steric number = 4), and VSEPR theory predicts tetrahedral geometry. There are individual dipole moments associated with each of the C–Cl bonds and each of the C–Br bonds. If all four dipole moments had the same magnitude, then we would expect them to completely cancel each other to give no molecular dipole moment (as in the case of CCl_4). However, because Cl is more electronegative than Br, each C–Cl bond is more polar than each C–Br bond. Therefore, 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:

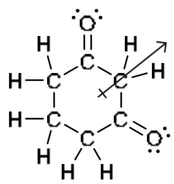


(e) The oxygen atom has two σ bonds and two lone pairs (steric number = 4), and VSEPR theory predicts bent geometry. As such, the dipole moments associated with the polar C–O bonds do not fully cancel each other, and the dipole moments associated with the lone pairs also do not fully cancel each other.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



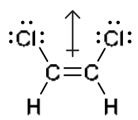
(f) There are individual dipole moments associated with each polar C–O bond and the lone pairs (as in the previous solution), but due to the symmetrical shape of the molecule in this case, they fully cancel each other to give no net molecular dipole moment.

(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 the polar bonds 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