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2nd Edition

Organic Chemistry I

WORKBOOK

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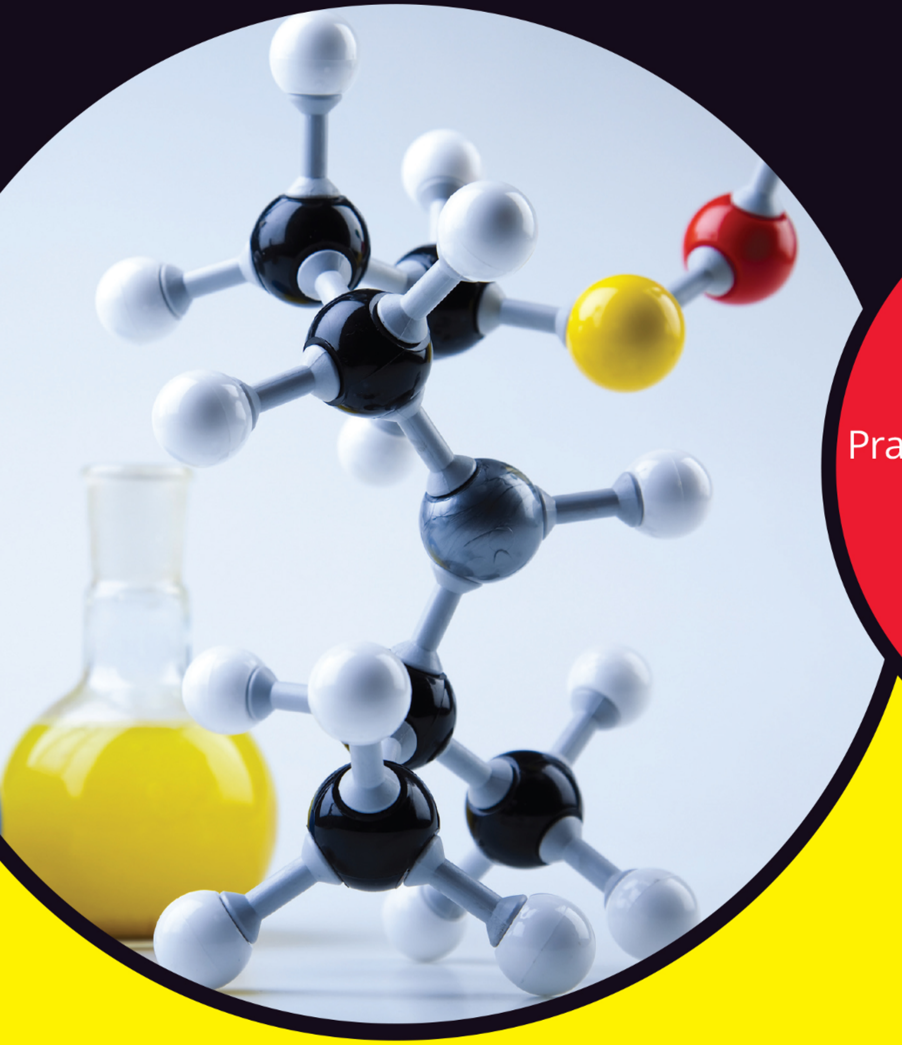

Review key organic chemistry concepts

Practice solving organic chemistry problems and structures

Get complete answer explanations

Arthur Winter, PhD

Chemistry Professor

Organic Chemistry I Workbook

2nd Edition

by Arthur Winter, PhD

for dummies®
A Wiley Brand

Organic Chemistry I Workbook For Dummies,® 2nd Edition

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Contents at a Glance

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Introduction

Organic chemistry is a subject that blends basic chemistry, logic problems, 3-D puzzles, and stick-figure art that looks like something out of a prehistoric cave. If you thirst for knowledge, taking organic chemistry will feel like drinking from a firehose.

Indeed, I've heard some students complain that the weight of their organic chemistry textbook is comparable to that of a small elephant. Rest assured, though, that these complaints represent shameless exaggerations: I have yet to find an ochem text that weighs even two-thirds as much.

Nevertheless, organic chemistry does cover so much material that you can't possibly hope to memorize it all. But good news! You don't need to memorize the vast majority of the material if you understand the basic concepts at a fundamental level, and indeed, memorization beyond the basic rules and conventions is even frowned upon. The catch is that to really understand the concepts, you have to practice at it by working problems. Lots of problems. Lots. Did I mention the whole working problems thing? Mastering organic chemistry without working problems is impossible — kind of like trying to become a chef by reading recipes and never practicing chopping up veggies.

This workbook is for getting hands-on experience. Organic chemistry exams are a lot like a gunfight. You act with discipline only if you've drilled the material. Classmates who haven't worked the problems will see the problems gunning at them on an exam and spook. They'll come down with a bad case of exam-block, let their nerves get the better of them, and get blown to smithereens. You, on the other hand, having been to boot camp and practiced by drilling the problems, will stare the exam down like you were Wyatt Earp or Annie Oakley. When the smoke clears, you'll emerge without a nick, and it'll be the exam that's carted away on a stretcher.

About This Book

Ideally, you should use this book in conjunction with some other reference book, such as a good introductory organic textbook or *Organic Chemistry I For Dummies*. This book doesn't cover the material in great detail; for each section, I give a brief overview of the topic followed by problems that apply the material.

The organization of this book follows the *For Dummies* text, which in turn is organized to follow most organic texts fairly closely. The basic layout of this workbook is to give you straightforward problems for each section to really drill the concepts and build your confidence — before spicing things up with a mischievous humdinger or two at the end of each section to make you don the old thinking cap.

For added convenience, the book is modular, meaning you can jump around to different chapters without having to have read or worked problems in other chapters. If you need to know some other concepts to get you up to speed, just follow the cross-references.

As with all *For Dummies* books, I try to write the answers in a simple conversational style, just as if you and I were having a one-on-one tutoring session, coffee in hand. Here are some other conventions I follow concerning the problems:

- At the beginning of each section, I present one or two example problems to show you the thought process involved in working that problem type before you take a stab at similar problems. You can refer back to the example while you're working the other problems in that section if you get stuck.
- Short answers appear in bold in the Answer Key, followed by a detailed breakdown of how I solved each problem. This includes my personal thought process of how to solve a particular problem type, such as where to start and how to proceed. Although other thought processes may lead to the same answer, my explanation can at least give you a guide for problems on which you get stuck.
- Sometimes, I discuss common mistakes that people make with a certain problem type. My basic philosophy is that I'd rather over-explain than give too little explanation.
- In naming molecules, I use official nomenclature of the International Union of Pure and Applied Chemistry (IUPAC).

Foolish Assumptions

When writing this book, I made a few general assumptions about you, the reader. You probably meet at least one of these assumptions:

- You have a background in general chemistry, and ideally, you've taken a one- or two-semester course in introductory chemistry.
- You're in the midst of or are getting ready to enter your organic chemistry I class in college, and you need some extra help practicing the concepts.
- You took organic chemistry a few years ago, and you want to review what you know.

No matter where you stand, this book provides multiple chances to practice organic chemistry problems in an easy-to-understand (and dare I say fun) way.

Icons Used in This Book

This book uses icons to direct you to important information. Here's your key to these icons:

TIP

The Tip icon highlights information that can save you time and cut down on the frustration factor.

REMEMBER

This symbol points out especially important concepts that you need to keep in mind as you work problems.

WARNING

The Warning icon helps you steer clear of organic chemistry pitfalls.

EXAMPLE

This icon directs you to the examples at the beginning of each set of problems.

Beyond the Book

In addition to what you're reading right now, this book comes with a free access-anywhere Cheat Sheet that includes handy information on the basics of organic chemistry and the periodic table of elements. To get this Cheat Sheet, simply go to `www.dummies.com` and type **Organic Chemistry I Workbook For Dummies Cheat Sheet** in the Search box.

Where to Go from Here

Organic chemistry builds on the concepts you picked up in general chemistry, so I strongly suggest starting with Chapter 1. I know, I know, you've already taken a class in introductory chemistry and have stuffed yourself silly with all that basic general-chemistry goodness — and that's all in the past, man, and you're now looking to move on to bigger and better things. However, winter breaks and days spent at the beach during summer vacations have a cruel tendency to swish the eraser around the old bean, particularly across the places that contain your vast, vast stores of chemistry knowledge. That's why I suggest you start with Chapter 1 for a quick refresher and that you at least breeze through the rest of Part 1. In a sense, Part 1 is the most important part of the book, because if you can get the hang of drawing structures and interpreting what they mean, you've reached the first major milestone. Getting versed in these fundamental skills can keep you out of organic purgatory.

Of course, this book is designed to be modular, so you're free to jump to whatever section you're having trouble with, without having to have done the problems in a previous chapter as reference. Feel free to flip through the Table of Contents or the Index to find the topic that most interests you.

1

The Fundamentals of Organic Chemistry

IN THIS PART . . .

You discover the words of the organic chemist — chemical structures. You start with drawing structures using the various drawing conventions and then see how you can assign charges, draw lone pairs, and predict the geometries around any atom in an organic molecule. With these basic tools under your belt, you get to resonance structures, which are patches chemists use to fix a few leaks in the Lewis structures of certain molecules. You also get to acid and base chemistry, the simplest organic reactions, and begin your mastery of depicting how reactions occur by drawing arrows to indicate the movement of electrons in a reaction.

IN THIS CHAPTER

- Diagramming Lewis structures
- Predicting bond dipoles and dipole moments of molecules
- Seeing atom hybridizations and geometries
- Discovering orbital diagrams

Chapter 1

Working with Models and Molecules

Organic chemists use models to describe molecules because atoms are tiny creatures with some very unusual behaviors, and models are a convenient way to describe on paper how the atoms in a molecule are bonded to each other, and where the electrons in an atom are located. Models are also convenient for helping you understand how reactions occur.

In this chapter, you use the Lewis structure, the most commonly used model for representing molecules in organic chemistry. You also practice applying the concept of atom hybridizations to construct orbital diagrams of molecules, explaining where electrons are distributed in simple organic structures. Along the way, you see how to determine dipoles for bonds and for molecules — an extremely useful tool for predicting solubility and reactivity of organic molecules.

Constructing Lewis Structures

The *Lewis structure* is the basic word of the organic chemist; these structures show which atoms in a molecule are bonded to each other and also show how many electrons are shared in each bond. You need to become a whiz at working with these structures so you can begin speaking the language of organic chemistry.

To draw a Lewis structure, follow four basic steps:

REMEMBER

1. **Determine the connectivity of the atoms in the molecule.**

   Figure out how the atoms are attached to each other. Here are some guidelines:

   - In general, the central atom in the molecule is the least electronegative element. (Electronegativity decreases as you go down and to the left on the periodic table.)
   - Hydrogen atoms and halide atoms (such as F, Cl, Br, and I) are almost always peripheral atoms (not the central atom) because these atoms usually form only one bond.

2. **Determine the total number of valence electrons (electrons in the outermost shell).**

   Add the valence electrons for each of the individual atoms in the molecule to obtain the total number of valence electrons in the molecule. If the molecule is charged, add one electron to this total for each negative charge or subtract one electron for each positive charge.

3. **Add the valence electrons to the molecule.**

   Follow these guidelines:

   - Start adding the electrons by making a bond between the central atom and each peripheral atom; subtract two valence electrons from your total for each bond you form.
   - Assign the remaining electrons by giving lone pairs of electrons to the peripheral atoms until each peripheral atom has a filled octet of electrons.
   - If electrons are left over after filling the octets of all peripheral atoms, then assign them to the central atom.

4. **Attempt to fill each atom's octet.**

   If you've completed Step 3 and the central atom doesn't have a full octet of electrons, you can share the electrons from one or more of the peripheral atoms with the central atom by forming double or triple bonds.

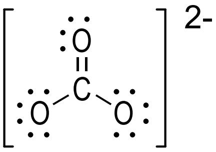
WARNING

You can't break the octet rule for second-row atoms; in other words, the sum of the bonds plus lone pairs around a second-row atom (like carbon) can't exceed four.

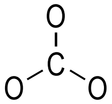
EXAMPLE

Q. Draw the Lewis structure of CO_3^{2-}.

A.

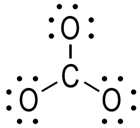


Most often, the *least* electronegative atom is the central atom. In this case, carbon is less electronegative than oxygen, so carbon is the central atom and the connectivity is the following:

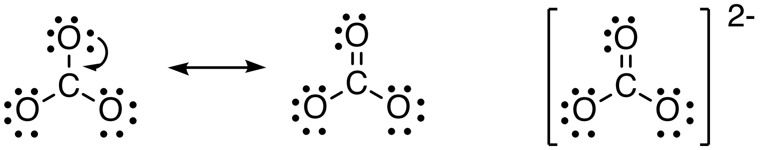


Carbon has four valence electrons because it's an atom in the fourth column of the periodic table, and oxygen has six valence electrons because it's in the sixth column. Therefore, the total number of valence electrons in the molecule is 4 + 6(3) + 2 = 24 valence electrons. You add the additional two electrons because the molecule has a charge of −2 (if the molecule were to have a charge of −3, you'd add three electrons; if −4, you'd add four; and so forth).

Start by forming a bond between the central carbon atom and each of the three peripheral oxygen atoms. This accounts for six of the electrons (two per bond). Then assign the remaining 18 electrons to the oxygens as lone pairs until their octets are filled. This gives you the following configuration:



The result of the preceding step leaves all the oxygen atoms happy because they each have a full octet of electrons, but the central carbon atom remains unsatisfied because this atom is still two electrons short of completing its octet. To remedy this situation, you move a lone pair from one of the oxygens toward the carbon to form a carbon-oxygen double bond. Because the oxygens are identical, which oxygen you take the lone pair from doesn't matter. In the final structure, the charge is also shown:



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① Draw the Lewis structure of BF4−.

2 Draw the Lewis structure of H_2CO.

3 Draw the Lewis structure of NO_2^-.

Predicting Bond Types

Bonds can form between a number of different atoms in organic molecules, but chemists like to broadly classify these bonds so they can get a rough feel for the reactivity of that bond. These bond types represent the extremes in bonding.

In chemistry, a bond is typically classified as one of three types:

- **Purely covalent:** The bonding electrons are shared equally between the two bonding atoms.
- **Polar covalent:** The electrons are shared between the two bonding atoms, but unequally, with the electrons spending more time around the more electronegative atom.
- **Ionic:** The electrons aren't shared. Instead, the more electronegative atom of the two bonding atoms selfishly grabs the two electrons for itself, giving this more electronegative atom a formally negative charge and leaving the other atom with a formal positive charge. The bond in an ionic bond is an attraction of opposite charges.

REMEMBER

You can often determine whether a bond is ionic or covalent by looking at the difference in electronegativity between the two atoms. The general rules are as follows:

- If the electronegativity difference between the two atoms is 0.0, the bond is purely covalent.
- If the electronegativity difference is between 0.0 and 2.0, the bond is considered polar covalent.
- If the electronegativity difference is greater than 2.0, the bond is considered ionic.

WARNING

Ionic and covalent bonding are extreme ends of a continuum of possibilities for how much the electrons are shared, so these numbers are just guidelines (some texts even give slightly different numbers as the cutoffs between covalent and ionic). For example, there is not a huge difference in the bonding situation arising between atoms having an electronegativity difference of 1.9 or between atoms having an electronegativity difference of 2.0, even though the first bond would be classified as polar covalent and the second one ionic. The bond with a 1.9 electronegativity difference would just have slightly more shared bonding electrons than the bond with a 2.0 difference, but in both cases the electrons would spend most of their time around the more electronegative element.

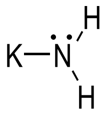
Figure 1-1 shows the electronegativity values.

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0					Br 2.8
						I 2.5

FIGURE 1-1: Electronegativity values for common atoms.

EXAMPLE

Q. Using the following figure, classify the bonds in potassium amide as purely covalent, polar covalent, or ionic.

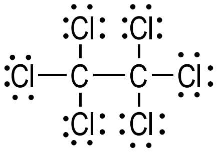


potassium amide

A. **You classify the N-H bonds as polar covalent and the N-K bond as ionic.** To determine the bond type, take the electronegativity difference between the two atoms in each bond. For the nitrogen-potassium (N-K) bond, the electronegativity value is 3.0 for nitrogen and 0.8 for potassium, giving an electronegativity difference of 2.2. Therefore, this bond is considered ionic. For the N-H bonds, the nitrogen has an electronegativity value of 3.0 and hydrogen has an electronegativity value of 2.2, so the electronegativity difference is 0.8. Therefore, the N-H bonds are classified as polar covalent.

4 Classify the bond in NaF as purely covalent, polar covalent, or ionic.

5 Using the following figure, classify the bonds in hexachloroethane as purely covalent, polar covalent, or ionic.



hexachloroethane

Determining Bond Dipoles

Most bonds in organic molecules are of the polar covalent variety. Consequently, although the electrons in a polar covalent bond are shared, on average they spend more time around the more electronegative atom of the two bonding atoms. This unequal sharing of the bonding electrons creates a separation of charge in the bond called a *bond dipole.*

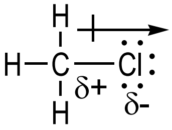
REMEMBER

Bond dipoles are used all the time to predict and explain the reactivity of organic molecules, so you need to understand what they mean and how to show them on paper. You represent this separation of charge on paper with a funny-looking arrow called the *dipole vector.* The head of the dipole vector points in the direction of the partially negatively charged atom (the more electronegative atom) and the tail (which looks like a + sign) points toward the partially positive atom of the bond (the less electronegative atom).

EXAMPLE

Q. Show the bond dipole of the C-Cl bond in CH_3Cl using the dipole vector.

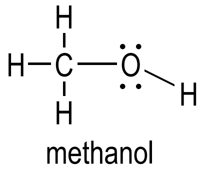
A.



Chlorine is more electronegative than carbon, so in this bond, the bonding electrons spend more time around chlorine than around carbon. Therefore, the chlorine holds a partial negative charge (the symbol δ indicates a partial charge), and the carbon holds a partial positive charge. To draw the dipole vector, the head of the vector points to the atom that has the partial negative charge (the more electronegative atom) — in this case, chlorine — while the tail points to the atom that has a partial positive charge (the less electronegative atom) — in this case, carbon.

6 Show the bond dipoles of the C-O bonds in CO_2 by using the dipole vector. (***Hint:*** Draw the Lewis structure of CO_2 first.)

7 Using the following figure, show the bond dipole of the C-O bond and the O-H bond in methanol by using the dipole vector.



Determining Dipole Moments for Molecules

The sum of all the bond dipoles on a molecule is referred to as the molecule's *dipole moment.* Molecule dipole moments are useful in predicting the solubility of organic molecules. For example, by using dipole moments, you can predict that oil and water won't mix and will be insoluble in each other, whereas water and alcohol will mix. Solubilities are important for practical organic chemistry because it's hard to get a reaction between two molecules that don't dissolve in the same solvent.

To determine the dipole moment of a molecule, follow these steps:

1. **Draw the bond dipole vector for each of the bonds in the molecule.**

   Draw a bigger dipole vector for bonds containing a larger difference in electronegativity between the bonded atoms than for bonds containing a smaller difference of electronegativities.

2. **Add the individual bond dipole vectors using mathematical vector addition to obtain the molecule's overall dipole moment.**

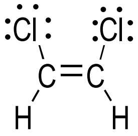
   A simple method to add vectors is to line them up head to tail and then draw a new vector that connects the tail of the first vector with the head of the second one.

REMEMBER

You can generally ignore contributions to the molecular dipole moment from C-H bonds because the electronegativity difference between carbon and hydrogen is so small that the C-H bond dipoles don't contribute in any significant way to the overall molecule dipole moment.

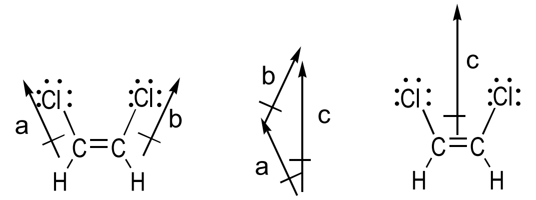
EXAMPLE

Q. Using the following figure, determine the dipole moment of *cis*-1,2-dichloroethene.



cis-1,2-dichloroethene

A.



individual bond dipoles vector addition molecular dipole

First draw the bond dipoles for each of the C-Cl bonds. You can ignore the bond dipoles from the other bonds in the molecule because C-H bonds have such small bond dipoles that you can ignore them and because C-C bonds have no bond dipole. After you draw the two C-Cl bond dipoles (labeled *a* and *b*), you add the vectors to give a third vector (labeled *c*). This new vector *(c)* is the molecule's overall dipole moment vector.

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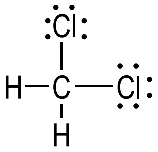
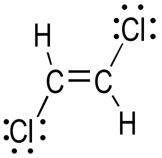
8 Determine the dipole moment of dichloromethane, CH_2Cl_2, shown here. For this problem, pretend that the molecule is flat as drawn.



9 Determine the dipole moment of *trans*-1,2-dichloroethene shown here.



trans-1,2-dichloroethene

Predicting Atom Hybridizations and Geometries

Organic molecules often have atoms stretched out into three-dimensional (3-D) space. Organic chemists care about how a molecule arranges itself in 3-D space because the geometry of a molecule often influences the molecule's physical properties (such as melting point, boiling point, and so on) and its reactivity. The 3-D shape of molecules also plays a large role in a molecule's biological activity, which is important if you want to make a drug, for example. To predict the geometry around an atom, you first need to determine the hybridization of that atom.

REMEMBER

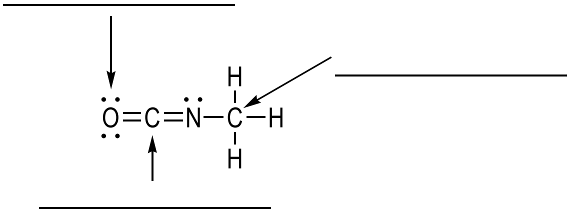
You can often predict the *hybridization* of an atom simply by counting the number of atoms to which that atom is bonded (plus the number of lone pairs on that atom). Table 1-1 breaks down this information for you.

Table 1-1 The Hybridization of an Atom

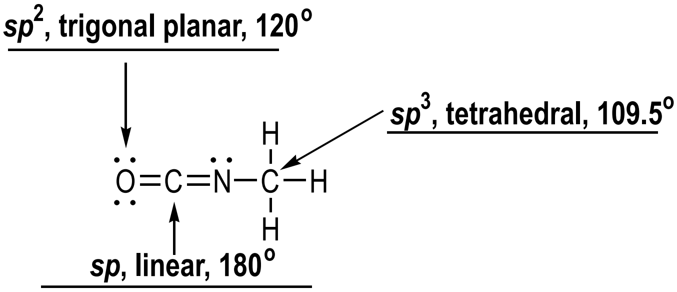
Number of Attached Atoms Plus Lone Pairs	Hybridization	Geometry	Approximate Angle
2	sp	Linear	180°
3	sp^2	Trigonal planar	120°
4	sp^3	Tetrahedral	109.5°

EXAMPLE

Q. Predict the hybridizations, geometries, and bond angles for each of the atoms where indicated in the shown molecule.



A.



The oxygen has three attachments from the adjacent carbon plus the two lone pairs, making this atom sp^2 hybridized. Atoms that are sp^2-hybridized have a trigonal planar geometry and bond angles of 120° separating the three attachments. ***Note:*** Don't take the oxygen's double bond into account; rather, simply count the number of attached atoms plus lone pairs. The carbon has two attachments and so is *sp* hybridized with a linear geometry and 180° bond angles between the attachments. And the right-most carbon, with four attachments, is sp^3 hybridized with a tetrahedral arrangement between the four attachments and bond angles of 109.5°.

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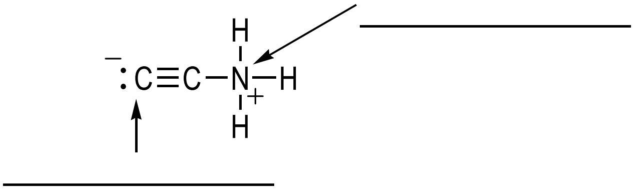
10 Predict the hybridizations, geometries, and bond angles for each of the atoms where indicated in the shown molecule.



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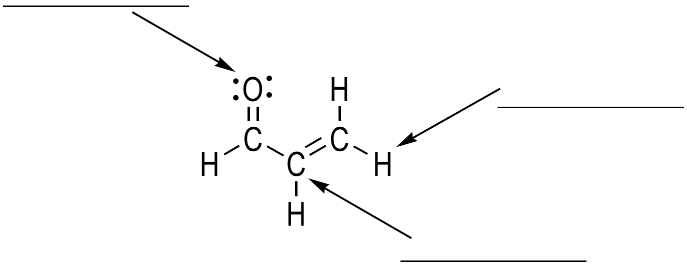
11 Predict the hybridizations, geometries, and bond angles for each of the atoms where indicated in the shown molecule.



Making Orbital Diagrams

An *orbital diagram* expands on a Lewis structure (check out the "Constructing Lewis Structures" section earlier in this chapter) by explicitly showing which orbitals on atoms overlap to form the bonds in a molecule. In order for a covalent bond to form, an atomic orbital on one atom must overlap in space with an atomic orbital on a second atom. This orbital overlap can be thought of as the quantum mechanical mechanism by which electrons are shared. Generally speaking, the more orbital overlap there is, the stronger the bond will be (and if there's no orbital overlap there is no covalent bond at all).

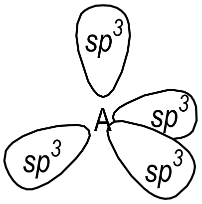
Organic chemists use such orbital diagrams extensively to explain the reactivity of certain bonds in a molecule, and the diagrams also do a better job than Lewis structures of showing exactly where electrons are distributed in a molecule. Follow these three steps to draw an orbital diagram:

1. **Determine the hybridization for each atom in the molecule.**

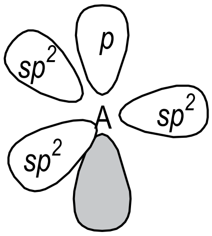
   Check out the preceding section for help on this step.

2. **Draw all the valence orbitals for each atom.**

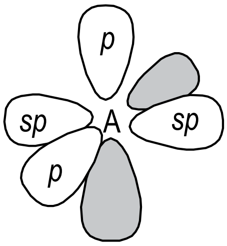
   Sp^3-hybridized atoms have four valence sp^3 orbitals; sp^2-hybridized atoms have three sp^2-hybridized orbitals and one *p* orbital; and *sp*-hybridized atoms have two *sp*-hybridized orbitals and two *p* orbitals. You may find the following templates helpful for constructing your orbital diagrams (where A represents the hybridized atom):



sp^3-hybridized



sp^2-hybridized



sp-hybridized

3. **Determine which orbitals overlap to form bonds.**

REMEMBER

   Single bonds are always *sigma bonds* — bonds that form from the overlapping of orbitals between the two nuclei of the bonding atoms. A double bond, on the other hand, consists of one sigma bond and one pi bond. A *pi bond* is formed from the side-by-side overlapping of two *p* orbitals above and below the nuclei of the two bonding atoms. A triple bond consists of two pi bonds and one sigma bond.

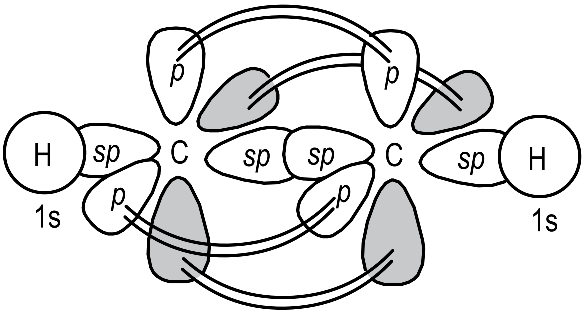
EXAMPLE

Q. Referring to the following figure, draw the orbital diagram of acetylene.

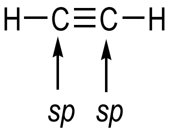
$H-C\equiv C-H$

acetylene

A.

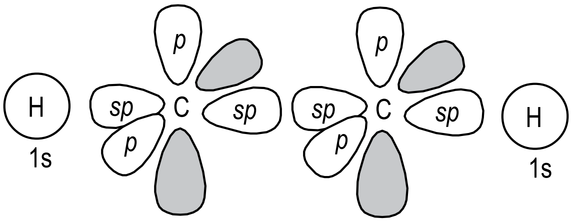


This problem is daunting, but you can tackle it step by step. The first thing to do is determine the hybridizations for all the atoms. The two carbons are *sp* hybridized because each atom is attached to two other atoms (see Table 1-1). The hydrogens, having only one electron, remain unhybridized (hydrogen is the only atom that doesn't rehybridize in organic molecules):



$$H-\underset{\overset{\uparrow}{sp}}{C}\equiv\underset{\overset{\uparrow}{sp}}{C}-H$$

Next, draw the valence orbitals as shown here. Hydrogen has only the 1*s* orbital, and you can use the earlier template for *sp*-hybridized atoms for each of the carbons.

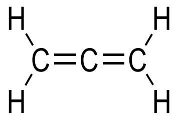


Next, you need to figure out which orbitals overlap to give rise to the bonds in acetylene. The C-H bonds form from overlap of the hydrogen 1s orbitals with the sp orbitals on carbon. Triple bonds consist of two pi bonds and one sigma bond. The one sigma bond comes from overlap of the two carbon sp orbitals. The two pi bonds come from overlap of the two p orbitals on each carbon, giving you the final answer shown earlier.

12 Draw the orbital diagram for methane, CH_4.

13 Draw the orbital diagram of formaldehyde, H_2CO. (***Hint:*** Draw the full Lewis structure first.)

14 Use the following figure to draw the orbital diagram for allene (very challenging).

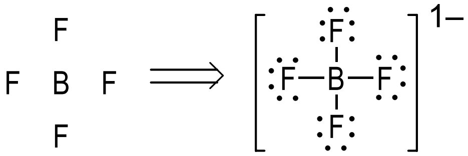


allene

Answer Key

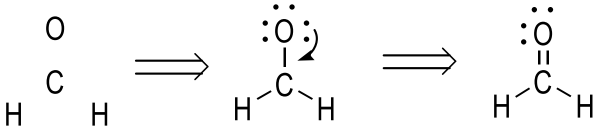
The following are the answers to the practice questions presented in this chapter.

①



Boron is the central atom because it's less electronegative than fluorine (and in any case, halogens such as F almost never form more than one single bond). Boron has three valence electrons, fluorine has seven, and the charge on the molecule is −1, so the total number of valence electrons in this molecule is 3 + 7(4) + 1= 32. Adding single bonds from boron to each of the four fluorines (for a total of eight electrons, two per bond) and adding the remaining 24 electrons to the fluorines as lone pairs gives the Lewis structure shown. Each atom is happy because it has a full octet of electrons, so there's no need to make multiple bonds.

②

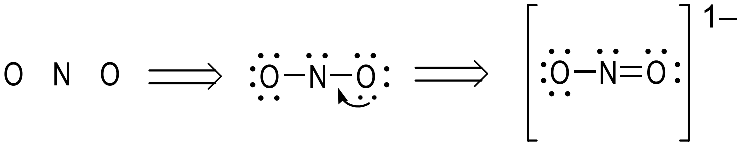


Carbon is the central atom because it's less electronegative than oxygen. A hydrogen can never be the central atom because hydrogens don't form more than one bond.

Hydrogen has one valence electron, carbon has four valence electrons, and oxygen has six valence electrons, so the total number of valence electrons is 2(1) + 4 + 6 = 12.

Adding a single bond from carbon to each of the two hydrogens and a single bond to the oxygen and peppering the remaining lone pairs onto the oxygen gives you the structure in the middle. Although oxygen is happy because it has a full octet of electrons, carbon isn't faring as well because it's two electrons short of its octet. Therefore, you push down one of the lone pairs from oxygen to form a double bond from oxygen to carbon. After that move is complete, all the atoms are happy because each atom has a full octet of electrons. ***Note:*** You can't give any lone pairs to hydrogen because with one bond already, hydrogen has satisfied its valence shell with two electrons (recall that the first shell holds only two electrons, and then it's eight in the second shell).

③



Nitrogen is the central atom in NO_2^- because nitrogen is less electronegative than oxygen.