GLOBAL EDITION

Organic Chemistry

EIGHTH EDITION

Paula Yurkanis Bruice

ALWAYS LEARNING

PEARSON

To the Student

Welcome to the fascinating world of organic chemistry. You are about to embark on an exciting journey. This book has been written with students like you in mind—those who are encountering the subject for the first time. The book's central goal is to make this journey through organic chemistry both stimulating and enjoyable by helping you understand central principles and asking you to apply them as you progress through the pages. You will be reminded about these principles at frequent intervals in references back to sections you have already mastered.

You should start by familiarizing yourself with the book. At the back of the book is information you may want to refer to often during the course. The list of Some Important Things to Remember and the Reaction Summary at each chapter's end provide helpful checklists of the concepts you should understand after studying the chapter. The Glossary at the end of the book can also be a useful study aid, as can the Appendices, which consolidate useful categories of information. The molecular models and electrostatic potential maps that you will find throughout the book are provided to give you an appreciation of what molecules look like in three dimensions and to show how charge is distributed within a molecule. Think of the margin notes as the author's opportunity to inject personal reminders of ideas and facts that are important to remember. Be sure to read them.

Work all the problems *within* each chapter. These are drill problems that you will find at the end of each section that allow you to check whether you have mastered the skills and concepts the particular section is teaching before you go on to the next section. Some of these problems are solved for you in the text. Short answers to some of the others—those marked with a diamond—are provided at the end of the book. Do not overlook the "Problem-Solving Strategies" that are also sprinkled throughout the text; they provide practical suggestions on the best way to approach important types of problems.

In addition to the *within-chapter* problems, work as many *end-of-chapter* problems as you can. The more problems you work, the more comfortable you will be with the subject matter and the better prepared you will be for the material in subsequent chapters. Do not let any problem frustrate you. Be sure to visit www.MasteringChemistry.com, where you can explore study tools including Exercise Sets, an Interactive Molecular Gallery, and Biographical Sketches of historically important chemists, and where you can access content on many important topics.

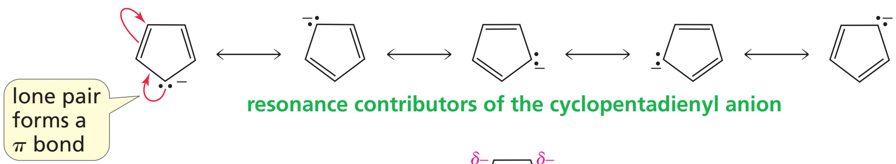
The most important advice to remember (and follow) in studying organic chemistry is DO NOT FALL BEHIND! The individual steps to learning organic chemistry are quite simple; each by itself is relatively easy to master. But they are numerous, and the subject can quickly become overwhelming if you do not keep up.

The key to succeeding in this course is paying attention to unifying principles. Before many of the theories and mechanisms were figured out, organic chemistry was a discipline that could be mastered only through memorization. Fortunately, that is no longer true. You will find many unifying principles that allow you to use what you have learned in one situation to predict what will happen in other situations. So, as you read the book and study your notes, always make sure that you understand *why* each chemical event or behavior happens. For example, when the reasons behind reactivity are understood, most reactions can be predicted. Approaching the course with the misconception that to succeed you must memorize hundreds of unrelated reactions could be your downfall. There is simply too much material to memorize. Understanding and reasoning, not memorization, provide the necessary foundation on which to lay subsequent learning. Nevertheless, from time to time some memorization will be required: some fundamental rules will have to be memorized, and you will need to learn the common names of a number of organic compounds. But that should not be a problem; after all, your friends have common names that you have been able to learn and remember.

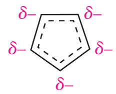
Students who study organic chemistry to gain entrance into medical school sometimes wonder why medical schools pay so much attention to this topic. The importance of organic chemistry is not in the subject matter alone, however. Mastering organic chemistry requires a thorough understanding of certain fundamental principles and the ability to use those fundamentals to analyze, classify, and predict. The study of medicine makes similar demands: a physician uses an understanding of certain fundamental principles to analyze, classify, and diagnose.

Good luck in your study. I hope you will enjoy studying organic chemistry and learn to appreciate the logic of this fascinating discipline. If you have any comments about the book or any suggestions for improving it, I would love to hear from you. Remember, positive comments are the most fun, but negative comments are the most useful.

Paula Yurkanis Bruice



resonance contributors of the cyclopentadienyl anion

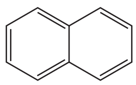


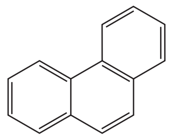
resonance hybrid

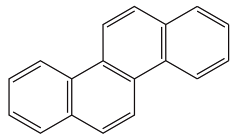
When drawing resonance contributors, remember that only electrons move; atoms never move.

The resonance hybrid shows that all the carbons in the cyclopentadienyl anion are equivalent. Each carbon has exactly one-fifth of the negative charge associated with the anion.

The criteria that determine whether a monocyclic hydrocarbon is aromatic can also be used to determine whether a polycyclic hydrocarbon is aromatic. Naphthalene (five pairs of π electrons), phenanthrene (seven pairs of π electrons), and chrysene (nine pairs of π electrons) are aromatic.


naphthalene


phenanthrene


chrysene

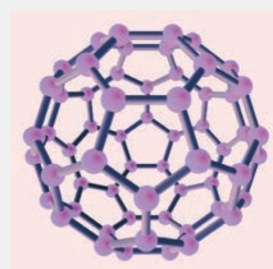
Buckyballs

We saw that diamond, graphite, and graphene are forms of pure carbon (Section 1.8). Another form of pure carbon was discovered unexpectedly in 1985, while scientists were conducting experiments designed to understand how long-chain molecules are formed in outer space. R. E. Smalley, R. F. Curl, Jr., and H. W. Kroto shared the 1996 Nobel Prize in Chemistry for discovering this new form of carbon. They named the substance *buckminsterfullerene* (often shortened to *fullerene*) because its structure reminded them of the geodesic domes popularized by R. Buckminster Fuller, an American architect and philosopher. Buckminsterfullerene's nickname is "buckyball."

Consisting of a hollow cluster of 60 carbons, fullerene is the most symmetrical large molecule known. Like graphite and graphene, fullerene has only sp^2 carbons, but instead of being arranged in layers, the carbons are arranged in rings that fit together like the seams of a soccer ball. Each molecule has 32 interlocking rings (20 hexagons and 12 pentagons). At first glance, fullerene appears to be aromatic because of its benzene-like rings. However, the curvature of the ball prevents the molecule from fulfilling the first criterion for aromaticity—it must be planar. Therefore, fullerene is not aromatic.

Buckyballs have extraordinary chemical and physical properties. For example, they are exceedingly rugged, as shown by their ability to survive the extreme temperatures of outer space. Because they are essentially hollow cages, they can be manipulated to make new materials. For example, when a buckyball is "doped" by inserting potassium or cesium into its cavity, it becomes an excellent organic superconductor. These molecules are now being studied for use in many other applications, including the development of new polymers, catalysts, and drug-delivery systems. The discovery of buckyballs is a strong reminder of the technological advances that can be achieved as a result of basic research.

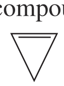

a geodesic dome.


C_{60}
buckminsterfullerene
"buckyball"

PROBLEM 50 ♦

Which compound in each set is aromatic? Explain your choice.

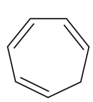
a.

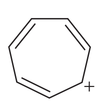

cyclopropene

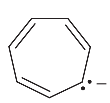

cyclopropenyl cation


cyclopropenyl anion

b.


cycloheptatriene

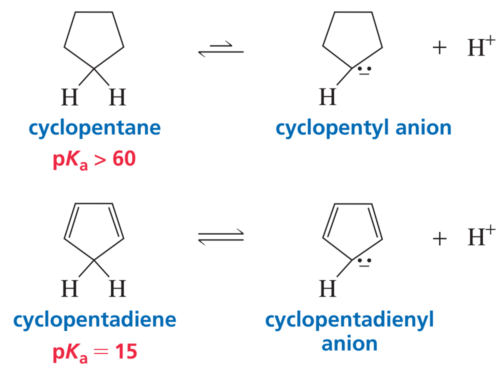

cycloheptatrienyl cation


cycloheptatrienyl anion

LEARN THE STRATEGY

PROBLEM 51 SOLVED

The pK_a of cyclopentane is > 60, which is about what is expected for a hydrogen that is bonded to an sp^3 carbon. Explain why cyclopentadiene is a much stronger acid (pK_a of 15) even though it too involves the loss of a proton from an sp^3 carbon.



SOLUTION To answer this question, we must look at the stabilities of the anions that are formed when the compounds lose a proton. (Recall that the strength of an acid is determined by the stability of its conjugate base: the more stable the base, the stronger its conjugate acid; Section 2.6). All the electrons in the cyclopentyl anion are localized. In contrast, the cyclopentadienyl anion is aromatic. As a result of its aromaticity, the cyclopentadienyl anion is an unusually stable carbanion, causing its conjugate acid to be an unusually strong acid compared to other compounds with hydrogens attached to sp^3 carbons.

USE THE STRATEGY

PROBLEM 52 ♦

a. Predict the relative pK_a values of cyclopentadiene and cycloheptatriene.
b. Predict the relative pK_a values of cyclopropene and cyclopropane.

PROBLEM 53 ♦

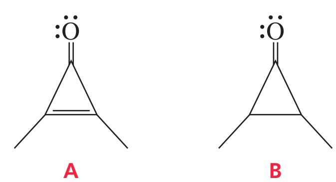
Which is more soluble in water: 3-bromocyclopropene or bromocyclopropane?

PROBLEM-SOLVING STRATEGY

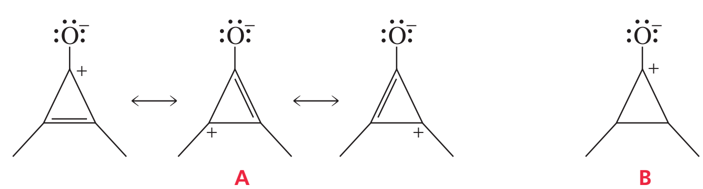
LEARN THE STRATEGY

Analyzing Electron Distribution in Compounds

Which of the following compounds has the greater dipole moment?



The dipole moment of these compounds results from the unequal sharing of electrons by carbon and oxygen. The dipole moment increases as the electron sharing becomes more unequal. So now the question becomes, which compound has a greater negative charge on its oxygen? To find out, we need to draw the structures with a negative charge on oxygen and determine their relative stabilities.

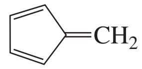


When the π bond is broken in order to put a negative charge on oxygen, we see that **A** has three resonance contributors, all of which are aromatic; **B** has no resonance contributors. Therefore, **A** has a greater concentration of negative charge on its oxygen, which gives **A** a greater dipole moment.

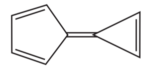
PROBLEM 54

USE THE STRATEGY

a. In what direction is the dipole moment in fulvene? Explain.
b. In what direction is the dipole moment in calicene? Explain.



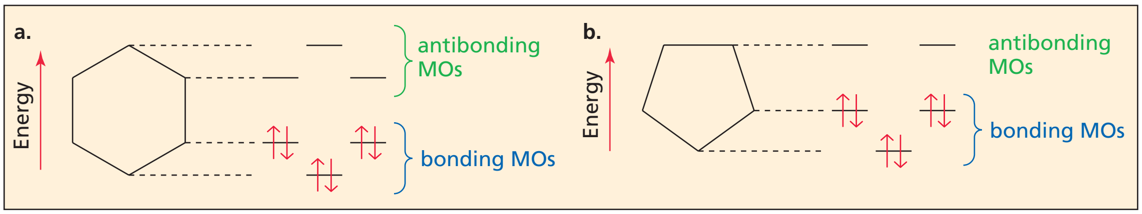
fulvene



calicene

8.19 A MOLECULAR ORBITAL DESCRIPTION OF AROMATICITY

The relative energies of the molecular orbitals of a compound that has a π cloud can be determined—without having to use any math—by drawing the cyclic compound with one of its vertices pointed down. The relative levels of the vertices correspond to the relative energies of the molecular orbitals (Figure 8.17). Notice that the number of molecular orbitals is the same as the number of atoms in the ring because each ring atom contributes a p orbital.



Aromatic compounds are stable because they have filled bonding molecular orbitals.

Figure 8.17
The distribution of electrons in the molecular orbitals of (a) benzene and (b) the cyclopentadienyl anion.

Molecular orbitals below the midpoint of the cyclic structure are bonding molecular orbitals, and those above the midpoint are antibonding molecular orbitals.

The six π electrons of benzene occupy its three bonding molecular orbitals, and the six π electrons of the cyclopentadienyl anion occupy its three bonding molecular orbitals. Notice that there is always an odd number of bonding molecular orbitals because one corresponds to the lowest vertex and the others come in degenerate pairs. Consequently, aromatic compounds—such as benzene and the cyclopentadienyl anion, with their odd number of pairs of π electrons—have completely filled bonding molecular orbitals. This is what gives aromatic molecules their stability.

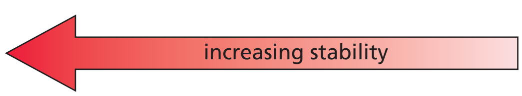
Antiaromatic Compounds

A compound is classified as **antiaromatic** if it fulfills the first criterion for aromaticity but does not fulfill the second. In other words, it must be a planar, cyclic compound with an uninterrupted ring of p orbital-bearing atoms, and the π cloud must contain an *even* number of pairs of π electrons. Because antiaromatic compounds cannot fill their bonding molecular orbitals, they are very unstable and highly reactive compounds. Thus, an aromatic compound is *more stable* than a cyclic compound with localized electrons, whereas an antiaromatic compound is *less stable* than a cyclic compound with localized electrons.

Antiaromatic compounds are very unstable.

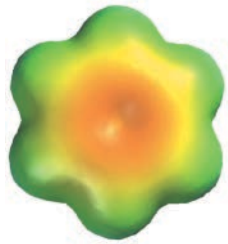
relative stabilities

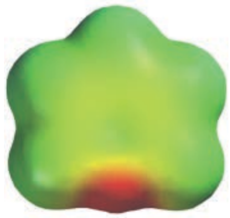
aromatic compound > cyclic compound with localized electrons > antiaromatic compound

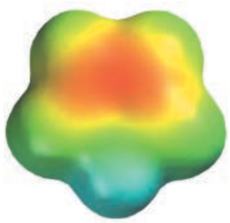


PROBLEM 55

Following the instructions for drawing the energy levels of the molecular orbitals for the compounds shown in Figure 8.17, draw the energy levels of the molecular orbitals for the cycloheptatrienyl cation, the cycloheptatrienyl anion, and the cyclopropenyl cation. For each compound, show the distribution of the π electrons. Which of the compounds are aromatic?


benzene

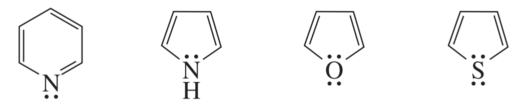

pyridine


pyrrole

8.20 AROMATIC HETEROCYCLIC COMPOUNDS

A compound does not have to be a hydrocarbon to be aromatic. Many *heterocyclic compounds* are aromatic. A **heterocyclic compound** is a cyclic compound in which one or more of the ring atoms is an atom other than carbon. The atom that is not carbon is called a **heteroatom.** The name comes from the Greek word *heteros*, which means "different." The most common heteroatoms encountered in organic compounds are N, O, and S.

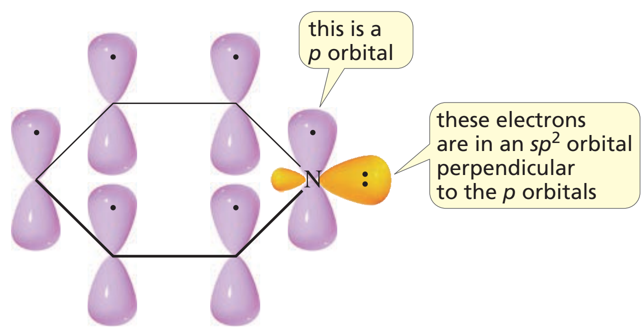
heterocyclic compounds



pyridine pyrrole furan thiophene

Pyridine

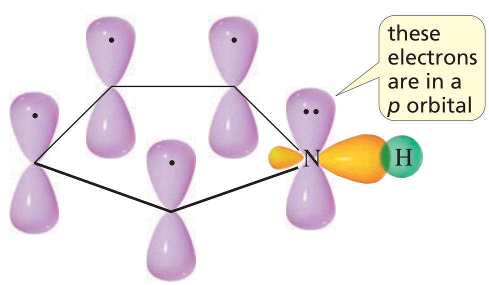
Pyridine is an aromatic heterocyclic compound. Each of the six ring atoms of pyridine is sp^2 hybridized, which means that each has a *p* orbital, and the molecule contains three pairs of π electrons. Do not be confused by the lone-pair electrons on the nitrogen—they are not π electrons. Recall that lone-pair electrons are π electrons only if they can be used to form a π bond in the ring of a resonance contributor (p. 401). Because nitrogen is sp^2 hybridized, it has three sp^2 orbitals and a *p* orbital. The *p* orbital is used to form the π bond. Two of nitrogen's sp^2 orbitals overlap the sp^2 orbitals of adjacent carbons, and its third sp^2 orbital contains the lone pair.



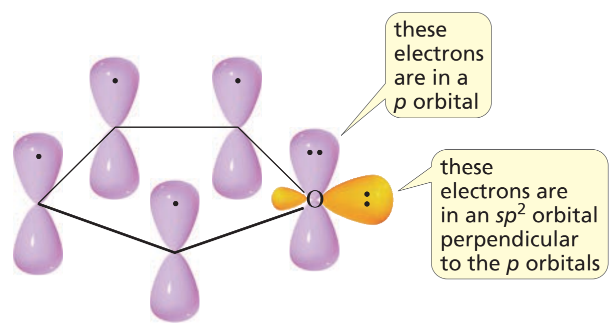
orbital structure of pyridine

Pyrrole, Furan, and Thiophene

The nitrogen atom of pyrrole is sp^2 hybridized. Thus, it has three sp^2 orbitals and a *p* orbital. It uses its three sp^2 orbitals to bond to two carbons and one hydrogen. The lone-pair electrons are in the *p* orbital that overlaps the *p* orbitals of adjacent carbons. Pyrrole, therefore, has three pairs of π electrons and is aromatic.

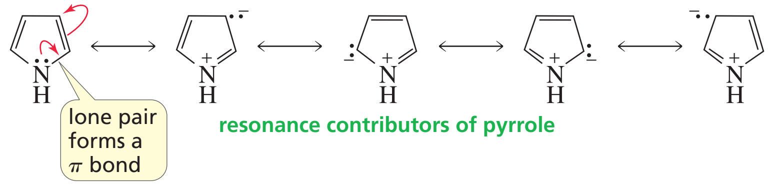


orbital structure of pyrrole



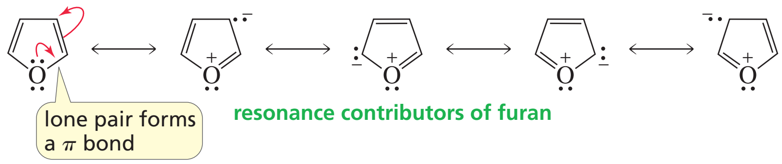
orbital structure of furan

The resonance contributors show that lone-pair electrons of pyrrole form a π bond in the ring of a resonance contributor; thus, they are π electrons.



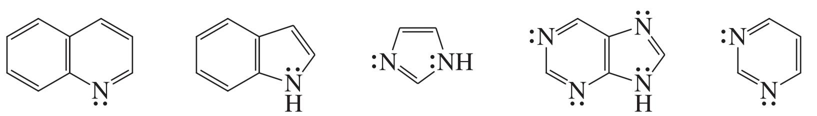
resonance contributors of pyrrole

Similarly, furan and thiophene are aromatic compounds. Both the oxygen in furan and the sulfur in thiophene are sp^2 hybridized and have one lone pair in an sp^2 orbital. The orbital picture of furan on the previous page shows that the second lone pair is in a p orbital that overlaps the p orbitals of adjacent carbons, forming a π bond. Thus, they are π electrons.



resonance contributors of furan

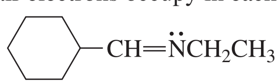
Quinoline, indole, imidazole, purine, and pyrimidine are other examples of heterocyclic aromatic compounds. The heterocyclic compounds discussed in this section will be examined in greater detail in Chapter 19.



quinoline · indole · imidazole · purine · pyrimidine

PROBLEM 56 ♦

What orbital do the lone-pair electrons occupy in each of the following compounds?

a. $CH_3CH_2\ddot{N}H_2$ **b.**  **c.** $CH_3CH_2C{\equiv}N{:}$

PROBLEM 57 ♦

What orbitals contain the electrons represented as lone pairs in the structures of quinoline, indole, imidazole, purine, and pyrimidine?

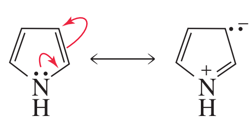
PROBLEM 58 SOLVED

LEARN THE STRATEGY

Which of the following compounds could be protonated without destroying its aromaticity?

SOLUTION Pyridine's lone-pair electrons are sp^2 electrons. They, therefore, are not part of the π cloud (only π electrons are in the π cloud), so they can be protonated without destroying the aromaticity of the pyridine ring.

We know that pyrrole's lone-pair electrons are π electrons because they can be used to form a π bond in a resonance contributor.

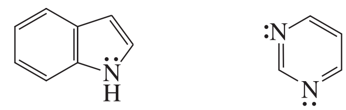


Because pyrrole's lone-pair electrons are one of the three pairs of π electrons in the π cloud, pyrrole's aromaticity is destroyed when it is protonated and, therefore, is no longer part of the π cloud.

USE THE STRATEGY

PROBLEM 59

Which of the following compounds could be protonated without destroying its aromaticity?



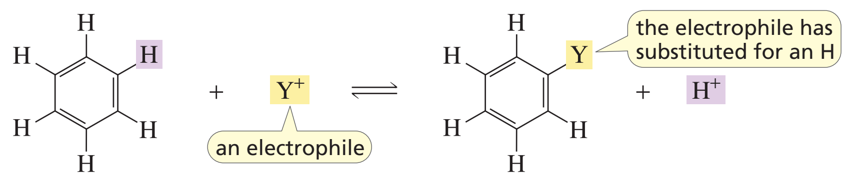
PROBLEM 60

Refer to the electrostatic potential maps on p. 404 to answer the following questions:

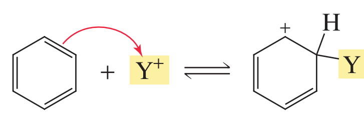
a. Why is the bottom part of the electrostatic potential map of pyrrole blue?
b. Why is the bottom part of the electrostatic potential map of pyridine red?
c. Why is the center of the electrostatic potential map of benzene more red than the center of the electrostatic potential map of pyridine?

8.21 HOW BENZENE REACTS

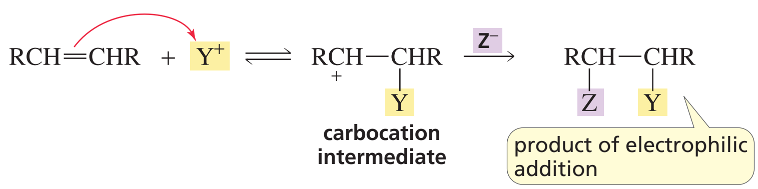
Aromatic compounds such as benzene undergo **electrophilic aromatic substitution reactions:** an electrophile substitutes for one of the hydrogens attached to the benzene ring.



Now let's look at why this substitution reaction occurs. The cloud of π electrons above and below the plane of its ring makes benzene a nucleophile, so it reacts with an electrophile (Y^+). When an electrophile attaches itself to a benzene ring, a carbocation intermediate is formed.



This description should remind you of the first step in an *electrophilic addition reaction* of an alkene: the nucleophilic alkene reacts with an electrophile and forms a carbocation intermediate (Section 6.0). In the second step of the reaction, the carbocation reacts with a nucleophile (Z^-) to form an addition product.



If the carbocation intermediate that is formed when benzene reacts with an electrophile were to react similarly (depicted as path *a* in Figure 8.18), then the *addition product* would not be aromatic. But, if the carbocation instead were to lose a proton from the site of electrophilic addition and form a *substitution product* (depicted as path *b* in Figure 8.18), then the aromaticity of the benzene ring would be restored.

Because the aromatic substitution product is much more stable than the nonaromatic addition product (Figure 8.19), benzene undergoes *electrophilic substitution reactions* that preserve aromaticity, rather than *electrophilic addition reactions*—the reactions characteristic of