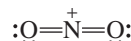


SOLUTION TO 10b The total number of valence electrons is 17 (5 for N and 6 for each of the two O's). Because the species has one positive charge, we must subtract 1 from the number of valence electrons, for a total of 16. The 16 electrons are used to form bonds and fill octets with lone-pair electrons.



Two double bonds are necessary to complete N's octet. The N has a formal charge of +1.



PROBLEM 11

- a. Draw two Lewis structures for $\text{C}_2\text{H}_6\text{O}$. b. Draw three Lewis structures for $\text{C}_3\text{H}_8\text{O}$.

(Hint: The two Lewis structures in part a are **constitutional isomers**; they have the same atoms, but differ in the way the atoms are connected. The three Lewis structures in part b are also constitutional isomers.)

PROBLEM 12

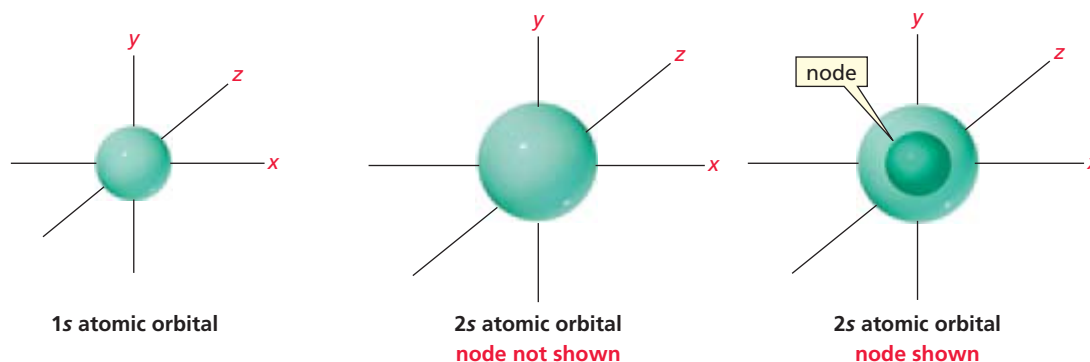
Expand the following condensed structures to show the covalent bonds and lone-pair electrons:

- a. $\text{CH}_3\text{NHCH}_2\text{CH}_3$ c. $(\text{CH}_3)_2\text{CHCHO}$
b. $(\text{CH}_3)_2\text{CHCl}$ d. $(\text{CH}_3)_3\text{C}(\text{CH}_2)_3\text{CH}(\text{CH}_3)_2$

1.5 Atomic Orbitals

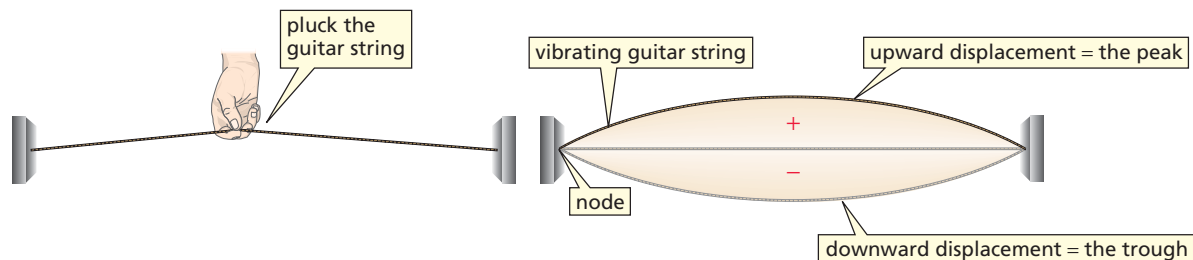
We have seen that electrons are distributed into different atomic orbitals (Table 1.2). An **orbital** is a three-dimensional region around the nucleus where there is a high probability of finding an electron. But what does an orbital look like? Mathematical calculations indicate that the *s* atomic orbital is a sphere with the nucleus at its center, and experimental evidence supports this theory. The **Heisenberg uncertainty principle** states that both the precise location and the momentum of an atomic particle cannot be simultaneously determined. This means that we can never say precisely where an electron is—we can only describe its probable location. Thus, when we say that an electron occupies a 1*s* atomic orbital, we mean that there is a greater than 90% probability that the electron is in the space defined by the sphere.

Because the average distance from the nucleus is greater for an electron in a 2s atomic orbital than for an electron in a 1s atomic orbital, a 2s atomic orbital is represented by a larger sphere. Consequently, the average electron density in a 2s atomic orbital is less than the average electron density in a 1s atomic orbital.



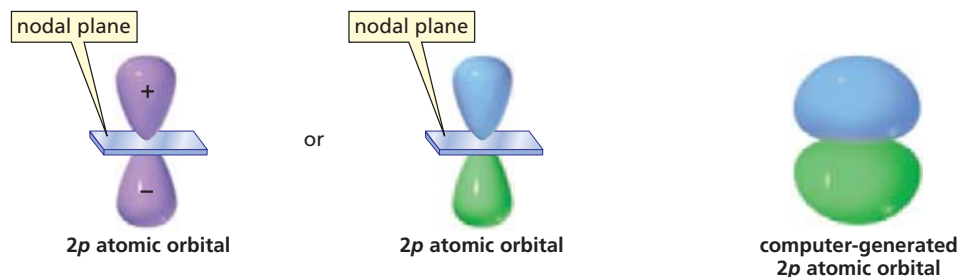
An electron in a $1s$ atomic orbital can be anywhere within the $1s$ sphere, but a $2s$ atomic orbital has a region where the probability of finding an electron falls to zero. This is called a **node**, or, more precisely—since the absence of electron density is at one set distance from nucleus—a **radial node**. So a $2s$ electron can be found anywhere within the $2s$ sphere—including the region of space defined by the $1s$ sphere—except in the node.

To understand why nodes occur, you need to remember that electrons have both particlelike and wavelike properties. A node is a consequence of the wavelike properties of an electron. Consider the following two types of waves: traveling waves and standing waves. Traveling waves move through space; light is an example of a traveling wave. A standing wave, in contrast, is confined to a limited space. A vibrating string of a guitar is an example of a standing wave—the string moves up and down, but does not travel through space. If you were to write a wave equation for the guitar string, the wave function would be (+) in the region above where the guitar string is at rest and (–) in the region below where the guitar string is at rest—the regions are of opposite phase. The region where the guitar string has no transverse displacement is called a *node*. A **node** is the region where a standing wave has an amplitude of zero.



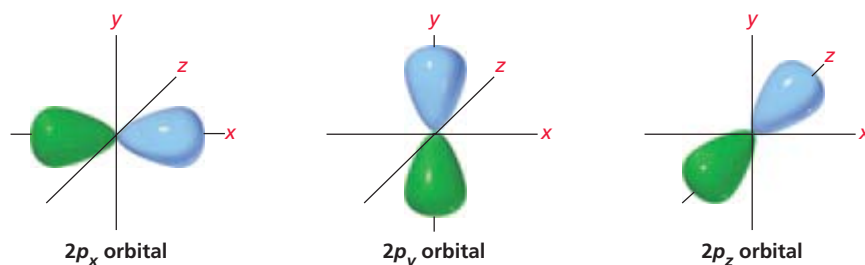
An electron behaves like a standing wave, but—unlike the wave created by a vibrating guitar string—it is three dimensional. This means that the node of a $2s$ atomic orbital is actually a surface—a spherical surface within the $2s$ atomic orbital. Because the electron wave has zero amplitude at the node, there is zero probability of finding an electron at the node.

Unlike s atomic orbitals that resemble spheres, p atomic orbitals have two lobes. Generally, the lobes are depicted as teardrop-shaped, but computer-generated representations reveal that they are shaped more like doorknobs. Like the vibrating guitar string, the lobes are of opposite phase, which can be designated by plus (+) and minus (–) signs or by two different colors. (In this context, + and – do not indicate charge, just the phase of the orbital.) The node of the p atomic orbital is a plane that passes through the center of the nucleus, bisecting its two lobes. This is called a **nodal plane**. There is zero probability of finding an electron in the nodal plane of the p orbital.



In Section 1.2, you saw that there are three degenerate p atomic orbitals. The p_x orbital is symmetrical about the x -axis, the p_y orbital is symmetrical about the y -axis, and the p_z orbital is symmetrical about the z -axis. This means that each p orbital is perpendicular to the other two p orbitals. The energy of a $2p$ atomic orbital is slightly greater than that of a $2s$ atomic orbital because the average location of an electron in a $2p$ atomic orbital is farther away from the nucleus.

Degenerate orbitals are orbitals that have the same energy.





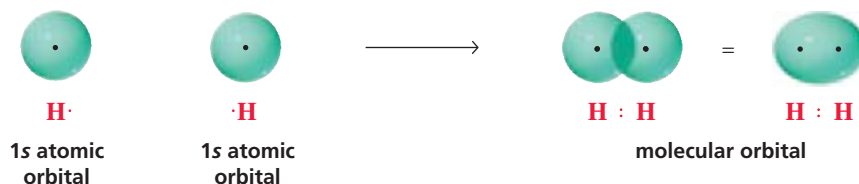
Movie:
H₂ bond formation

1.6 An Introduction to Molecular Orbital Theory

How do atoms form covalent bonds in order to form molecules? The Lewis model, which describes how atoms attain a complete octet by sharing electrons, tells us only part of the story. A drawback of the model is that it treats electrons like particles and does not take into account their wavelike properties.

Molecular orbital (MO) theory combines the tendency of atoms to fill their octets by sharing electrons (the Lewis model) with their wavelike properties—assigning electrons to a volume of space called an orbital. According to MO theory, covalent bonds result from the combination of atomic orbitals to form **molecular orbitals**—orbitals that belong to the whole molecule rather than to a single atom. Like an atomic orbital that describes the volume of space around the nucleus of an atom where an electron is likely to be found, a molecular orbital describes the volume of space around a molecule where an electron is likely to be found. Like atomic orbitals, molecular orbitals have specific sizes, shapes, and energies.

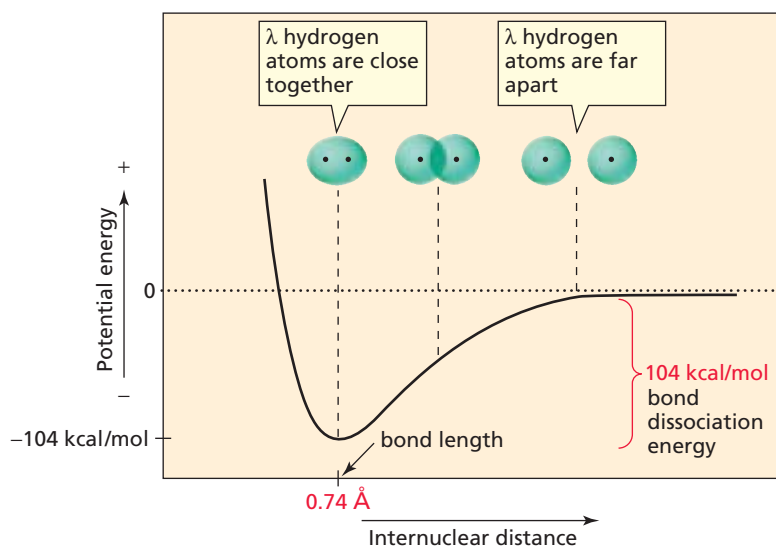
Let's look first at the bonding in a hydrogen molecule (H₂). As the 1s atomic orbital of one hydrogen atom approaches the 1s atomic orbital of a second hydrogen atom, they begin to overlap. As the atomic orbitals move closer together, the amount of overlap increases until the orbitals combine to form a molecular orbital. The covalent bond that is formed when the two s atomic orbitals overlap is called a **sigma (σ) bond**. A σ bond is cylindrically symmetrical—the electrons in the bond are symmetrically distributed about an imaginary line connecting the centers of the two atoms joined by the bond. (The term σ comes from the fact that cylindrically symmetrical molecular orbitals possess σ symmetry.)



During bond formation, energy is released as the two orbitals start to overlap, because the electron in each atom not only is attracted to its own nucleus but also is attracted to the positively charged nucleus of the other atom (Figure 1.2). Thus, the attraction of the negatively charged electrons for the positively charged nuclei is what holds the atoms together. The more the orbitals overlap, the more the energy decreases

Figure 1.2 ►

The change in energy that occurs as two 1s atomic orbitals approach each other. The internuclear distance at minimum energy is the length of the H—H covalent bond.



until the atoms approach each other so closely that their positively charged nuclei start to repel each other. This repulsion causes a large increase in energy. We see that maximum stability (i.e., minimum energy) is achieved when the nuclei are a certain distance apart. This distance is the **bond length** of the new covalent bond. The length of the H—H bond is 0.74 Å.

As Figure 1.2 shows, energy is released when a covalent bond forms. When the H—H bond forms, 104 kcal/mol (or 435 kJ/mol)* of energy is released. Breaking the bond requires precisely the same amount of energy. Thus, the **bond strength**—also called the **bond dissociation energy**—is the energy required to break a bond, or the energy released when a bond is formed. Every covalent bond has a characteristic bond length and bond strength.

Orbitals are conserved—the number of molecular orbitals formed must equal the number of atomic orbitals combined. In describing the formation of an H—H bond, however, we combined two atomic orbitals, but discussed only one molecular orbital. Where is the other molecular orbital? It is there, but it contains no electrons.

Atomic orbitals can combine in two different ways: constructively and destructively. They can combine in a constructive, additive manner, just as two light waves or sound waves may reinforce each other (Figure 1.3). This is called a **σ (sigma) bonding molecular orbital**. Atomic orbitals can also combine in a destructive way, canceling each other. The cancellation is similar to the darkness that occurs when two light waves cancel each other or to the silence that occurs when two sound waves cancel each other (Figure 1.3). This destructive type of interaction is called a **σ^* antibonding molecular orbital**. An antibonding orbital is indicated by an asterisk (*).

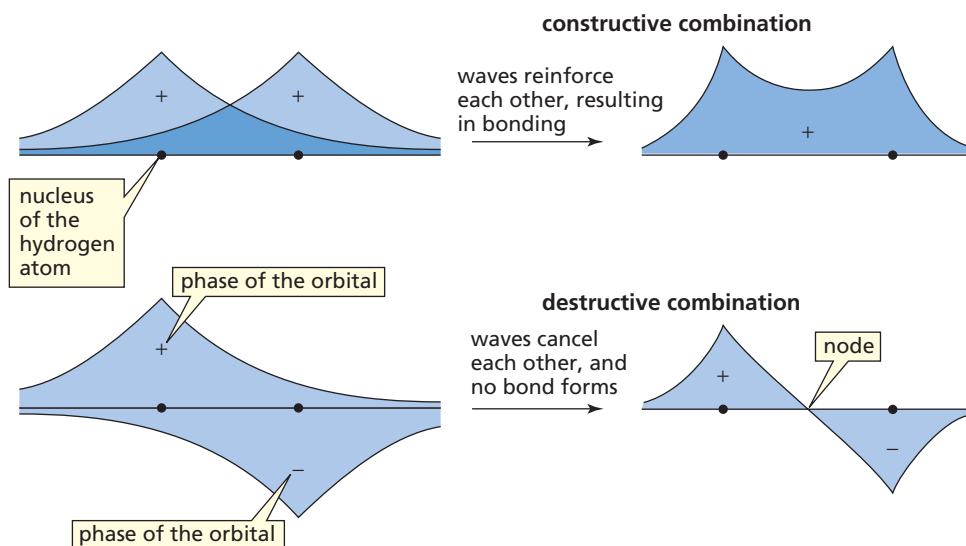


Figure 1.3

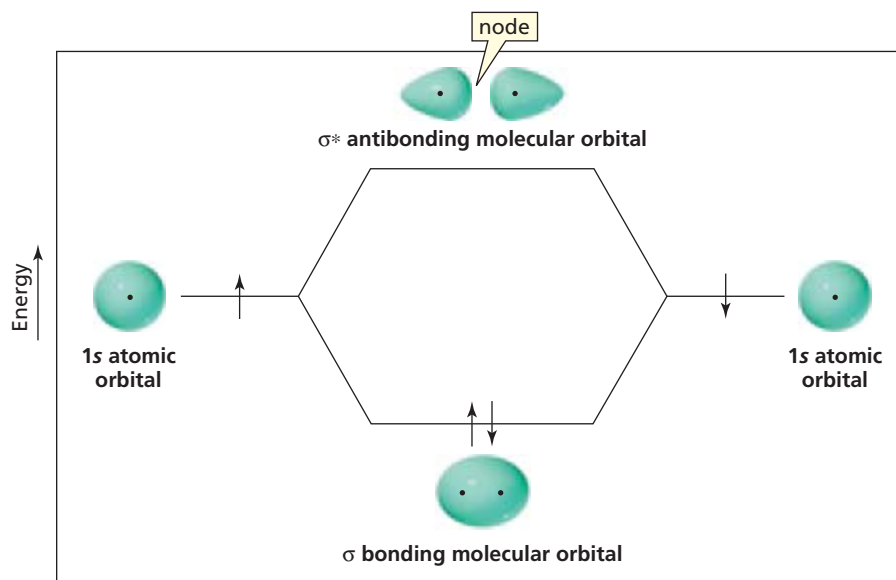
The wave functions of two hydrogen atoms can interact to reinforce, or enhance, each other (top) or can interact to cancel each other (bottom). Note that waves that interact constructively are in-phase, whereas waves that interact destructively are out-of-phase.

The σ bonding molecular orbital and σ^* antibonding molecular orbital are shown in the molecular orbital diagram in Figure 1.4. In an MO diagram, the energies are represented as horizontal lines; the bottom line is the lowest energy level, the top line the highest energy level. We see that any electrons in the bonding orbital will most likely be found between the nuclei. This increased electron density between the nuclei is what binds the atoms together. Because there is a node between the nuclei in the antibonding molecular orbital, any electrons that are in that orbital are more likely to be found anywhere except between the nuclei, so the nuclei are more exposed to one another and will be forced apart by electrostatic repulsion. Thus, electrons that occupy this orbital detract from, rather than aid, the formation of a bond between the atoms.

*1 kcal = 4.184 kJ. Joules are the Système International (SI) units for energy, although many chemists use calories. We will use both in this book.

Figure 1.4 ▶

Atomic orbitals of H_2 . Before covalent bond formation, each electron is in an atomic orbital. After covalent bond formation, both electrons are in the bonding molecular orbital. The antibonding molecular orbital is empty.



When two atomic orbitals overlap, two molecular orbitals are formed—one lower in energy and one higher in energy than the atomic orbitals.

The MO diagram shows that the bonding molecular orbital is more stable—is lower in energy—than the individual atomic orbitals. This is because the more nuclei an electron “feels,” the more stable it is. The antibonding molecular orbital, with less electron density between the nuclei, is less stable—is of higher energy—than the atomic orbitals.

After the MO diagram is constructed, the electrons are assigned to the molecular orbitals. The aufbau principle and the Pauli exclusion principle, which apply to electrons in atomic orbitals, also apply to electrons in molecular orbitals: Electrons always occupy available orbitals with the lowest energy, and no more than two electrons can occupy a molecular orbital. Thus, the two electrons of the H—H bond occupy the lower energy bonding molecular orbital (Figure 1.4), where they are attracted to both positively charged nuclei. It is this electrostatic attraction that gives a covalent bond its strength. Therefore, the greater the overlap of the atomic orbitals, the stronger is the covalent bond. The strongest covalent bonds are formed by electrons that occupy the molecular orbitals with the lowest energy.

The MO diagram in Figure 1.4 allows us to predict that H_2^+ would not be as stable as H_2 because H_2^+ has only one electron in the bonding orbital. We can also predict that He_2 does not exist: Because each He atom would bring two electrons, He_2 would have four electrons—two filling the lower energy bonding molecular orbital and the remaining two filling the higher energy antibonding molecular orbital. The two electrons in the antibonding molecular orbital would cancel the advantage to bonding gained by the two electrons in the bonding molecular orbital.

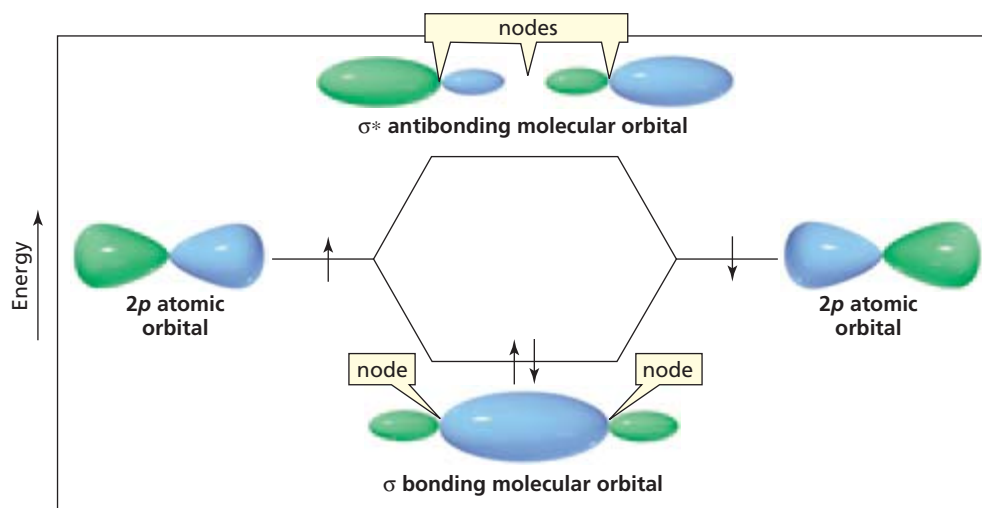
In-phase overlap forms a bonding MO; out-of-phase overlap forms an antibonding MO.

PROBLEM 13♦

Predict whether or not He_2^+ exists.

Two p atomic orbitals can overlap either end-on or side-to-side. Let’s first look at end-on overlap. End-on overlap forms a σ bond. If the overlapping lobes of the p orbitals are in-phase (a blue lobe of one p orbital overlaps a blue lobe of the other p orbital), a σ bonding molecular orbital is formed (Figure 1.5). The electron density of the σ bonding molecular orbital is concentrated between the nuclei, which causes the back lobes (the nonoverlapping lobes) of the molecular orbital to be quite small. The σ bonding molecular orbital has two nodes—a nodal plane passing through each of the nuclei.

If the overlapping lobes of the p orbitals are out-of-phase (a blue lobe of one p orbital overlaps a green lobe of the other p orbital), a σ^* antibonding molecular orbital is



◀ **Figure 1.5**

End-on overlap of two p orbitals to form a σ bonding molecular orbital and a σ^* antibonding molecular orbital.

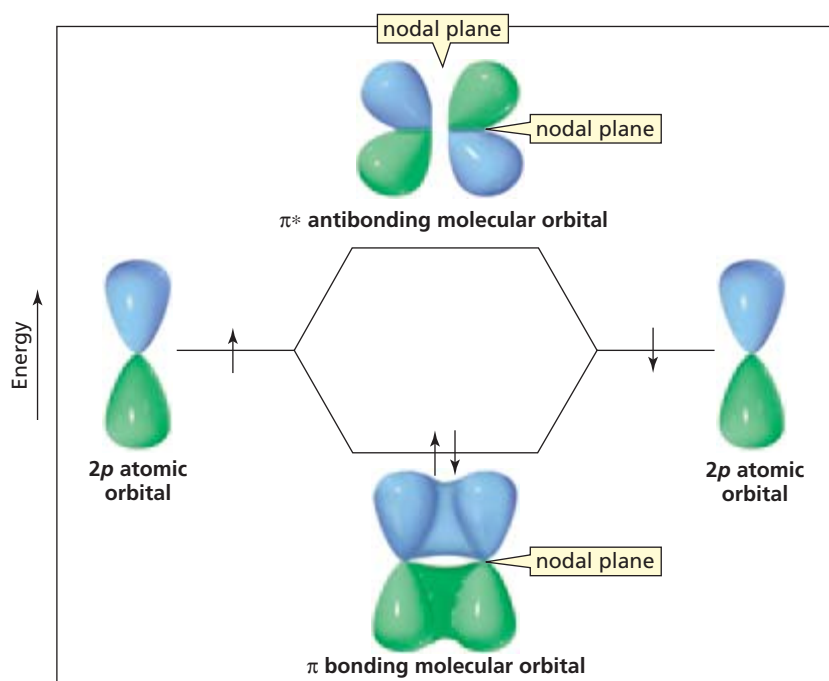
formed. The σ^* antibonding molecular orbital has *three* nodes. (Notice that after each node, the phase of the molecular orbital changes.)

Unlike the σ bond formed as a result of end-on overlap, side-to-side overlap of two p atomic orbitals forms a **pi (π) bond** (Figure 1.6). Side-to-side overlap of two in-phase p atomic orbitals forms a π bonding molecular orbital, whereas side-to-side overlap of two out-of-phase p orbitals forms a π^* antibonding molecular orbital. The π bonding molecular orbital has one node—a nodal plane that passes through both nuclei. The π^* antibonding molecular orbital has two nodal planes. Notice that σ bonds are cylindrically symmetrical, but π bonds are not.

The extent of overlap is greater when p orbitals overlap end-on than when they overlap side-to-side. This means that a σ bond formed by the end-on overlap of p orbitals is stronger than a π bond formed by the side-to-side overlap of p orbitals. It also means that a σ bonding molecular orbital is more stable than a π bonding molecular orbital because the stronger the bond, the more stable it is. Figure 1.7 shows a molecular orbital diagram of two identical atoms using their three degenerate atomic orbitals to form three bonds—one σ bond and two π bonds.

Side-to-side overlap of two p atomic orbitals forms a π bond. All other covalent bonds in organic molecules are σ bonds.

A σ bond is stronger than a π bond.

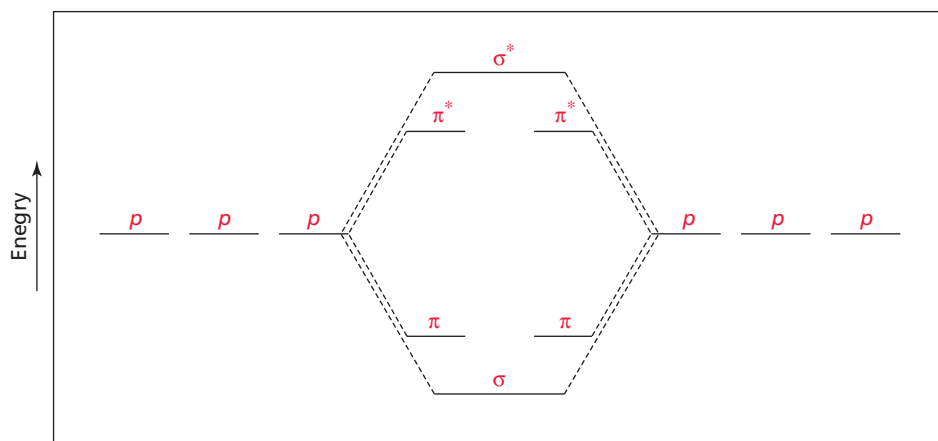


◀ **Figure 1.6**

Side-to-side overlap of two parallel p orbitals to form a π bonding molecular orbital and a π^* antibonding molecular orbital.

Figure 1.7 ▶

p Orbitals can overlap end-on to form σ bonding and σ^* antibonding molecular orbitals, or can overlap side-to-side to form π bonding and π^* antibonding molecular orbitals. The relative energies of the molecular orbitals are $\sigma < \pi < \pi^* < \sigma^*$.

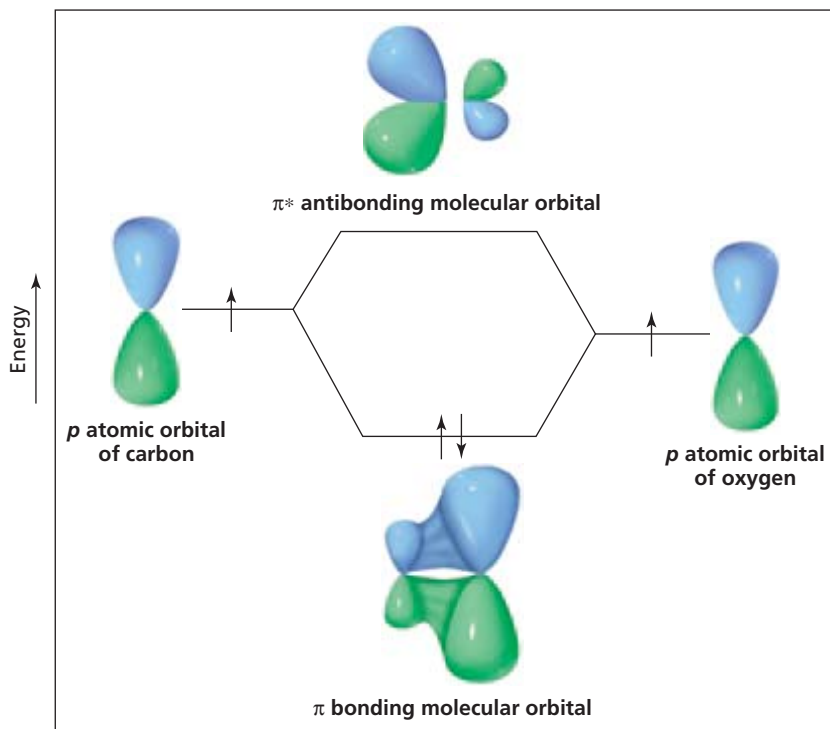


Now let's look at the molecular orbital diagram for side-to-side overlap of a p orbital of carbon with a p orbital of oxygen—the orbitals are the same, but they belong to different atoms (Figure 1.8). When the two p atomic orbitals combine to form molecular orbitals, they do so unsymmetrically. The atomic orbital of the more electronegative atom contributes more to the bonding molecular orbital, and the atomic orbital of the less electronegative atom contributes more to the antibonding molecular orbital. This means that if we were to put electrons in the bonding MO, they would be more apt to be around the oxygen atom than around the carbon atom. Thus, both the Lewis theory and molecular orbital theory tell us that the electrons shared by carbon and oxygen are not shared equally—the oxygen atom of a carbon–oxygen bond has a partial negative charge and the carbon atom has a partial positive charge.

Organic chemists find that the information obtained from MO theory, where valence electrons occupy bonding and antibonding molecular orbitals, does not always yield the needed information about the bonds in a molecule. The **valence-shell electron-pair repulsion (VSEPR) model** combines the Lewis concept of shared electron pairs and lone-pair electrons with the concept of atomic orbitals and adds a third principle: *the minimization of electron repulsion*. In this model, atoms share electrons by overlapping

Figure 1.8 ▶

Side-to-side overlap of a p orbital of carbon with a p orbital of oxygen to form a π bonding molecular orbital and a π^* antibonding molecular orbital.

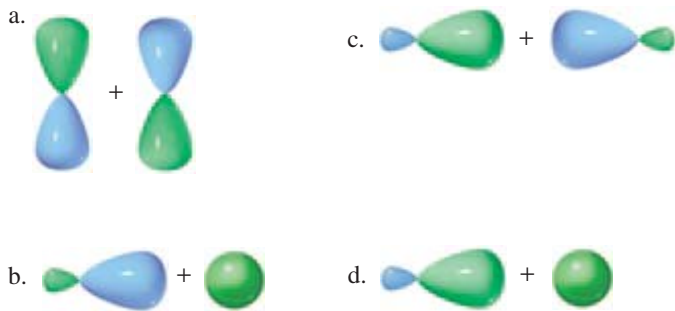


their atomic orbitals, and because electron pairs repel each other, the bonding electrons and lone-pair electrons around an atom are positioned as far apart as possible.

Because organic chemists generally think of chemical reactions in terms of the changes that occur in the bonds of the reacting molecules, the VSEPR model often provides the easiest way to visualize chemical change. However, the model is inadequate for some molecules because it does not allow for antibonding orbitals. We will use both the MO and the VSEPR models in this book. Our choice will depend on which model provides the best description of the molecule under discussion. We will use the VSEPR model in Sections 1.7–1.13.

PROBLEM 14♦

Indicate the kind of molecular orbital (σ , σ^* , π , or π^*) that results when the orbitals are combined as indicated:



1.7 Bonding in Methane and Ethane: Single Bonds

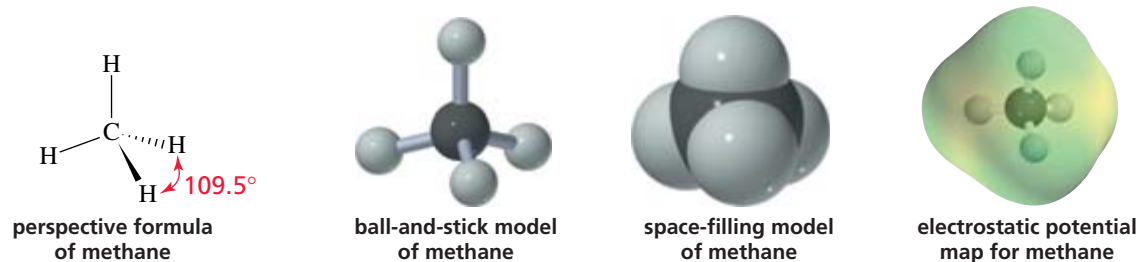
We will begin the discussion of bonding in organic compounds by looking at the bonding in methane, a compound with only one carbon atom. Then we will examine the bonding in ethane (a compound with two carbons and a carbon–carbon single bond), in ethene (a compound with two carbons and a carbon–carbon double bond), and in ethyne (a compound with two carbons and a carbon–carbon triple bond).

Next, we will look at bonds formed by atoms other than carbon that are commonly found in organic compounds—bonds formed by oxygen, nitrogen, and the halogens. Because *the orbitals used in bond formation determine the bond angles in a molecule*, you will see that if we know the bond angles in a molecule, we can figure out which orbitals are involved in bond formation.

Bonding in Methane

Methane (CH_4) has four covalent C—H bonds. Because all four bonds have the same length and all the bond angles are the same (109.5°), we can conclude that the four C—H bonds in methane are identical.

Four different ways to represent a methane molecule are shown here.



In a perspective formula, bonds in the plane of the paper are drawn as solid lines, bonds protruding out of the plane of the paper toward the viewer are drawn as solid wedges, and those protruding back from the plane of the paper away from the viewer are drawn as hatched wedges.



Roald Hoffmann was born in Poland in 1937 and came to the United States when he was 12. He received a B.S. from Columbia and a Ph.D. from Harvard. When the conservation of orbital symmetry theory was proposed, he and Woodward were both on the faculty at Harvard. Hoffmann is presently a professor of chemistry at Cornell.

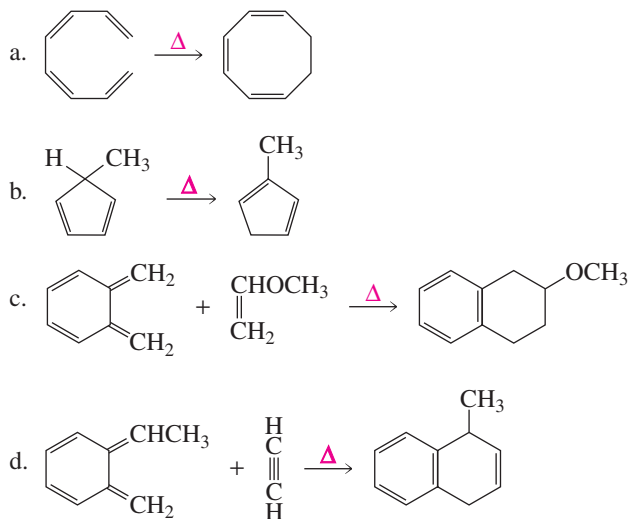
Kenichi Fukui (1918–1998) was born in Japan. He was a professor at Kyoto University until 1982 when he became president of the Kyoto Institute of Technology. He was the first Japanese to receive the Nobel Prize in chemistry.

AU: OK bulleted list here?
Please check

According to the conservation of orbital symmetry theory, whether a compound will undergo a pericyclic reaction under particular conditions *and* what product will be formed both depend on molecular orbital symmetry. To understand pericyclic reactions, therefore, we must now review molecular orbital theory. We will then be able to understand how the symmetry of a molecular orbital controls both the conditions under which a pericyclic reaction takes place and the configuration of the product that is formed.

PROBLEM 1♦

Examine the following pericyclic reactions. For each reaction, indicate whether it is an electrocyclic reaction, a cycloaddition reaction, or a sigmatropic rearrangement.

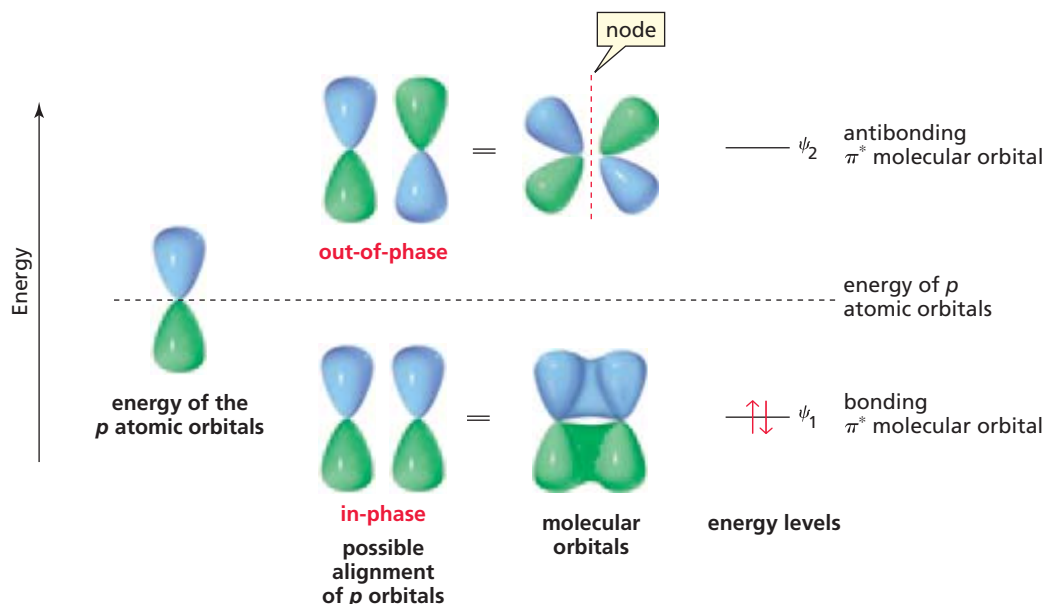


29.2 Molecular Orbitals and Orbital Symmetry

The overlap of p atomic orbitals to form π molecular orbitals can be described mathematically using quantum mechanics. The result of the mathematical treatment can be described simply in nonmathematical terms by **molecular orbital (MO) theory**. You were introduced to molecular orbital theory in Sections 1.6 and 7.11. Take a few minutes to review the following key points raised in these sections.

- The two lobes of a p orbital have opposite phases. When two in-phase atomic orbitals interact, a covalent bond is formed. When two out-of-phase atomic orbitals interact, a node is created between the two nuclei.
- Electrons fill molecular orbitals according to the same rules—the aufbau principle, the Pauli exclusion principle, Hund's rule—that govern how they fill atomic orbitals: An electron goes into the available molecular orbital with the lowest energy, and only two electrons can occupy a particular molecular orbital (Section 1.2).
- Because the π -bonding portion of a molecule is perpendicular to the framework of the σ bonds, the π bonds can be treated independently. Each carbon atom that forms a π bond has a p orbital, and the p orbitals of the carbon atoms combine to produce a π molecular orbital. Thus, a molecular orbital can be described by the **linear combination of atomic orbitals (LCAO)**. In a π molecular orbital, each electron that previously occupied a p atomic orbital surrounding an individual carbon nucleus now surrounds the entire part of the molecule that is included in the interacting p orbitals.

A molecular orbital description of ethene is shown in Figure 29.1. (To show the different phases of the two lobes of a p orbital, one phase is represented by a blue lobe and the other phase by a green lobe.)¹ Because ethene has one π bond, it has two p atomic orbitals that combine to produce two π molecular orbitals. The in-phase interaction of the two p atomic orbitals gives a **bonding π molecular orbital**, designated by ψ_1 (ψ is the Greek letter psi). The bonding molecular orbital is of lower energy than the isolated p atomic orbitals. The two p atomic orbitals of ethene can also interact out-of-phase. Interaction of out-of-phase orbitals gives an **antibonding π^* molecular orbital**, ψ_2 , which is of higher energy than the p atomic orbitals. The bonding molecular orbital results from additive interaction of the atomic orbitals, whereas the antibonding molecular orbital results from subtractive interaction. In other words, the interaction of in-phase orbitals holds atoms together, while the interaction of out-of-phase orbitals pushes atoms apart. Because electrons reside in the available molecular orbitals with the lowest energy and two electrons can occupy a molecular orbital, the two π electrons of ethene reside in the bonding π molecular orbital. This molecular orbital picture describes all molecules with one carbon–carbon double bond.



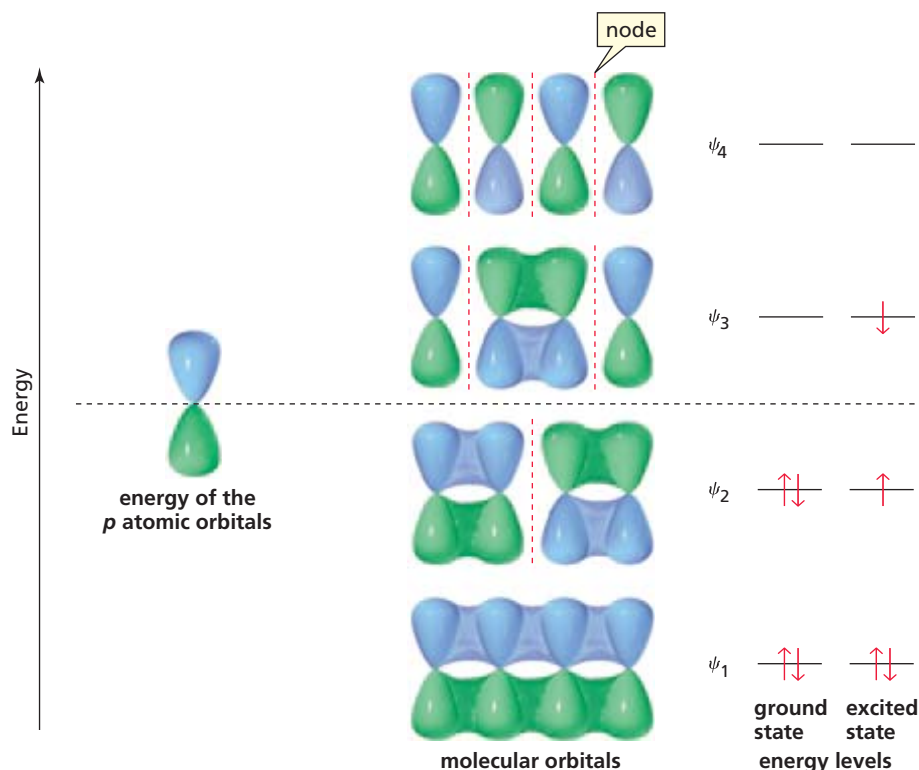
▲ Figure 29.1

Interaction of in-phase p atomic orbitals gives a bonding π molecular orbital that is lower in energy than the p atomic orbitals. Interaction of out-of-phase π atomic orbitals gives an antibonding π^* molecular orbital that is higher in energy than the p atomic orbitals.

1,3-Butadiene has two conjugated π bonds, so it has four p atomic orbitals (Figure 29.2). Four atomic orbitals can combine linearly in four different ways. Consequently, there are four π molecular orbitals: ψ_1 , ψ_2 , ψ_3 , and ψ_4 . Notice that orbitals are conserved: Four atomic orbitals combine to produce four molecular orbitals. Half are bonding molecular orbitals (ψ_1 and ψ_2) and the other half are antibonding molecular orbitals (ψ_3 and ψ_4). Because the four π electrons will reside in the available molecular orbitals with the lowest energy, two electrons are in ψ_1 and two are in ψ_2 . Remember that although the molecular orbitals have different energies, they are all valid and they all coexist. This molecular orbital picture describes all molecules with two conjugated carbon–carbon double bonds.

Orbitals are conserved—two atomic orbitals combine to produce two molecular orbitals, four atomic orbitals combine to produce four molecular orbitals, six atomic orbitals combine to produce six molecular orbitals, etc.

¹Because the different phases of the p orbital result from the different mathematical signs (+ and −) of the wave function of the electron, some chemists represent the different phases by a (+) and a (−).



▲ Figure 29.2

Four p atomic orbitals interact to give the four π molecular orbitals of 1,3-butadiene.



Tutorial:
 π Molecular orbitals

If you examine the interacting orbitals in Figure 29.2, you will see that in-phase orbitals interact to give a bonding interaction and out-of-phase orbitals interact to create a node. Recall that a node is a place in which there is zero probability of finding an electron (Section 1.5). You will also see that as the energy of the molecular orbital increases, the number of bonding interactions decreases and the number of nodes *between* the nuclei increases. For example, ψ_1 has three bonding interactions and zero nodes between the nuclei, ψ_2 has two bonding interactions and one node between the nuclei, ψ_3 has one bonding interaction and two nodes between the nuclei, and ψ_4 has zero bonding interactions and three nodes between the nuclei. Notice that a molecular orbital is bonding if the number of bonding interactions is greater than the number of nodes between the nuclei, and a molecular orbital is antibonding if the number of bonding interactions is fewer than the number of nodes between the nuclei.

The normal electronic configuration of a molecule is known as its **ground state**. In the ground state of 1,3-butadiene, the *highest occupied molecular orbital (HOMO)* is ψ_2 , and the *lowest unoccupied molecular orbital (LUMO)* is ψ_3 . If a molecule absorbs light of an appropriate wavelength, the light will promote an electron from its ground-state HOMO to its LUMO (from ψ_2 to ψ_3). The molecule is then in an **excited state**. In the excited state, the HOMO is ψ_3 and the LUMO is ψ_4 . In a thermal reaction the reactant is in its ground state; in a photochemical reaction the reactant is in an excited state.

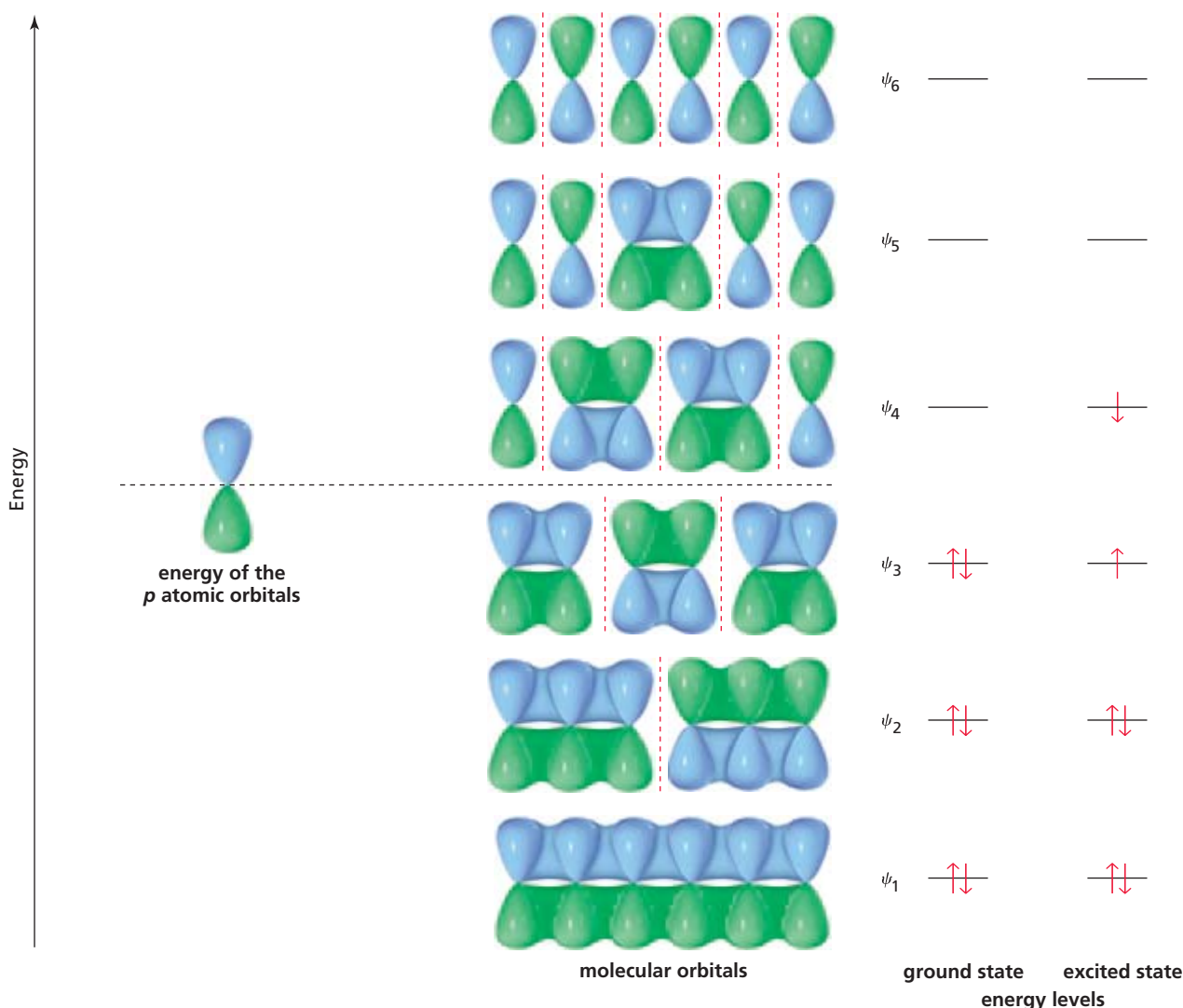
Some molecular orbitals are *symmetric* and some are *asymmetric* (also called *dissymmetric*), and they are easy to distinguish. If the p orbitals at the ends of the molecular orbital are in-phase (both have blue lobes on the top and green lobes on the bottom), the molecular orbital is symmetric. If the two end p orbitals are out-of-phase, the molecular orbital is asymmetric. In Figure 29.2, ψ_1 and ψ_3 are **symmetric molecular orbitals** and ψ_2 and ψ_4 are **asymmetric molecular orbitals**. Notice that as the molecular orbitals increase in energy, they alternate in being symmetric and

asymmetric. Therefore, *the ground-state HOMO and the excited-state HOMO always have opposite symmetries—one is symmetric and the other is asymmetric.* A molecular orbital description of 1,3,5-hexatriene, a compound with three conjugated double bonds, is shown in Figure 29.3. As a review, examine the figure and note

The ground-state HOMO and the excited-state HOMO have opposite symmetries.

- the distribution of electrons in the ground and excited states
- that the number of bonding interactions decreases and the number of nodes increases as the molecular orbitals increase in energy
- that the molecular orbitals alternate from symmetric to asymmetric as the molecular orbitals increase in energy

Although the chemistry of a compound is determined by all its molecular orbitals, we can learn a great deal about the chemistry of a compound by looking at only the **highest occupied molecular orbital (HOMO)** and the **lowest unoccupied molecular orbital (LUMO)**. These two molecular orbitals are known as the **frontier orbitals**. We will now see that simply by evaluating *one* of the frontier molecular orbitals of the reactant(s) in a pericyclic reaction, we can predict the conditions under which the reaction will occur (thermal or photochemical, or both) and the products that will be formed.



▲ **Figure 29.3**

Six p atomic orbitals interact to give the six π molecular orbitals of 1,3,5-hexatriene.

PROBLEM 2♦

Answer the following questions for the π molecular orbitals of 1,3,5-hexatriene:

- Which are the bonding orbitals, and which are the antibonding orbitals?
- Which orbitals are the HOMO and the LUMO in the ground state?
- Which orbitals are the HOMO and the LUMO in the excited state?
- Which orbitals are symmetric, and which are asymmetric?
- What is the relationship between HOMO and LUMO and symmetric and asymmetric orbitals?

PROBLEM 3♦

- How many π molecular orbitals does 1,3,5,7-octatetraene have?
- What is the designation of its HOMO (ψ_1 , ψ_2 , etc.)?
- How many nodes does its highest-energy π molecular orbital have between the nuclei?

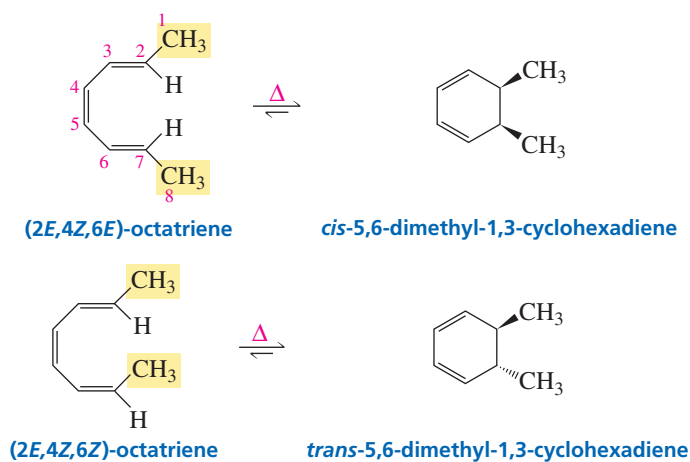
PROBLEM 4

Give a molecular orbital description for each of the following:

- | | |
|-------------------|-------------------------|
| a. 1,3-pentadiene | c. 1,3,5-heptatriene |
| b. 1,4-pentadiene | d. 1,3,5,8-nonatetraene |

29.3 Electrocyclic Reactions

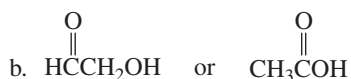
An *electrocyclic reaction* is an intramolecular reaction in which the rearrangement of π electrons leads to a cyclic product that has one fewer π bond than the reactant. An electrocyclic reaction is completely stereoselective—it preferentially forms one stereoisomer. For example, when (2*E*,4*Z*,6*E*)-octatriene undergoes an electrocyclic reaction under thermal conditions, only the cis product is formed; when (2*E*,4*Z*,6*Z*)-octatriene undergoes an electrocyclic reaction under thermal conditions, only the trans product is formed. Recall that *E* means the high-priority groups are on opposite sides of the double bond, and *Z* means the high-priority groups are on the same side of the double bond (Section 3.5).



However, when the reactions are carried out under photochemical conditions, the products have opposite configurations: The compound that forms the *cis* isomer under

PROBLEM 11♦

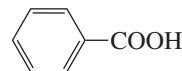
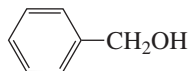
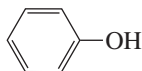
Which is a stronger acid?

**PROBLEM 12♦**

Which is a stronger base?

**PROBLEM 13♦**

Rank the following compounds in order of decreasing acid strength:

**7.11 A Molecular Orbital Description of Stability**

We have used contributing resonance structures to show why compounds are stabilized by electron delocalization. Why compounds are stabilized by electron delocalization can also be explained by molecular orbital (MO) theory.

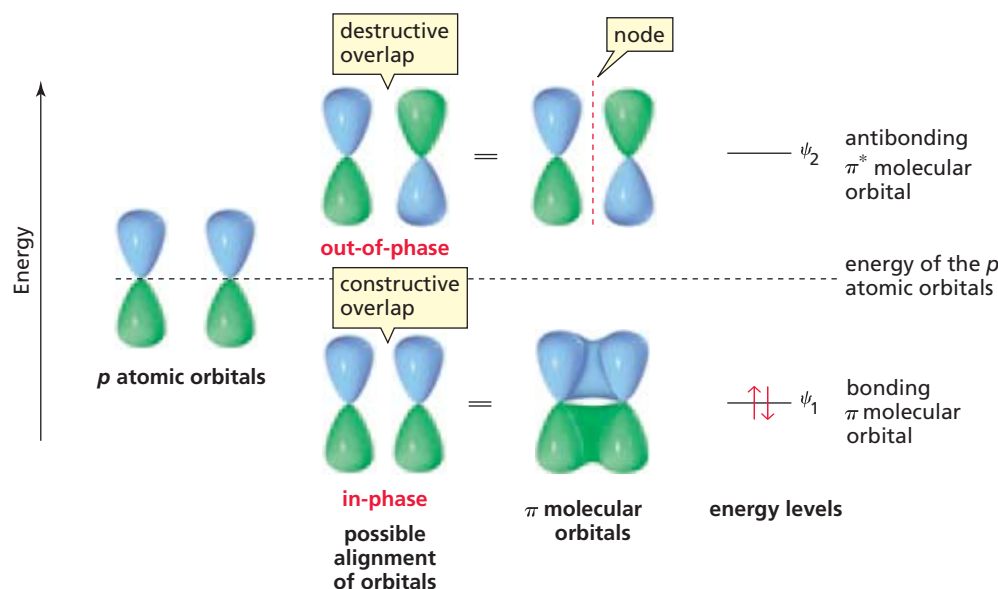
In Section 1.5, we saw that the two lobes of a p orbital have opposite phases. We also saw that when two in-phase p orbitals overlap, a covalent bond is formed, and when two out-of-phase p orbitals overlap, they cancel each other and produce a node between the two nuclei (Section 1.6). A *node* is a region where there is zero probability of finding an electron.

Let's review how the π molecular orbitals of ethene are constructed. An MO description of ethene is shown in Figure 7.8. The two p orbitals can be either in-phase or out-of-phase. (The different phases are indicated by different colors.) Notice that the number of orbitals is conserved—the number of molecular orbitals equals the number of atomic orbitals that produced them. Thus, the two atomic p orbitals of ethene overlap to produce two molecular orbitals. Side-to-side overlap of in-phase p orbitals (lobes of the same color) produces a **bonding molecular orbital** designated ψ_1 (the Greek letter psi). The bonding molecular orbital is lower in energy than the p atomic orbitals, and it encompasses both carbons. In other words, each electron in the bonding molecular orbital spreads over both carbon atoms.

Side-to-side overlap of out-of-phase p orbitals produces an **antibonding molecular orbital**, ψ_2 , which is higher in energy than the p atomic orbitals. The antibonding molecular orbital has a node between the lobes of opposite phases. The bonding MO arises from *constructive overlap* of the atomic orbitals, whereas the antibonding MO arises from *destructive overlap*. In other words, the overlap of in-phase orbitals holds atoms together—it is a bonding interaction—whereas the overlap of out-of-phase orbitals pulls atoms apart—it is an antibonding interaction.

The π electrons are placed in molecular orbitals according to the same rules that govern the placement of electrons in atomic orbitals (Section 1.2): the aufbau principle (orbitals are filled in order of increasing energy), the Pauli exclusion principle (each

Take a few minutes to review
Section 1.6.



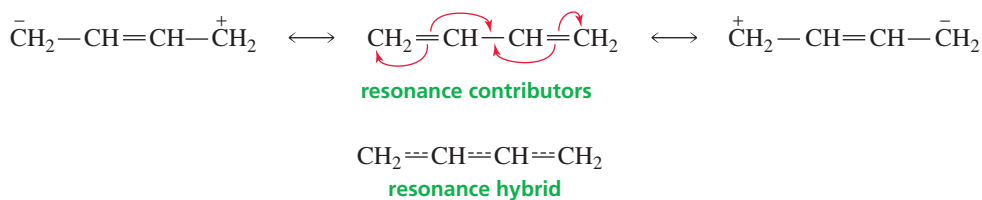
▲ Figure 7.8

The distribution of electrons in ethene. Overlapping of in-phase p orbitals produces a bonding molecular orbital that is lower in energy than the p atomic orbitals. Overlapping of out-of-phase p orbitals produces an antibonding molecular orbital that is higher in energy than the p atomic orbitals.

orbital can hold two electrons of opposite spin), and Hund's rule (an electron will occupy an empty degenerate orbital before it will pair up with an electron that is already present in an orbital).

1,3-Butadiene and 1,4-Pentadiene

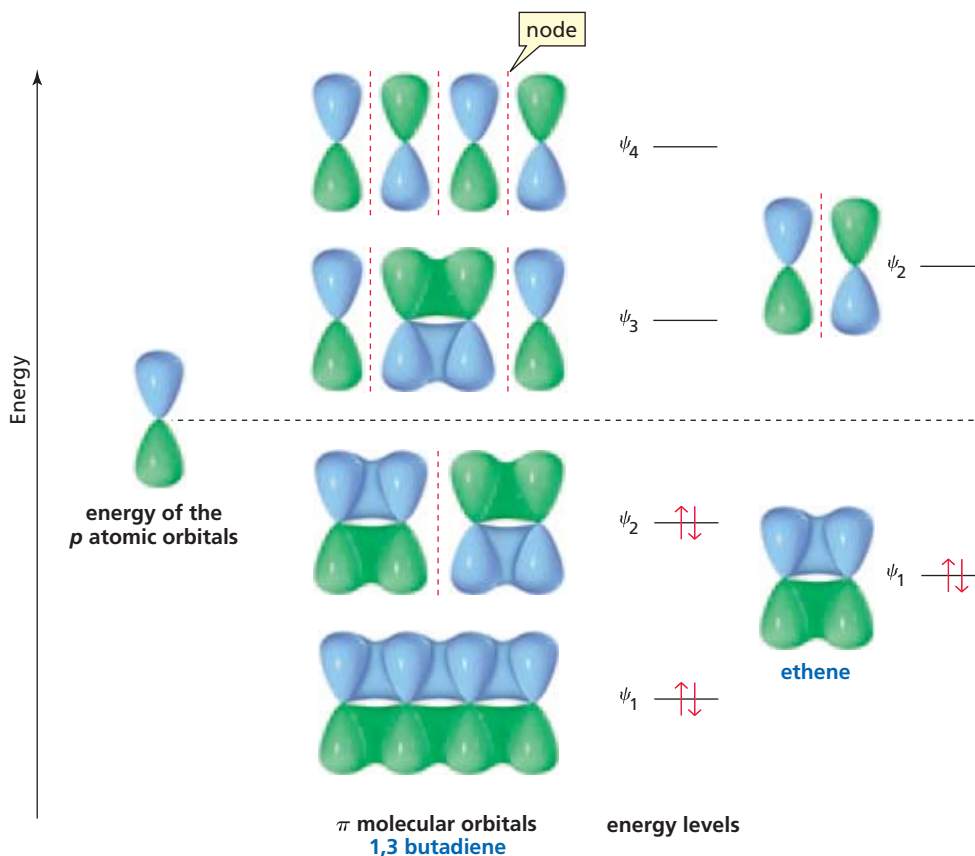
The π electrons in 1,3-butadiene are delocalized over four sp^2 carbons. In other words, there are four carbons in the π system. A molecular orbital description of 1,3-butadiene is shown in Figure 7.9.



Each of the four carbons contributes one p atomic orbital, and the four p atomic orbitals combine to produce four π molecular orbitals: ψ_1 , ψ_2 , ψ_3 , and ψ_4 . Thus, a molecular orbital results from the **linear combination of atomic orbitals (LCAO)**. Half of the MOs are bonding (π) MOs (ψ_1 and ψ_2), and the other half are antibonding (π^*) MOs (ψ_3 and ψ_4), and they are given the designations ψ_1 , ψ_2 , ψ_3 , and ψ_4 , in order of increasing energy. The energies of the bonding and antibonding MOs are symmetrically distributed above and below the energy of the p atomic orbitals.

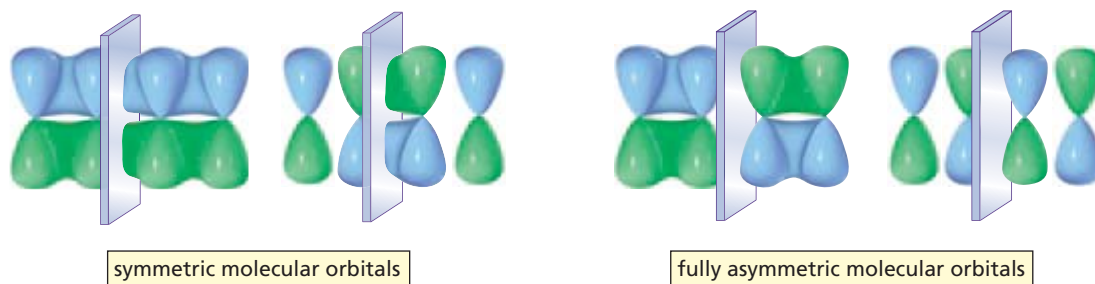
Notice that as the MOs increase in energy, the number of nodes increases and the number of bonding interactions decreases. The lowest-energy MO (ψ_1) has only the node that bisects the p orbitals—it has no nodes between the nuclei because all the blue lobes overlap on one face of the molecule and all the green lobes overlap on the other face; ψ_1 has three bonding interactions; ψ_2 has one node between the nuclei and two bonding interactions (for a net of one bonding interaction); ψ_3 has two nodes between the nuclei and one bonding interaction (for a net of one antibonding interaction); and ψ_4 has three nodes between the nuclei—three antibonding interactions—and no bonding interactions. The four π electrons of 1,3-butadiene reside in ψ_1 and ψ_2 .

Four p atomic orbitals overlap to produce four molecular orbitals in 1,3-butadiene, and two p atomic orbitals overlap to produce two molecular orbitals in ethene. In both compounds, the bonding MOs are filled and the antibonding MOs are empty.



1,3-Butadiene's lowest-energy MO (ψ_1) is particularly stable because it has three bonding interactions and its two electrons are delocalized over all four nuclei—they encompass all the carbons in the π system. The MO next in energy (ψ_2) is also a bonding MO because it has one more bonding interaction than antibonding interaction; it is not as strongly bonding or as low in energy as ψ_1 . These two bonding MOs show that the greatest π electron density in a compound with two double bonds joined by one single bond is between C-1 and C-2 and between C-3 and C-4, but there is some π electron density between C-2 and C-3—just as the resonance contributors show. They also show why 1,3-butadiene is most stable in a planar conformation: If 1,3-butadiene weren't planar, there would be little or no overlap between C-2 and C-3. Overall, ψ_3 is an antibonding MO: It has one more antibonding interaction than bonding interaction, but it is not as strongly antibonding as ψ_4 , which has no bonding interactions and three antibonding interactions.

Both ψ_1 and ψ_3 are **symmetric molecular orbitals**; they have a plane of symmetry, so one half is the mirror image of the other half. Both ψ_2 and ψ_4 are *fully asymmetric*; they do not have a plane of symmetry, but would have one if one half of the MO were turned upside down. Notice that as the MOs increase in energy, they alternate from being symmetric to asymmetric.



The energies of the MOs of 1,3-butadiene and ethene are compared in Figure 7.9. Notice that the average energy of the electrons in 1,3-butadiene is lower than the electrons in ethene. This lower energy is the resonance energy. In other words, 1,3-butadiene is stabilized by electron delocalization (resonance).

PROBLEM 14♦

What is the total number of nodes in the ψ_3 and ψ_4 molecular orbitals of 1,3-butadiene?

The highest-energy molecular orbital of 1,3-butadiene that contains electrons is ψ_2 . Therefore, ψ_2 is called the **highest occupied molecular orbital (HOMO)**. The lowest-energy molecular orbital of 1,3-butadiene that does not contain electrons is ψ_3 ; ψ_3 is called the **lowest unoccupied molecular orbital (LUMO)**.

The molecular orbital description of 1,3-butadiene shown in Figure 7.9 represents the electronic configuration of the molecule in its ground state. If the molecule absorbs light of an appropriate wavelength, the light will promote an electron from its HOMO to its LUMO (from ψ_2 to ψ_3). The molecule then is in an excited state (Section 1.2). The excitation of an electron from the HOMO to the LUMO is the basis of ultraviolet and visible spectroscopy (Section 8.9).

HOMO = the highest occupied molecular orbital.

LUMO = the lowest unoccupied molecular orbital.

PROBLEM 15♦

Answer the following questions for the π molecular orbitals of 1,3-butadiene:

- Which are the bonding MOs and which are the antibonding MOs?
- Which MOs are symmetric and which are asymmetric?
- Which MO is the HOMO and which is the LUMO in the ground state?
- Which MO is the HOMO and which is the LUMO in the excited state?
- What is the relationship between the HOMO and the LUMO and symmetric and asymmetric orbitals?

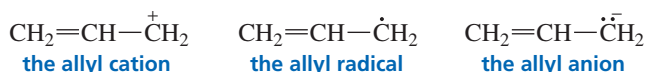
Now let's look at the π molecular orbitals of 1,4-pentadiene.



1,4-Pentadiene, like 1,3-butadiene, has four π electrons. However, unlike the delocalized π electrons in 1,3-butadiene, the π electrons in 1,4-pentadiene are completely separate from one another. In other words, the electrons are localized. The molecular orbitals of 1,4-pentadiene have the same energy as those of ethene—a compound with one pair of localized π electrons. Thus, molecular orbital theory and contributing resonance structures are two different ways to show that the π electrons in 1,3-butadiene are delocalized and that electron delocalization stabilizes a molecule.

The Allyl Cation, the Allyl Radical, and the Allyl Anion

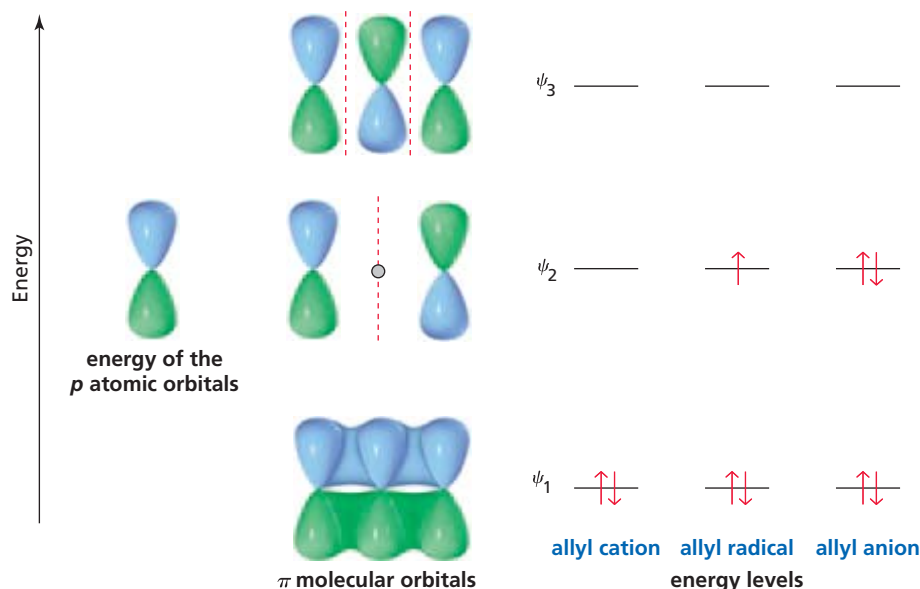
Let's now look at the molecular orbitals of the allyl cation, the allyl radical, and the allyl anion.



The three p atomic orbitals of the allyl group combine to produce three π molecular orbitals: ψ_1 , ψ_2 , and ψ_3 (Figure 7.10). The bonding MO (ψ_1) encompasses all the

Figure 7.10 ►

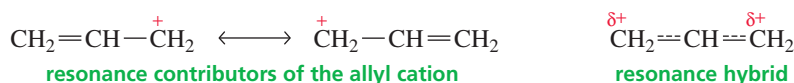
The distribution of electrons in the molecular orbitals of the allyl cation, the allyl radical, and the allyl anion. Three p atomic orbitals overlap to produce three π molecular orbitals.



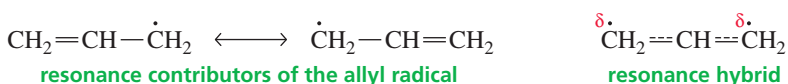
carbons in the π system. In an acyclic π system, the number of bonding MOs always equals the number of antibonding MOs. Therefore, when there is an odd number of MOs, one of them must be a **nonbonding molecular orbital**. In an allyl system, ψ_2 is a nonbonding MO. We have seen that as the energy of the MO increases, the number of nodes increases. Consequently, the ψ_2 MO must have a node—in addition to the one that ψ_1 has that bisects the p orbitals. The only symmetrical position for a node in ψ_2 is for it to pass through the middle carbon. (You also know that it needs to pass through the middle carbon because that is the only way ψ_2 can be fully asymmetric, which it must be, since ψ_1 and ψ_3 are symmetric.)

You can see from Figure 7.10 why ψ_2 is called a nonbonding molecular orbital: There is no overlap between the p orbital on the middle carbon and the p orbital on either of the end carbons. Notice that a nonbonding MO has the same energy as the isolated p atomic orbitals. The third molecular orbital (ψ_3) is an antibonding MO.

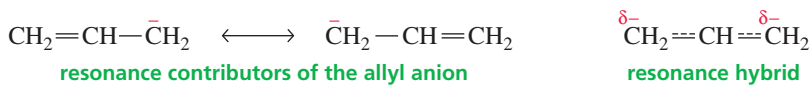
The two π electrons of the allyl cation are in the bonding MO, which means that they are spread over all three carbons. Consequently, the two carbon–carbon bonds in the allyl cation are identical, with each having some double-bond character. The positive charge is shared equally by the end carbon atoms, which is another way of showing that the stability of the allyl cation is due to electron delocalization.



The allyl radical has two electrons in the bonding π molecular orbital, so these electrons are spread over all three carbon atoms. The third electron is in the nonbonding MO. The molecular orbital diagram shows that the third electron is shared equally by the end carbons, with none of the electron density on the middle carbon. This is in agreement with what the resonance contributors show: Only the end carbons have radical character.



Finally, the allyl anion has two electrons in the nonbonding MO. These two electrons are shared equally by the end carbon atoms. This again agrees with what the resonance contributors show.

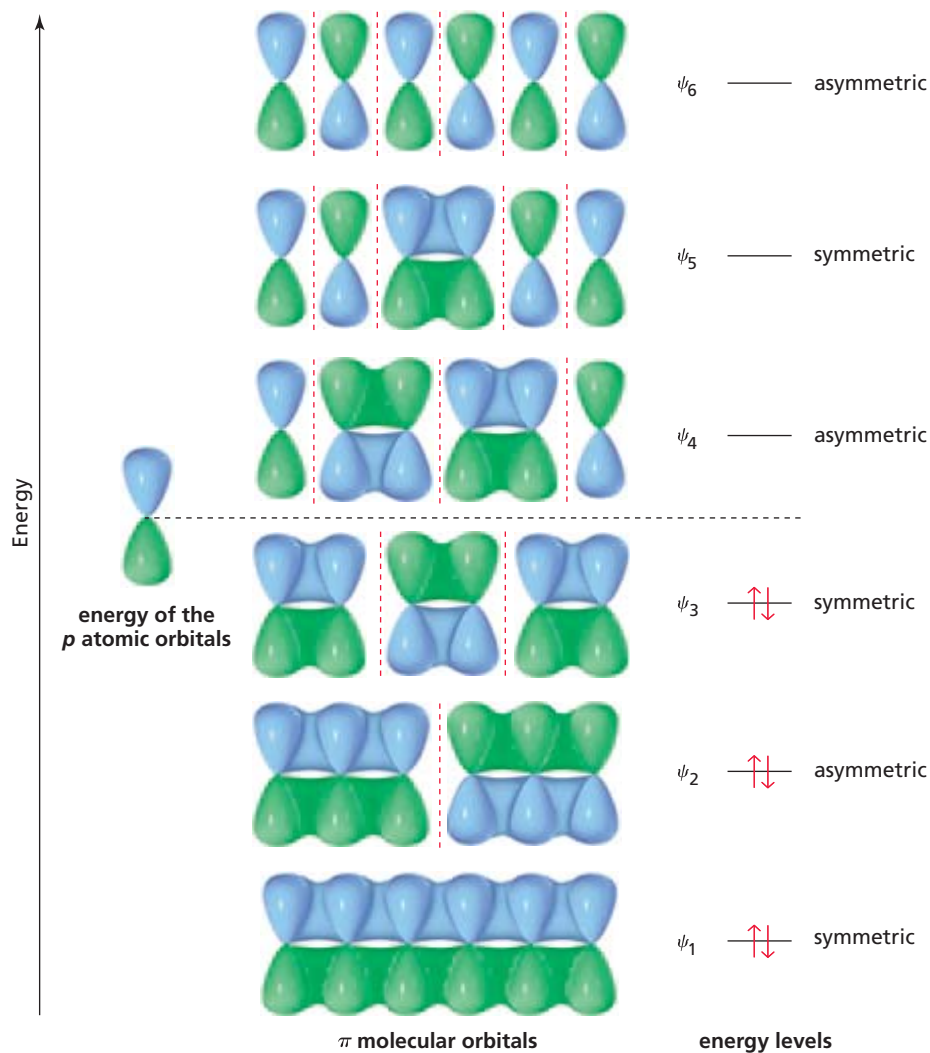


1,3,5-Hexatriene and Benzene

1,3,5-Hexatriene, with six carbon atoms, has six p atomic orbitals.



The six p atomic orbitals combine to produce six π molecular orbitals: $\psi_1, \psi_2, \psi_3, \psi_4, \psi_5$, and ψ_6 (Figure 7.11). Half of the MOs (ψ_1, ψ_2 , and ψ_3) are bonding MOs, and the other half (ψ_4, ψ_5 , and ψ_6) are antibonding. 1,3,5-Hexatriene's six π electrons occupy the three bonding MOs (ψ_1, ψ_2 , and ψ_3), and two of the electrons (those in ψ_1) are delocalized over all six carbons. Thus, molecular orbital theory and resonance contributors are two different ways of showing that the π electrons in 1,3,5-hexatriene are delocalized. Notice in the figure that as the MOs increase in energy, the number of nodes increases, the number of bonding interactions decreases, and the MOs alternate from being symmetric to being asymmetric.



◀ **Figure 7.11**
Six p atomic orbitals overlap to produce the six π molecular orbitals of 1,3,5-hexatriene. The six electrons occupy the three bonding molecular orbitals ψ_1, ψ_2 , and ψ_3 .

PROBLEM 16♦

Answer the following questions for the π molecular orbitals of 1,3,5-hexatriene:

- Which are the bonding MOs and which are the antibonding MOs?
- Which MOs are symmetric and which are asymmetric?
- Which MO is the HOMO and which is the LUMO in the ground state?
- Which MO is the HOMO and which is the LUMO in the excited state?
- What is the relationship between the HOMO and the LUMO and symmetric and asymmetric orbitals.

Like 1,3,5-hexatriene, benzene has a six-carbon π system. The six-carbon π system in benzene, however, is cyclic. The six p atomic orbitals combine to produce six π molecular orbitals (Figure 7.12). Three of the MOs are bonding (ψ_1 , ψ_2 , and ψ_3) and three are antibonding (ψ_4 , ψ_5 , and ψ_6). Benzene's six π electrons occupy the three lowest-energy MOs (the bonding MOs). The two electrons in ψ_1 are delocalized over the six carbon atoms. The method used to determine the relative energies of the MOs of compounds with cyclic π systems is described in Section 15.6.

Figure 7.12 ▶

Benzene has six π molecular orbitals, three bonding (ψ_1 , ψ_2 , ψ_3) and three antibonding (ψ_4 , ψ_5 , ψ_6). The six π electrons occupy the three bonding molecular orbitals.

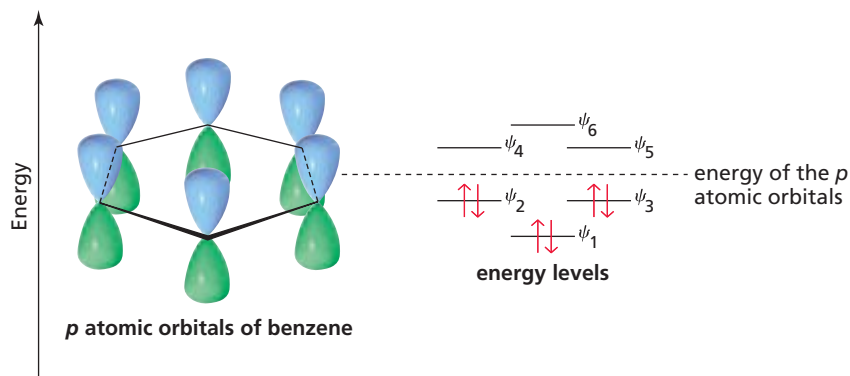


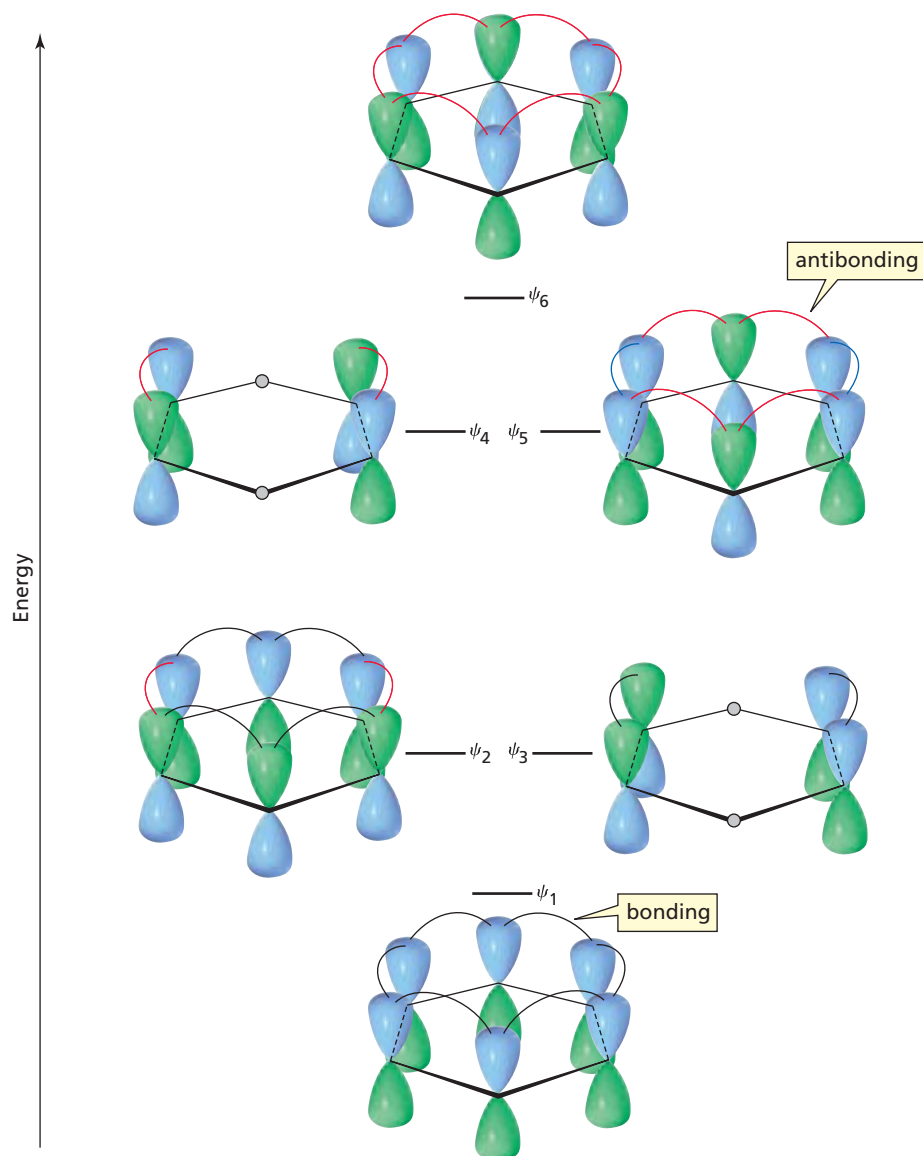
Figure 7.13 shows that there are *six* bonding interactions in the lowest-energy MO (ψ_1) of benzene—one more than in the lowest-energy MO of 1,3,5-hexatriene (Figure 7.12). In other words, putting the three double bonds into a ring is accompanied by an increase in stabilization. Each of the other two bonding MOs of benzene (ψ_2 and ψ_3) has a node in addition to the node that bisects the p orbitals. These two orbitals are degenerate: ψ_2 has four bonding interactions and two antibonding interactions, for a net of two bonding interactions, and ψ_3 also has two bonding interactions. Thus, ψ_2 and ψ_3 are bonding MOs, but they are not as strongly bonding as ψ_1 .

The energy levels of the MOs of ethene, 1,3-butadiene, 1,3,5-hexatriene, and benzene are compared in Figure 7.14. You can see that benzene is a particularly stable molecule—more stable than 1,3,5-hexatriene and much more stable than a molecule with one or more isolated double bonds. Compounds such as benzene that are unusually stable because of large delocalization energies are called **aromatic compounds**. The structural features that cause a compound to be aromatic are discussed in Section 15.1.

PROBLEM 17♦

How many bonding interactions are there in the ψ_1 and ψ_2 molecular orbitals of the following compounds?

- 1,3-butadiene
- 1,3,5,7-octatetraene

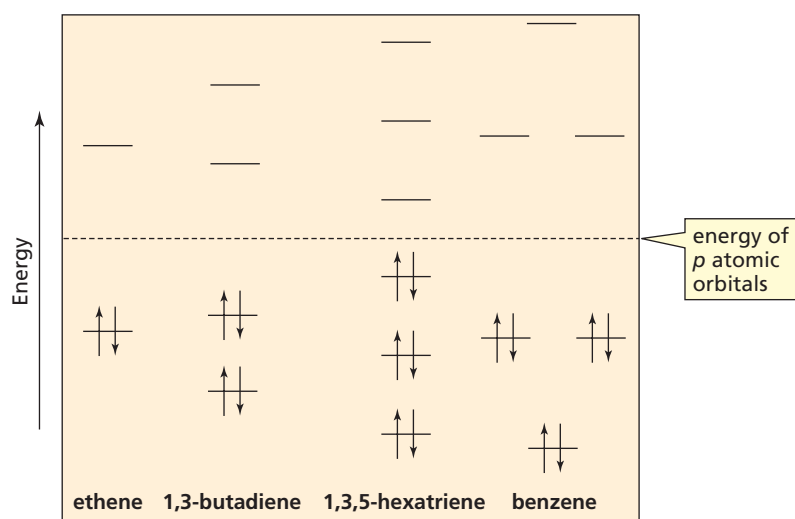


◀ **Figure 7.13**

As the energy of the π molecular orbitals increases, the number of nodes increases and the net number of bonding interactions decreases.



Tutorial:
Common terms



◀ **Figure 7.14**

A comparison of the energy levels of the π molecular orbitals of ethene, 1,3-butadiene, 1,3,5-hexatriene, and benzene.

Summary

Localized electrons belong to a single atom or are confined to a bond between two atoms. **Delocalized electrons** are shared by more than two atoms; they result when a p orbital overlaps the p orbitals of more than one adjacent atom. Electron delocalization occurs only if all the atoms sharing the delocalized electrons lie in or close to the same plane.

Benzene is a planar molecule. Each of its six carbon atoms is sp^2 hybridized, with bond angles of 120° . A p orbital of each carbon overlaps the p orbitals of both adjacent carbons. The six π electrons are shared by all six carbons. Compounds such as benzene that are unusually stable because of large **delocalization energies** are called **aromatic compounds**.

Chemists use **resonance contributors**—structures with localized electrons—to approximate the actual structure of a compound that has delocalized electrons: **the resonance hybrid**. To draw resonance contributors, move only π electrons, lone pairs, or unpaired electrons toward an sp^2 hybridized atom. The total number of electrons and the numbers of paired and unpaired electrons do not change.

The greater the **predicted stability** of the resonance contributor, the more it contributes to the hybrid and the more similar it is to the real molecule. The predicted stability is decreased by (1) an atom with an incomplete octet, (2) a negative (positive) charge not on the most electronegative (electropositive) atom, or (3) charge separation. A resonance hybrid is more stable than the predicted stability of any of its resonance contributors.

The extra stability a compound gains from having delocalized electrons is called **resonance energy**. It tells us how much more stable a compound with delocalized electrons is than it would be if its electrons were localized. The greater the number of relatively stable resonance contributors and the more nearly equivalent they are, the greater is the reso-

nance energy of the compound. Allylic and benzylic cations (and radicals) have delocalized electrons, so they are more stable than similarly substituted carbocations (and radicals) with localized electrons. Donation of a lone pair is called **resonance electron donation**.

Electron delocalization can affect the nature of the product formed in a reaction and the pK_a of a compound. A carboxylic acid and a phenol are more acidic than an alcohol such as ethanol, and a protonated aniline is more acidic than a protonated amine because electron withdrawal stabilizes their conjugate bases and the loss of a proton is accompanied by an increase in resonance energy.

A **molecular orbital** results from the **linear combination of atomic orbitals**. The number of orbitals is conserved: The number of molecular orbitals equals the number of atomic orbitals that produced them. Side-to-side overlap of in-phase p orbitals produces a **bonding molecular orbital**, which is more stable than the atomic orbitals. Side-to-side overlap of out-of-phase p orbitals produces an **antibonding molecular orbital**, which is less stable than the atomic orbitals. The **highest occupied molecular orbital (HOMO)** is the highest-energy MO that contains electrons. The **lowest unoccupied molecular orbital (LUMO)** is the lowest-energy MO that does not contain electrons.

As the MOs increase in energy, the number of **nodes** increases and the number of bonding interactions decreases, and they alternate from being **symmetric** to **asymmetric**. When there is an odd number of molecular orbitals, one must be a **nonbonding molecular orbital**. **Molecular orbital theory** and contributing resonance structures both show that electrons are delocalized and that electron delocalization makes a molecule more stable.

Key Terms

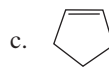
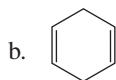
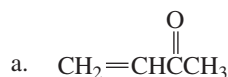
allylic carbon (p. 278)
allylic cation (p. 278)
antibonding molecular orbital (p. 286)
aromatic compounds (p. 292)
asymmetric molecular orbital (p. 288)
benzylic carbon (p. 278)
benzylic cation (p. 278)
bonding molecular orbital (p. 286)
contributing resonance structure (p. 267)
delocalization energy (p. 275)

delocalized electrons (p. 263)
electron delocalization (p. 275)
highest occupied molecular orbital (HOMO) (p. 289)
linear combination of atomic orbitals (LCAO) (p. 287)
localized electrons (p. 263)
lowest unoccupied molecular orbital (LUMO) (p. 289)
nonbonding molecular orbital (p. 290)

resonance (p. 275)
resonance contributor (p. 267)
resonance electron donation (p. 282)
resonance energy (p. 275)
resonance hybrid (p. 268)
resonance structure (p. 267)
separated charges (p. 273)
symmetric molecular orbital (p. 288)

Problems

18. Which of the following compounds have delocalized electrons?



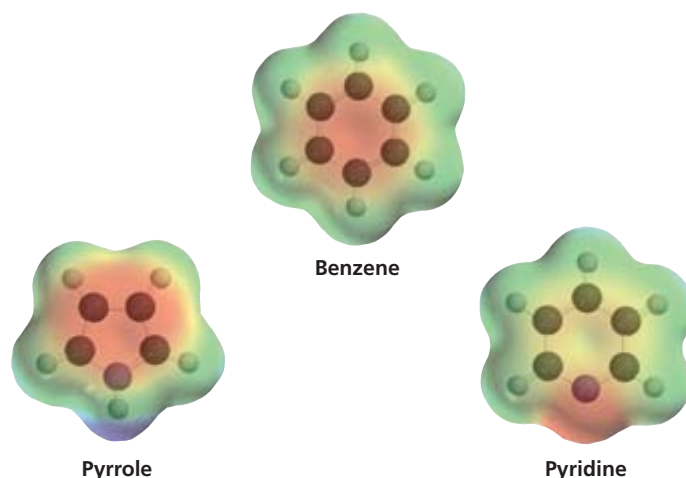
Michael Faraday (1791–1867) was born in England, a son of a blacksmith. At the age of 14, he was apprenticed to a bookbinder and educated himself by reading the books that he bound. He became an assistant to Sir Humphry Davy in 1812 and taught himself chemistry. In 1825, he became the director of a laboratory at the Royal Institution, and, in 1833, he became a professor of chemistry there. He is best known for his work on electricity and magnetism.

Eilhardt Mitscherlich (1794–1863) was born in Germany. He studied oriental languages at the University of Heidelberg and the Sorbonne, where he concentrated on Farsi, hoping that Napoleon would include him in a delegation he intended to send to Persia. That ambition ended with Napoleon's defeat. Mitscherlich returned to Germany to study science, simultaneously receiving a doctorate in Persian studies. He was a professor of chemistry at the University of Berlin.

The compound we know as benzene was first isolated in 1825 by Michael Faraday, who extracted the compound from a liquid residue obtained after heating whale oil under pressure to produce a gas used to illuminate buildings in London. Because of its origin, chemists suggested that it should be called “pheno” from the Greek word *phainein* (“to shine”).

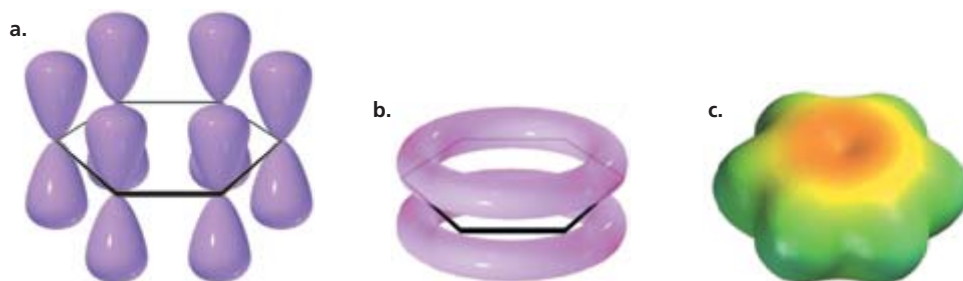
In 1834, Eilhardt Mitscherlich correctly determined benzene's molecular formula (C_6H_6) and decided to call it benzin because of its relationship to benzoic acid, a known substituted form of the compound. Later its name was changed to benzene.

Compounds like benzene, which have relatively few hydrogens in relation to the number of carbons, are typically found in oils produced by trees and other plants. Early chemists called such compounds **aromatic** compounds because of their pleasing fragrances. In this way, they were distinguished from **aliphatic** compounds, with higher hydrogen-to-carbon ratios, that were obtained from the chemical degradation of fats. The chemical meaning of the word “aromatic” now signifies certain kinds of chemical structures. We will now examine the criteria that a compound must satisfy to be classified as aromatic.



15.1 Criteria for Aromaticity

In Chapter 7, we saw that benzene is a planar, cyclic compound with a cyclic cloud of delocalized electrons above and below the plane of the ring (Figure 15.1). Because its π electrons are delocalized, all the C—C bonds have the same length—partway between the length of a typical single and a typical double bond. We also saw that benzene is a particularly stable compound because it has an unusually large resonance energy (36 kcal/mol or 151 kJ/mol). Most compounds with delocalized electrons



◀ **Figure 15.1**

(a) Each carbon of benzene has a p orbital. (b) The overlap of the p orbitals forms a cloud of π electrons above and below the plane of the benzene ring. (c) The electrostatic potential map for benzene shows that all the carbon–carbon bonds have the same electron density.

have much smaller resonance energies. Compounds such as benzene with unusually large resonance energies are called aromatic compounds. How can we tell whether a compound is aromatic by looking at its structure? In other words, what structural features do aromatic compounds have in common?

To be classified as aromatic, a compound must meet both of the following criteria:

1. *It must have an uninterrupted cyclic cloud of π electrons (often called a π cloud) above and below the plane of the molecule. Let's look a little more closely at what this means:*

For the π cloud to be cyclic, the molecule must be cyclic.

For the π cloud to be uninterrupted, every atom in the ring must have a p orbital.

For the π cloud to form, each p orbital must overlap with the p orbitals on either side of it. Therefore, the molecule must be planar.

2. *The π cloud must contain an odd number of pairs of π electrons.*

Benzene is an aromatic compound because it is cyclic and planar, every carbon in the ring has a p orbital, and the π cloud contains *three* pairs of π electrons.

The German chemist Erich Hückel was the first to recognize that an aromatic compound must have an odd number of pairs of π electrons. In 1931, he described this requirement by what has come to be known as **Hückel's rule**, or the **$4n + 2$ rule**. The rule states that for a planar, cyclic compound to be aromatic, its uninterrupted π cloud must contain $(4n + 2)\pi$ electrons, where n is any whole number. According to Hückel's rule, then, an aromatic compound must have 2 ($n = 0$), 6 ($n = 1$), 10 ($n = 2$), 14 ($n = 3$), 18 ($n = 4$), etc., π electrons. Because there are two electrons in a pair, Hückel's rule requires that an aromatic compound have 1, 3, 5, 7, 9, etc., pairs of π electrons. Thus, Hückel's rule is just a mathematical way of saying that an aromatic compound must have an *odd* number of pairs of π electrons.

Aromatic compounds are particularly stable.

For a compound to be aromatic, it must be cyclic and planar and have an uninterrupted cloud of π electrons. The π cloud must contain an odd number of pairs of π electrons.

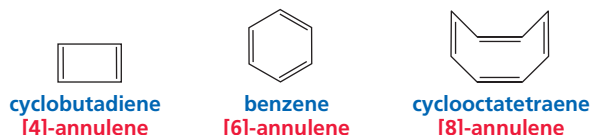
Erich Hückel (1896–1980) was born in Germany. He was a professor of chemistry at the University of Stuttgart and at the University of Marburg.

PROBLEM 1 ♦

- a. What is the value of n in Hückel's rule when a compound has nine pairs of π electrons?
- b. Is such a compound aromatic?

15.2 Aromatic Hydrocarbons

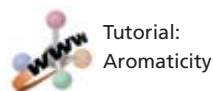
Monocyclic hydrocarbons with alternating single and double bonds are called **annulenes**. A prefix in brackets denotes the number of carbons in the ring. Cyclobutadiene, benzene, and cyclooctatetraene are examples.



3-D Molecules:
Cyclobutadiene;
Benzene;
Cyclooctatetraene

Cyclobutadiene has two pairs of π electrons, and cyclooctatetraene has four pairs of π electrons. Unlike benzene, these compounds are *not* aromatic because they have an *even* number of pairs of π electrons. There is an additional reason why cyclooctatetraene is not aromatic—it is not planar but, instead, tub-shaped. Earlier, we saw that, for an eight-membered ring to be planar, it must have bond angles of 135° (Chapter 2, Problem 28), and we know that sp^2 carbons have 120° bond angles. Therefore, if cyclooctatetraene were planar, it would have considerable angle strain. Because cyclobutadiene and cyclooctatetraene are not aromatic, they do not have the unusual stability of aromatic compounds.

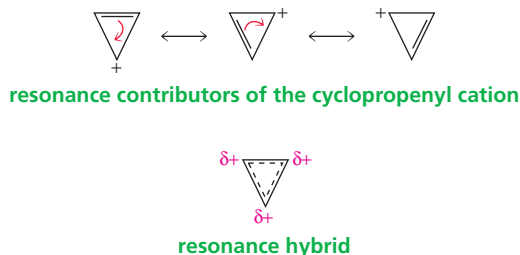
Now let's look at some other compounds and determine whether they are aromatic. Cyclopropene is not aromatic because it does not have an uninterrupted ring of p orbital-bearing atoms. One of its ring atoms is sp^3 hybridized, and only sp^2 and sp hybridized carbons have p orbitals. Therefore, cyclopropene does not fulfill the first criterion for aromaticity.



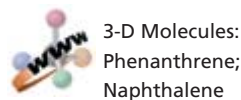
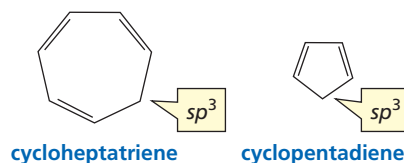
Tutorial:
Aromaticity

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

The cyclopropenyl cation is aromatic because it has an uninterrupted ring of p orbital-bearing atoms and the π cloud contains *one* (an odd number) pair of delocalized π electrons. The cyclopropenyl anion is not aromatic because although it has an uninterrupted ring of p orbital-bearing atoms, its π cloud has *two* (an even number) pairs of π electrons.

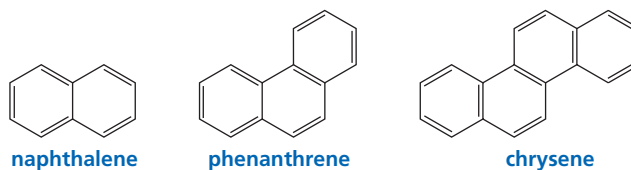


Cycloheptatriene is not aromatic. Although it has the correct number of pairs of π electrons (three) to be aromatic, it does not have an uninterrupted ring of p orbital-bearing atoms because one of the ring atoms is sp^3 hybridized. Cyclopentadiene is also not aromatic: It has an even number of pairs of π electrons (two pairs), *and* it does not have an uninterrupted ring of p orbital-bearing atoms. Like cycloheptatriene, cyclopentadiene has an sp^3 hybridized carbon.



3-D Molecules:
Phenanthrene;
Naphthalene

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





BUCKYBALLS AND AIDS

In addition to diamond and graphite (Section 1.1), a third form of pure carbon was discovered 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, the discoverers of this new form of carbon, shared the 1996 Nobel Prize in chemistry for their discovery. They named this new form buckminsterfullerene (often shortened to fullerene) because it reminded them of the geodesic domes popularized by R. Buckminster Fuller, an American architect and philosopher. The substance is nicknamed “buckyball.” Consisting of a hollow cluster of 60 carbons, fullerene is the most symmetrical large molecule known. Like graphite, fullerene has only sp^2 hybridized carbons, but instead of being arranged in layers, the carbons are arranged in rings, forming a hollow cluster of 60 carbons 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 would appear to be aromatic because of its benzene-like rings. However, it does not undergo electrophilic substitution reactions; instead, it undergoes electrophilic addition reactions like an alkene. Fullerene’s lack of aromaticity is apparently caused by the curvature of the ball, which prevents the molecule from fulfilling the first criterion for aromaticity—that it must be planar.

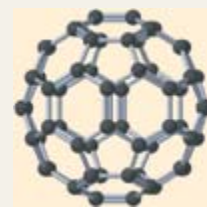
Buckyballs have extraordinary chemical and physical properties. They are exceedingly rugged and are capable of surviving the extreme temperatures of outer space. Because they are essentially hollow cages, they can be manipulated to make materials never before known. For example, when a buckyball is “doped” by inserting potassium or cesium into its cavity, it becomes an excellent

organic superconductor. These molecules are presently being studied for use in many other applications, such as new polymers and catalysts and new drug delivery systems. The discovery of buckyballs is a strong reminder of the technological advances that can be achieved as a result of conducting basic research.

Scientists have even turned their attention to buckyballs in their quest for a cure for AIDS. An enzyme that is required for HIV to reproduce exhibits a nonpolar pocket in its three-dimensional structure. If this pocket is blocked, the production of the virus ceases. Because buckyballs are nonpolar and have approximately the same diameter as the pocket of the enzyme, they are being considered as possible blockers. The first step in pursuing this possibility was to equip the buckyball with polar side chains to make it water soluble so that it could flow through the bloodstream. Scientists have now modified the side chains so that they bind to the enzyme. It’s still a long way from a cure for AIDS, but this represents one example of the many and varied approaches that scientists are taking to find a cure for this disease.



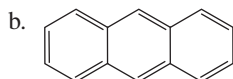
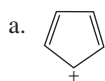
A geodesic dome



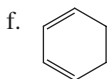
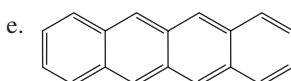
C_{60}
buckminsterfullerene
“buckyball”

PROBLEM 2 ♦

Which of the following compounds are aromatic?



c. cycloheptatrienyl cation



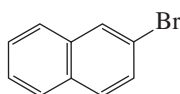
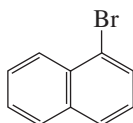
g. cyclononatetraenyl anion

h. $CH_2=CHCH=CHCH=CH_2$

PROBLEM 3 SOLVED

- How many monobromonaphthalenes are there?
- How many monobromophenanthrenes are there?

SOLUTION TO 3a There are two monobromonaphthalenes. Substitution cannot occur at either of the carbons shared by both rings, because those carbons are not bonded to a hydrogen. Naphthalene is a flat molecule, so substitution for a hydrogen at any other carbon will result in one of the compounds shown.



Richard E. Smalley was born in 1943 in Akron, Ohio. He received a B.S. from the University of Michigan and a Ph.D. from Princeton University. He is a professor of chemistry at Rice University.

Robert F. Curl, Jr., was born in Texas in 1933. He received a B.A. from Rice University and a Ph.D. from the University of California, Berkeley. He is a professor of chemistry at Rice University.

Sir Harold W. Kroto was born in 1939 in England and is a professor of chemistry at the University of Sussex.



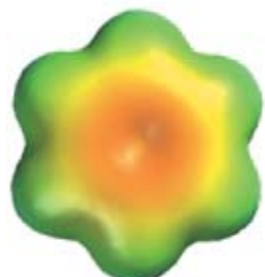
3-D Molecules:
1-Chloronaphthalene;
2-Chloronaphthalene

PROBLEM 4

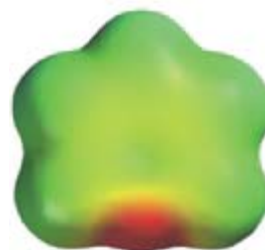
The [10]- and [12]-annulenes have been synthesized, and neither has been found to be aromatic. Explain.

15.3 Aromatic Heterocyclic Compounds

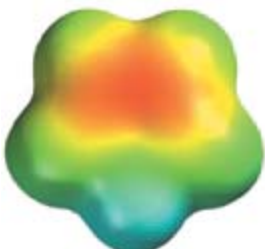
A compound does not have to be a hydrocarbon to be aromatic. Many *heterocyclic compounds* are aromatic. A **heterocyclic compound** is a cyclic compound in which one or more of the ring atoms is an atom other than carbon. A ring atom that is not carbon is called a **heteroatom**. The name comes from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



benzene

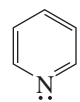


pyridine



pyrrole

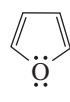
heterocyclic compounds



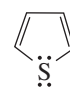
pyridine



pyrrole

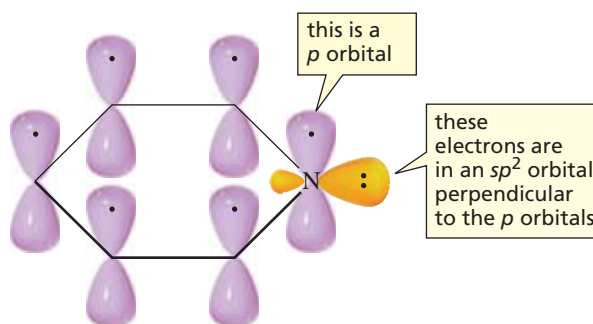


furan



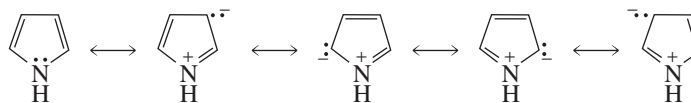
thiophene

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. Don't be confused by the lone-pair electrons on the nitrogen; they are not π electrons. 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 carbon atoms, and nitrogen's third sp^2 orbital contains the lone pair.

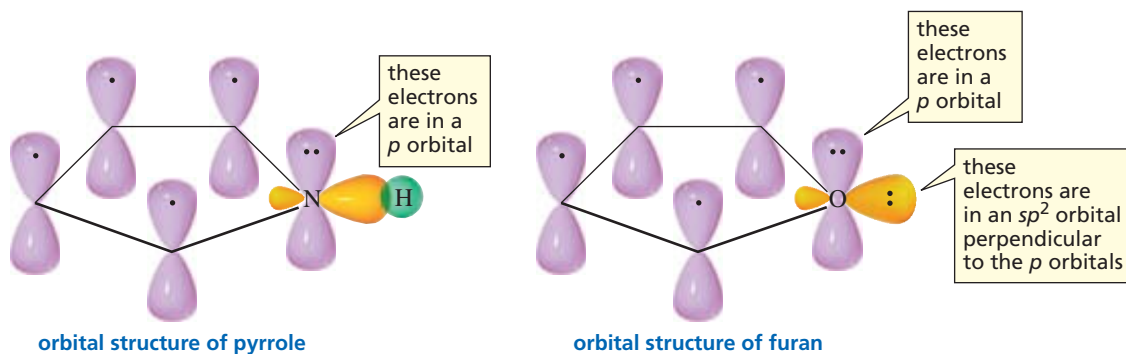


orbital structure of pyridine

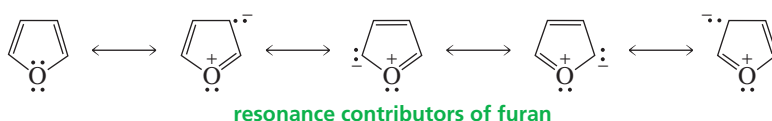
It is not immediately apparent that the electrons represented as lone-pair electrons on the nitrogen atom of pyrrole are π electrons. The resonance contributors, however, show that the nitrogen atom is sp^2 hybridized and uses its three sp^2 orbitals to bond to two carbons and one hydrogen. The lone-pair electrons are in a p orbital that overlaps the p orbitals on adjacent carbons, forming a π bond—thus, they are π electrons. Pyrrole, therefore, has three pairs of π electrons and is aromatic.



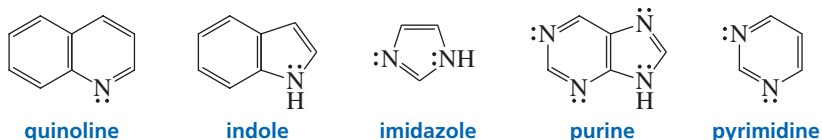
resonance contributors of pyrrole



Similarly, furan and thiophene are stable aromatic compounds. Both the oxygen in the former and the sulfur in the latter are sp^2 hybridized and have one lone pair in an sp^2 orbital. 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.



Quinoline, indole, imidazole, purine, and pyrimidine are other examples of heterocyclic aromatic compounds. The heterocyclic compounds discussed in this section are examined in greater detail in Chapter 21.



PROBLEM 5 ♦

In what orbitals are the electrons represented as lone pairs when drawing the structures of quinoline, indole, imidazole, purine, and pyrimidine?

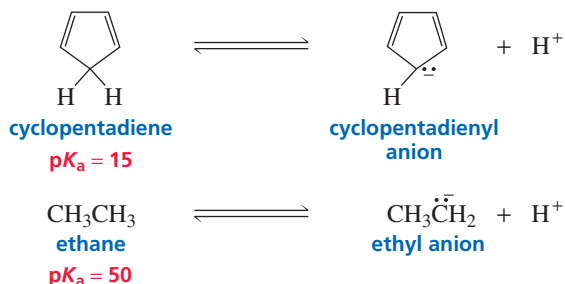
PROBLEM 6

Answer the following questions by examining the electrostatic potential maps on p. 598:

- Why is the bottom part of the electrostatic potential map of pyrrole blue?
- Why is the bottom part of the electrostatic potential map of pyridine red?
- Why is the center of the electrostatic potential map of benzene more red than the center of the electrostatic potential map of pyridine?

15.4 Some Chemical Consequences of Aromaticity

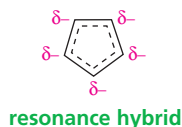
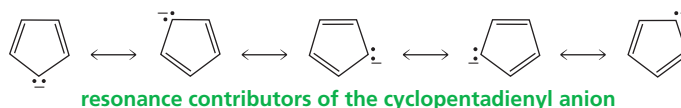
The pK_a of cyclopentadiene is 15, which is extraordinarily acidic for a hydrogen that is bonded to an sp^3 hybridized carbon. Ethane, for example, has a pK_a of 50.





Tutorial:
Aromaticity and acidity

Why is the pK_a of cyclopentadiene so much lower than that of ethane? 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 its conjugate base, the stronger is the acid; see Section 1.18.) All the electrons in the ethyl anion are localized. In contrast, the anion that is formed when cyclopentadiene loses a proton fulfills the requirements for aromaticity: It is cyclic and planar, each atom in the ring has a p orbital, and the π cloud has three pairs of delocalized π electrons. The negatively charged carbon in the cyclopentadienyl anion is sp^2 hybridized because if it were sp^3 hybridized, the ion would not be aromatic. 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.



As a result of its aromaticity, the cyclopentadienyl anion is an unusually stable carbanion. This is why cyclopentadiene has an unusually low pK_a . In other words, it is the stability conveyed by the aromaticity of the cyclopentadienyl anion that makes the hydrogen much more acidic than hydrogens bonded to other sp^3 carbons.

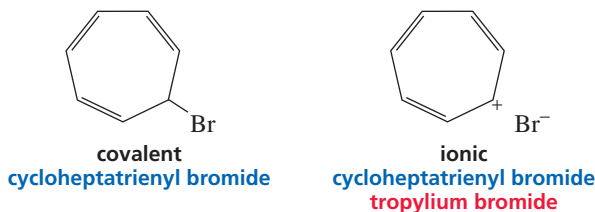
PROBLEM 7♦

Predict the relative pK_a values of cyclopentadiene and cycloheptatriene.

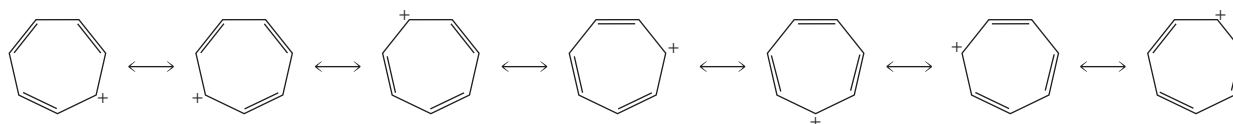
PROBLEM 8

- a. Draw arrows to show the movement of electrons in going from one resonance contributor to the next in
 1. the cyclopentadienyl anion
 2. pyrrole
- b. How many ring atoms share the negative charge in
 1. the cyclopentadienyl anion?
 2. pyrrole?

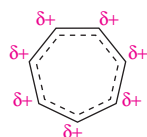
Another example of the influence of aromaticity on chemical reactivity is the unusual chemical behavior exhibited by cycloheptatrienyl bromide. Recall from Section 2.9 that alkyl halides tend to be relatively nonpolar covalent compounds—they are soluble in nonpolar solvents and insoluble in water. Cycloheptatrienyl bromide, however, is an alkyl halide that behaves like an ionic compound—it is insoluble in nonpolar solvents, but readily soluble in water.



Cycloheptatrienyl bromide is an ionic compound because its cation is aromatic. The alkyl halide is *not* aromatic in the covalent form because it has an sp^3 hybridized carbon, so it does *not* have an uninterrupted ring of p orbital-bearing atoms. In the ionic form, however, the cycloheptatrienyl cation (also known as the tropylium cation) *is* aromatic because it is a planar cyclic ion, all the ring atoms are sp^2 hybridized (which means that each ring atom has a p orbital), and it has three pairs of delocalized π electrons. The stability associated with the aromatic cation causes the alkyl halide to exist in the ionic form.



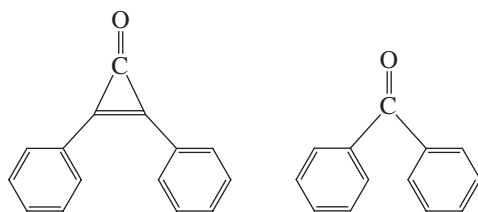
resonance contributors of the cycloheptatrienyl cation



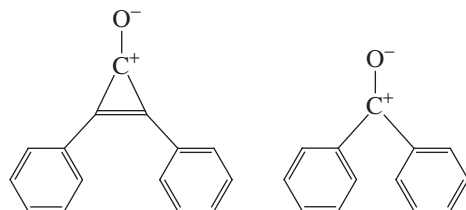
resonance hybrid

PROBLEM-SOLVING STRATEGY

Which of the following compounds has the greater dipole moment?



Before attempting to answer this kind of question, make sure that you know exactly what the question is asking. You know that the dipole moment of these compounds results from the unequal sharing of electrons by carbon and oxygen. Therefore, the more unequal the sharing, the greater is the dipole moment. So now the question becomes, which compound has a greater negative charge on its oxygen atom? Draw the structures with separated charges, and determine their relative stabilities. In the case of the compound on the left, the three-membered ring becomes aromatic when the charges are separated. In the case of the compound on the right, the structure with separated charges is not aromatic. Because being aromatic makes a compound more stable, the compound on the left has the greater dipole moment.

**PROBLEM 9**

Draw the resonance contributors of the cyclooctatrienyl dianion.

- Which of the resonance contributors is the least stable?
- Which of the resonance contributors makes the smallest contribution to the hybrid?

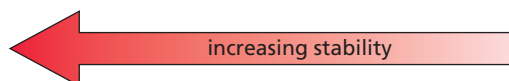
Antiaromatic compounds are highly unstable.

15.5 Antiaromaticity

An aromatic compound is *more stable* than an analogous cyclic compound with localized electrons. In contrast, an **antiaromatic** compound is *less stable* than an analogous cyclic compound with localized electrons. *Aromaticity is characterized by stability, whereas antiaromaticity is characterized by instability.*

relative stabilities

aromatic compound > cyclic compound with localized electrons > antiaromatic compound



A compound is classified as being antiaromatic if it fulfills the first criterion for aromaticity but does not fulfill the second criterion. 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. Hückel would state that the π cloud must contain $4n$ π electrons, where n is any whole number—a mathematical way of saying that the cloud must contain an *even* number of pairs of π electrons.

Cyclobutadiene is a planar, cyclic molecule with two pairs of π electrons. Hence, it is expected to be antiaromatic and highly unstable. In fact, it is too unstable to be isolated, although it has been trapped at very cold temperatures. The cyclopentadienyl cation also has two pairs of π electrons, so we can conclude that it is antiaromatic and unstable.



cyclobutadiene



cyclopentadienyl cation

PROBLEM 10♦

- Predict the relative pK_a values of cyclopropene and cyclopropane.
- Which is more soluble in water, 3-bromocyclopropene or bromocyclopropane?

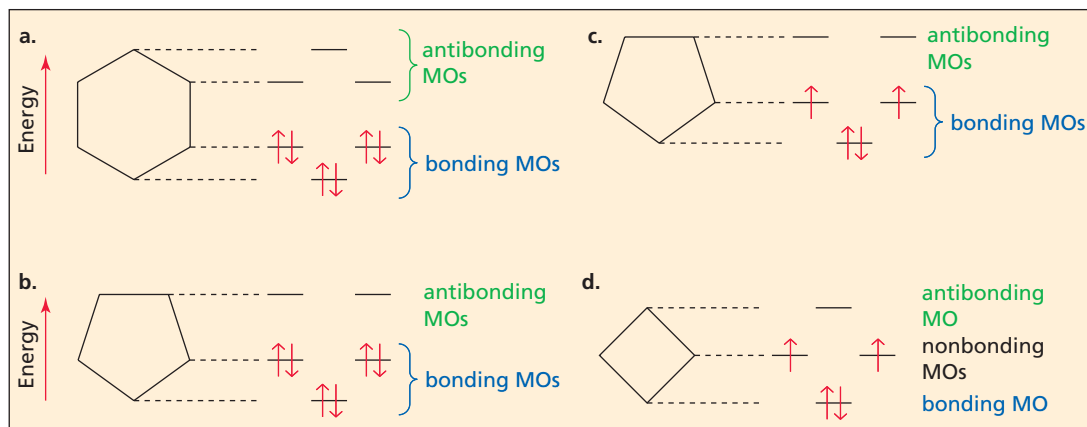
PROBLEM 11♦

Which of the compounds in Problem 2 are antiaromatic?

15.6 A Molecular Orbital Description of Aromaticity and Antiaromaticity

Why are planar molecules with uninterrupted cyclic π electron clouds highly stable (aromatic) if they have an odd number of pairs of π electrons and highly unstable (antiaromatic) if they have an even number of pairs of π electrons? To answer this question, we must turn to molecular orbital theory.

The relative energies of the π molecular orbitals of a planar molecule with an uninterrupted cyclic π electron cloud can be determined—without having to use any math—by first drawing the cyclic compound with one of its vertices pointed down. The relative energies of the π molecular orbitals correspond to the relative levels of the vertices (Figure 15.2). Molecular orbitals below the midpoint of the cyclic structure are bonding molecular orbitals, those above the midpoint are antibonding molecular orbitals, and any at the midpoint are nonbonding molecular orbitals. This scheme is sometimes called a Frost device (or a Frost circle) in honor of Arthur A. Frost, an



▲ **Figure 15.2**

The distribution of electrons in the π molecular orbitals of (a) benzene, (b) the cyclopentadienyl anion, (c) the cyclopentadienyl cation, and (d) cyclobutadiene. The relative energies of the π molecular orbitals in a cyclic compound correspond to the relative levels of the vertices. Molecular orbitals below the midpoint of the cyclic structure are bonding, those above the midpoint are antibonding, and those at the midpoint are nonbonding.

American scientist who devised this simple method. Notice that the number of π molecular orbitals is the same as the number of atoms in the ring because each ring atom contributes a p orbital. (Recall that orbitals are conserved; Section 7.11.)

The six π electrons of benzene occupy its three bonding π molecular orbitals, and the six π electrons of the cyclopentadienyl anion occupy *its* three bonding π molecular orbitals. Notice that there is always an odd number of bonding orbitals because one corresponds to the lowest vertex and the others come in degenerate pairs. This means that aromatic compounds—such as benzene and the cyclopentadienyl anion—with an odd number of pairs of π electrons have completely filled bonding orbitals and no electrons in either nonbonding or antibonding orbitals. This is what gives aromatic molecules their stability. (A more in-depth description of the molecular orbitals in benzene is given in Section 7.11.)

Antiaromatic compounds have an even number of pairs of π electrons. Therefore, either they are unable to fill their bonding orbitals (cyclopentadienyl cation) or they have a pair of π electrons left over after the bonding orbitals are filled (cyclobutadiene). Hund's rule requires that these two electrons go into two degenerate orbitals (Section 1.2). The unpaired electrons are responsible for the instability of antiaromatic molecules.



Tutorial:
Molecular orbital description
of aromaticity

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

PROBLEM 12♦

How many bonding, nonbonding, and antibonding π molecular orbitals does cyclobutadiene have? In which molecular orbitals are the π electrons?

PROBLEM 13♦

Can a radical be aromatic?

PROBLEM 14

Following the instructions for drawing the π molecular orbital energy levels of the compounds shown in Figure 15.2, draw the π molecular orbital energy levels 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? Which are antiaromatic?