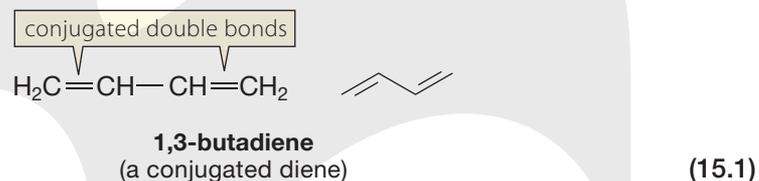


15 | DIENES AND AROMATICITY

Dienes are compounds with two carbon–carbon double bonds. Their nomenclature was discussed along with the nomenclature of other alkenes in Sec. 4.2A. Dienes are classified according to the relative position of their double bonds. In **conjugated dienes**, two double bonds are separated by one single bond. These double bonds are called **conjugated double bonds**.

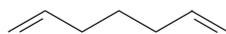


Cumulenes are compounds in which one carbon participates in two carbon–carbon double bonds; these double bonds are called **cumulated double bonds**. Propadiene (common name, allene) is the simplest cumulene. The term *allene* is also sometimes used as a family name for compounds containing only two cumulated double bonds.



Conjugated dienes and cumulenes have unique structures and chemical properties that are the basis for much of the discussion here in Chapter 15.

Dienes in which the double bonds are separated by two or more single bonds have structures and chemical properties more or less like those of simple alkenes and do not require special discussion. We refer to these dienes as “ordinary” dienes.



1,6-heptadiene
(an ordinary diene)

In this chapter, the interaction of two functional groups within the same molecule—in this case, two carbon–carbon double bonds—can result in special reactivity. In particular, we explain how conjugated double bonds differ in their reactivity from ordinary double bonds. This discussion leads to a consideration of benzene, a cyclic hydrocarbon in which the effects of conjugation are particularly unique. The chemistry of benzene and the effects of conjugation on chemical properties continue as central themes through Chapter 18.

15.1 STRUCTURE AND STABILITY OF DIENES

A. Stability of Conjugated Dienes. Molecular Orbitals

The heats of formation listed in **Table 15.1** provide information about the relative stabilities of dienes. The effect of conjugation on the stability of dienes can be deduced from a comparison of the heats of formation for (*E*)-1,3-hexadiene, a conjugated diene, and (*E*)-1,4-hexadiene, an unconjugated isomer. The heats of formation show that the conjugated diene is 19.7 kJ mol^{-1} ($4.7 \text{ kcal mol}^{-1}$) more stable than its unconjugated isomer. Because the double bonds in these two compounds have the same number of branches and the same stereochemistry, this stabilization of nearly 20 kJ mol^{-1} (5 kcal mol^{-1}) is due to conjugation.

TABLE 15.1 Heats of Formation of Dienes and Alkynes

| Compound | Structure | ΔH_f° (25 °C, gas phase) | |
|-----------------------------|---|---------------------------------------|------------------------|
| | | kJ mol^{-1} | kcal mol^{-1} |
| (<i>E</i>)-1,3-hexadiene | | 54.4 | 13.0 |
| (<i>E</i>)-1,4-hexadiene | | 74.1 | 17.7 |
| 1-pentyne | $\text{HC}\equiv\text{CCH}_2\text{CH}_2\text{CH}_3$ | 144 | 34.5 |
| 2-pentyne | $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$ | 129 | 30.8 |
| (<i>E</i>)-1,3-pentadiene | | 75.8 | 18.1 |
| 1,4-pentadiene | $\text{H}_2\text{C}=\text{CHCH}_2\text{CH}=\text{CH}_2$ | 106 | 25.4 |
| 1,2-pentadiene | $\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{CH}_3$ | 141 | 33.6 |
| 2,3-pentadiene | $\text{CH}_3\text{CH}=\text{C}=\text{CHCH}_3$ | 133 | 31.8 |

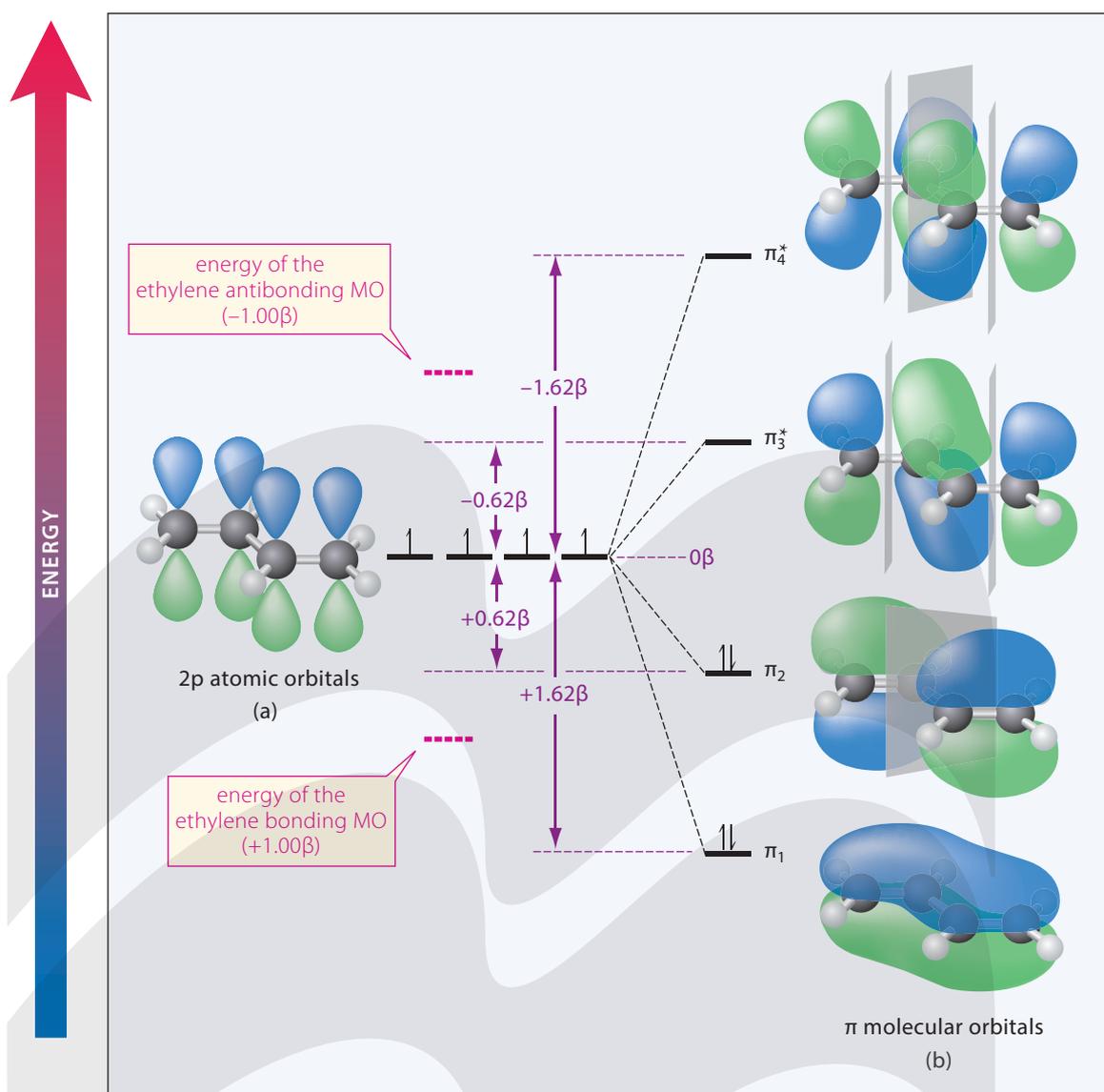


FIGURE 15.1 An orbital interaction diagram showing π molecular orbital (MO) formation in 1,3-butadiene. (a) Arrangement of 2p orbitals in 1,3-butadiene, the simplest conjugated diene. The axes of the 2p orbitals are properly aligned for overlap. (b) Interaction of the four 2p orbitals (dashed black lines) gives four π MOs. Nodal planes are shown in gray. Nodes occur between peaks and troughs in the MOs, indicated by blue and green, respectively. (The original nodal plane of the starting 2p orbitals in the plane of the molecule, which is also present in all of the MOs, is not shown.) The four 2p electrons both go into π_1 and π_2 , the bonding MOs. The violet arrows and numbers show the relative energies of the MOs in β units. (β is a negative number.) The relative energies of the ethylene MOs are shown in red.

The major reason for the greater stability of conjugated dienes is the overlap of 2p orbitals across the carbon–carbon single bond connecting the two alkene units. That is, not only does π bonding occur *within* each of the alkene units, but *between* them as well. **Figure 15.1a** shows the alignment of carbon 2p orbitals in 1,3-butadiene, the simplest conjugated diene. Notice that the 2p orbitals on the central carbons are in the parallel alignment necessary for overlap.

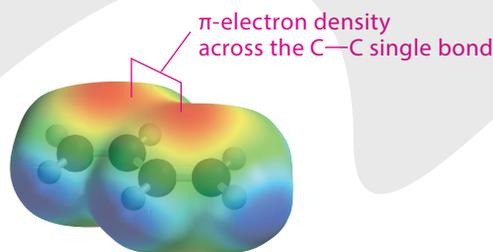
As we showed when we considered π bonding in ethylene (see Fig. 4.3, Sec. 4.1C), the overlap of 2p orbitals results in the formation of π molecular orbitals. The overlap of j 2p orbitals results in the formation of j molecular orbitals. In the case of a conjugated diene, $j = 4$. Therefore, four molecular orbitals (MOs) are formed. For a conjugated diene, half of the MOs are bonding—they have a lower energy than an isolated 2p atomic orbital. The other half are antibonding—they have a higher energy than an isolated 2p atomic orbital. These four MOs for 1,3-butadiene, the simplest conjugated diene, are shown in **Fig. 15.1b**. First of all, each π MO retains a node in the plane of the molecule like the 2p orbitals from which it is formed. (This node is not shown in

Fig. 15.1.) The MO of lowest energy, π_1 , has no additional nodes. Each MO of successively higher energy has one additional planar node, and these nodes are symmetrically arranged within the π system. Therefore, the second bonding MO, π_2 , has one additional planar node between the two interior carbons. The antibonding MOs π_3^* and π_4^* have two and three additional planar nodes, respectively. (The asterisk indicates their antibonding character.)

1,3-Butadiene has four 2p electrons; these electrons are distributed into the four MOs. Because each MO can accommodate two electrons, two electrons are placed into π_1 and two into π_2 . These two bonding MOs, then, are the ones we want to examine to understand the bonding and stability of conjugated dienes. Consider first the energies of these bonding MOs. These are shown to scale relative to the energies of the ethylene MOs (see Fig. 4.3, Sec. 4.1C). The energy unit conventionally used with π MOs is called **beta** (β), which, for conjugated alkenes, has a value of roughly -50 kJ mol^{-1} ($-12 \text{ kcal mol}^{-1}$). By convention, β is a negative number. The π_1 MO of butadiene has a relative energy of 1.62β , and π_2 has a relative energy of 0.62β . Each π electron in butadiene contributes to the molecule the energy of its MO. Therefore, the two electrons in π_1 contribute $2 \times (1.62\beta) = 3.24\beta$, and the two electrons in π_2 contribute $2 \times (0.62\beta) = 1.24\beta$. The total π electron energy for 1,3-butadiene, then, is 4.48β .

To calculate the bonding advantage of a conjugated diene due to π -electron delocalization, we compare it to the π -electron energy of two isolated ethylene molecules—that is, two π -electron systems in which there is no overlap between the double bonds. As Fig. 15.1 shows, the bonding MO of ethylene lies at 1.00β ; the two bonding π electrons of ethylene contribute a π -electron energy of 2.00β , and the π electrons of two isolated ethylenes contribute 4.00β . It follows that the energetic advantage of conjugation—orbital overlap—in 1,3-butadiene is $4.48\beta - 4.00\beta = 0.48\beta$. This energetic advantage must result from π_1 , which is the MO with lower energy than the bonding MO of ethylene.

Half of the total π -electron density in 1,3-butadiene is contributed by the two electrons in π_1 and half by the two electrons in π_2 . Consider now the nodal structure of these two molecular orbitals. The π_2 MO has a node that divides the molecule into two isolated “ethylene halves;” so, the electrons in this MO contribute some isolated double-bond character to the π -electron structure of 1,3-butadiene. However, the π_1 MO has no node perpendicular to the plane of the molecule; consequently, the π -electron density in this MO is spread across the entire molecule—that is, the electrons in π_1 are **delocalized**. In particular, this MO contributes to bonding between the two central carbons—the carbons connected by the “single bond.” The delocalization of π electrons across the central single bond is also evident from the electrostatic potential maps (EPM) of 1,3-butadiene.



EPM of 1,3-butadiene

(15.3)

This analysis shows that electron delocalization, which is not adequately conveyed by Lewis structures, is responsible for the additional stability associated with conjugation. *Conjugation results in additional bonding that makes a molecule more stable.*

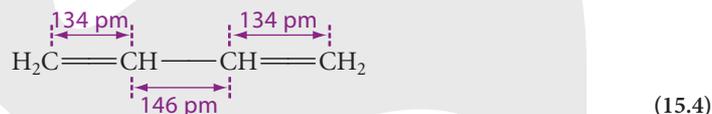
The energetic advantage of conjugation is called the **delocalization energy**. This name colorfully describes its origin—the delocalization of electrons in π_1 . Because β is negative, the delocalization energy describes the *reduction* in energy (that is, the increased stability) of a conjugated diene relative to two isolated, unconjugated ethylenes. In other words, the delocalization energy is energy that the molecule “doesn’t have.” Therefore, the delocalization energy of 0.48β for 1,3-butadiene means that this conjugated diene is more stable than two unconjugated ethylene molecules by 0.48β .

Focused Problems

- 15.1 The conjugated triene (*E*)-1,3,5-hexatriene has six π molecular orbitals with relative energies $\pm 1.80\beta$, $\pm 1.25\beta$, and $\pm 0.44\beta$. (a) Sketch these MOs. Indicate which are bonding and which are antibonding. (b) Tell how many nodes each has. (c) Show the position of the nodes in π_1 , π_2 , and π_6^* .
- 15.2 Calculate the delocalization energy for (*E*)-1,3,5-hexatriene.
- 15.3 Explain why there is a larger *difference* between the heats of formation of (*E*)-1,3-pentadiene and 1,4-pentadiene (29.3 kJ mol^{-1} or $7.1 \text{ kcal mol}^{-1}$) than between (*E*)-1,3-hexadiene and (*E*)-1,4-hexadiene (19.7 kJ mol^{-1} or $4.7 \text{ kcal mol}^{-1}$).

B. Structure of Conjugated Dienes

The length of the carbon-carbon single bond in 1,3-butadiene reflects the hybridization of the orbitals from which it is constructed. At 146 pm, this $\text{sp}^2\text{-sp}^2$ single bond is considerably shorter than both the $\text{sp}^2\text{-sp}^3$ carbon-carbon single bond in propene (150 pm) and the $\text{sp}^3\text{-sp}^3$ carbon-carbon bond in ethane (154 pm).



Section 4.1B noted that, as the fraction of *s* character in the component orbitals increases, the length of the bond decreases. (See Display 4.2, Sec. 4.1C.)

Conjugated dienes such as 1,3-butadiene undergo rapid internal rotation about the central single bond of the diene unit. 1,3-Butadiene has two stable conformations. The most stable conformation is the ***s*-trans conformation**. (The *s* prefix emphasizes that this refers to rotation about a *single* bond.) This conformation is sometimes called the **anti conformation**. The second conformation is the **gauche** or **skew conformation**. These conformations and their relative standard free energies are shown in Fig. 15.2a; Newman projections are shown in Fig. 15.2b. (The *s*-trans conformation is shown in Fig. 15.1 as well.) In the *s*-trans conformation, the 2p orbitals of all carbons are coplanar and can overlap. In the gauche conformation, the 2p orbitals of one double bond are twisted 38° relative to those of the other, at the cost of some orbital overlap. The partial loss of overlap accounts for the higher energy of the gauche conformation. The energy barrier between the two conformations, which is greatest at 102° , largely reflects the complete loss of overlap at this angle. The third conformation shown in Fig. 15.2a, the ***s*-cis conformation**, is unstable. In this conformation, the 2p orbitals are coplanar, but van der Waals repulsions between two of the hydrogens (shown in Fig. 15.2a) destabilize this conformation; in the gauche conformation, the offending hydrogens are further apart. Despite the instability of the *s*-cis conformation, it is important in some reactions of conjugated dienes (Sec. 15.3).

Focused Problem

- 15.4 Draw the *s*-cis and *s*-trans conformations of (*2E,4E*)-2,4-hexadiene and (*2E,4Z*)-2,4-hexadiene. Which diene contains the *greater* proportion of the gauche conformation? Why? (Use the *s*-cis conformation as an approximation of the gauche conformation in your drawing.)

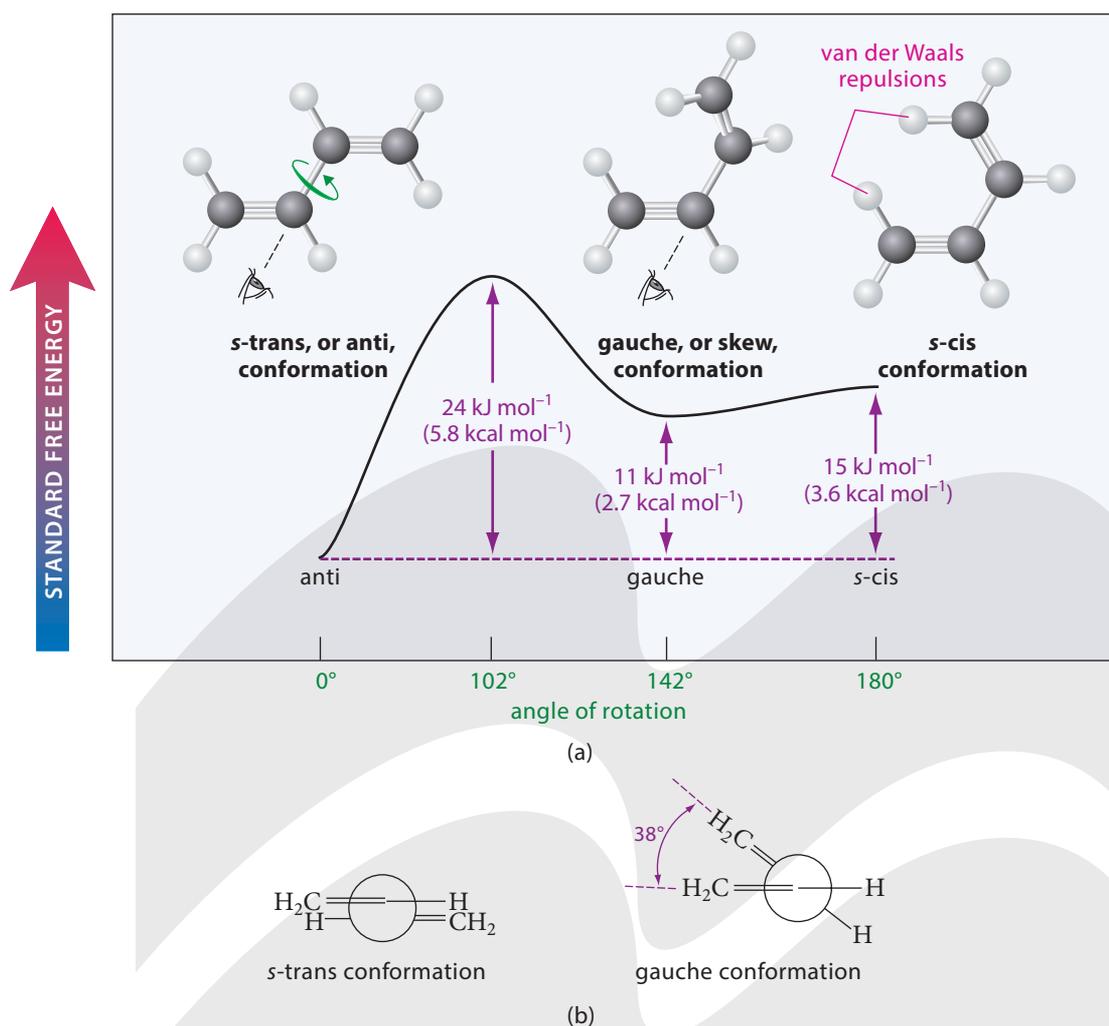


FIGURE 15.2 (a) The conformations of 1,3-butadiene and their relative standard free energies. Internal rotation occurs about the central carbon–carbon single bond (green arrow; rotation angles are shown in green along the horizontal axis). (b) Newman projections of the two stable conformations obtained by sighting along the central carbon–carbon single bond, as shown by the eyeball in (a).

C. Structure and Stability of Cumulated Dienes

The structure of allene is shown in **Fig. 15.3**. Because the central carbon of allene is bound to two groups, the carbon skeleton of this molecule is linear (Sec. 1.3B). A carbon atom with 180° bond angles is sp -hybridized (Sec. 1.7D). Therefore, the central carbon of allene, like the carbons in an alkyne triple bond, is sp -hybridized; it is much like the carbon in CO_2 (Display 1.73, Sec. 1.7D). The two remaining carbons of the cumulated diene are sp^2 -hybridized and have trigonal planar geometry.

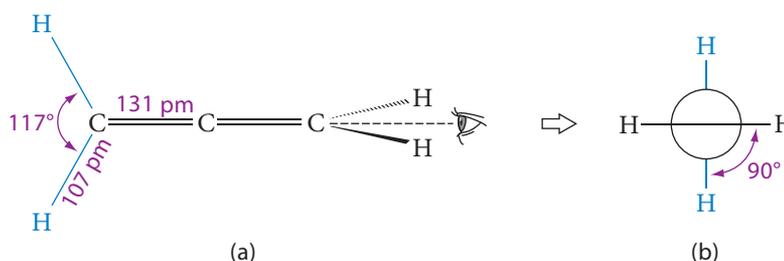
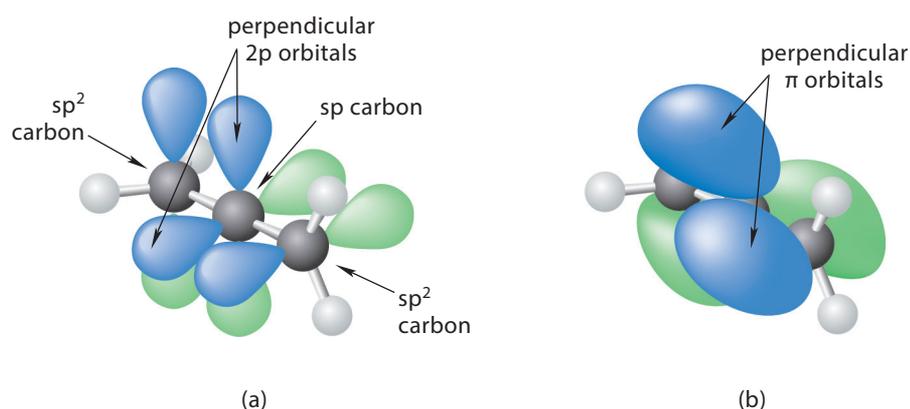
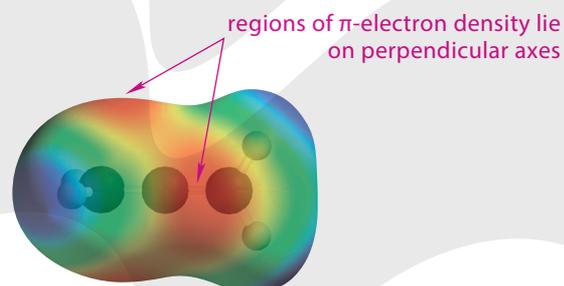


FIGURE 15.3 The structure of allene, the simplest cumulated diene. (a) Lewis structure showing the bond angles and bond lengths. (b) A Newman projection along the carbon–carbon double bond as seen by the eyeball. The CH_2 groups at opposite ends of the molecule lie in perpendicular planes. (A model is shown in Fig. 15.4.)

FIGURE 15.4 The π -electron structure of allene. The blue and green orbital colors represent wave peaks and wave troughs. (a) The component 2p orbitals of the double bonds. Because the central carbon is sp -hybridized, it has two mutually perpendicular 2p orbitals. (b) The π molecular orbitals that result from overlap of the 2p orbitals are mutually perpendicular and do not overlap.



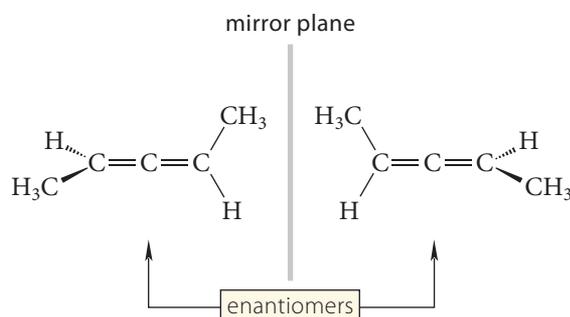
The two π bonds in allenes are mutually perpendicular, as required by the sp hybridization of the central carbon atom (Fig. 15.4). Consequently, the $H-C-H$ plane at one end of the allene molecule is perpendicular to the $H-C-H$ plane at the other end, as shown by the Newman projection in Fig. 15.3. Notice the difference in the bonding arrangements in allene and the conjugated diene 1,3-butadiene. In the conjugated diene, the π -electron systems of the two double bonds are coplanar and can overlap; all carbon atoms are sp^2 -hybridized. In contrast, allene contains two mutually perpendicular π systems, each spanning two carbons; the central carbon is part of both. Because these two π systems are perpendicular, they do *not* overlap. The perpendicular π orbitals of allene are reflected in the EPM of allene, which shows areas of π -electron density above and below each double bond.



EPM of allene

(15.5)

Because of their geometries, some allenes are chiral even though they do not contain an asymmetric carbon atom. 2,3-Pentadiene is a chiral allene:



(15.6)

This is an example of *twist chirality*, which was discussed in Sec. 6.8.

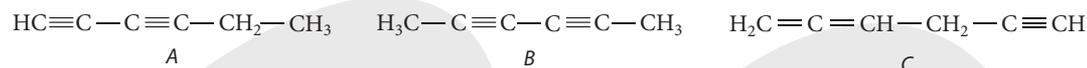
The sp hybridization of allenes is reflected in their $C=C$ stretching absorptions in the infrared spectrum. This absorption occurs near 1950 cm^{-1} , not far from the $C\equiv C$ stretching absorption of alkynes.

The data in Table 15.1 show that allenes have greater heats of formation than other types of isomeric dienes. For example, 1,2-pentadiene is considerably less stable than 1,3-pentadiene or 1,4-pentadiene. Therefore, the cumulated arrangement is the least stable arrangement of two double bonds. A comparison of the heats of formation of 2-pentyne and 2,3-pentadiene shows that allenes are somewhat less stable than isomeric alkynes as well. In fact, a common reaction of allenes is isomerization to alkynes.

Although a few naturally occurring allenes are known, allenes are relatively rare in nature.

Focused Problem

15.5 Rank the following compounds in order of increasing stability (decreasing heats of formation). Give reasons for your choices.



15.2 ULTRAVIOLET–VISIBLE SPECTROSCOPY AND FLUORESCENCE

The IR and NMR spectra of conjugated dienes are very similar to the spectra of ordinary alkenes. However, another type of spectroscopy can be used to analyze and identify organic compounds containing conjugated double and triple bonds. In this type of spectroscopy, called **ultraviolet–visible spectroscopy**, the absorption of radiation in the ultraviolet or visible region of the spectrum is recorded as a function of wavelength. The part of the ultraviolet spectrum of greatest interest to organic chemists is the *near ultraviolet* (wavelength range 200×10^{-9} to 400×10^{-9} m). Visible light, as the name implies, is electromagnetic radiation visible to the human eye (wavelengths from 400×10^{-9} to 750×10^{-9} m). Because there is a common physical basis for the absorption of both ultraviolet and visible radiation by chemical compounds, both ultraviolet and visible spectroscopy are considered together as one type of spectroscopy, often called simply **UV–vis spectroscopy**.

Some molecules, after absorption of UV or visible radiation, can lose some of the energy gained during absorption by emission of light. We conclude this section with a description of one type of light emission, called *fluorescence*, which is a particularly important analytical technique in biology.

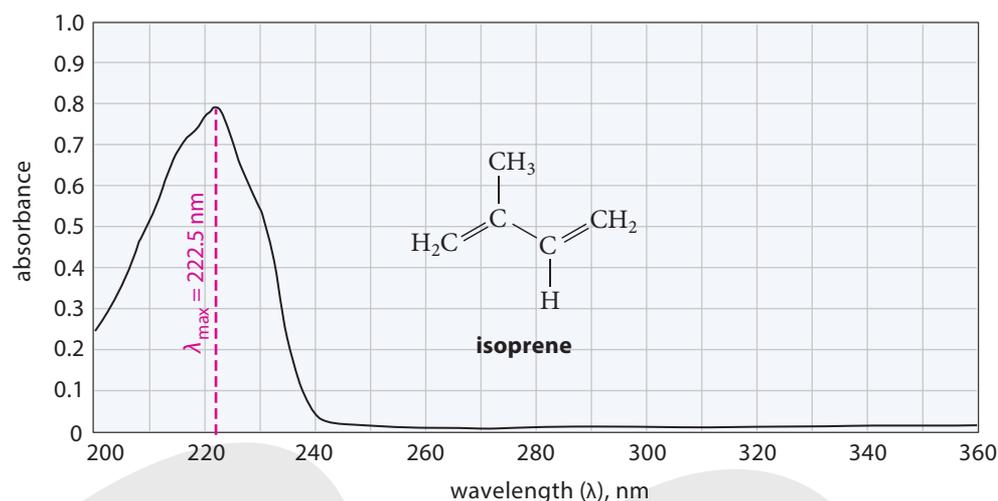
A. The UV–Vis Spectrum

Like any other absorption spectrum, the **UV–vis spectrum** of a substance is the graph of radiation absorption by the substance versus the wavelength of the radiation. The instrument used to measure a UV–vis spectrum is called a **UV–vis spectrophotometer**. Except for the fact that it is designed to operate in a different part of the electromagnetic spectrum, it is conceptually much like any other absorption spectrometer (see Fig. 13.3, Sec. 13.1A).

A typical UV spectrum, that of 2-methyl-1,3-butadiene (isoprene), is shown in Fig. 15.5. Because isoprene does not absorb visible light, only the ultraviolet region of the spectrum is shown. On the horizontal axis of the UV spectrum is plotted the wavelength λ of the radiation. In UV spectroscopy, the conventional unit of wavelength is the *nanometer* (abbreviated nm). One **nanometer** equals 10^{-9} meter. (In older literature, the term *millimicron*, abbreviated m μ , was used; a millimicron is the same as a nanometer.) The relationship between the energy of the electromagnetic radiation and its frequency or wavelength should be reviewed again (Sec. 13.1A).

The vertical axis of a UV spectrum shows the **absorbance**. (Absorbance is sometimes called **optical density**, abbreviated OD.) The absorbance is a measure of the amount of radiant energy

FIGURE 15.5 Ultraviolet-visible spectrum of isoprene in methanol. The λ_{max} (red) is the wavelength at which the absorption maximum occurs; for isoprene, $\lambda_{\text{max}} = 222.5 \text{ nm}$.



absorbed. Suppose the radiation entering a sample has intensity I_0 , and the light emerging from the sample has intensity I . The absorbance A is defined as the logarithm of the ratio I_0/I :

$$A = \log(I_0/I) \quad (15.7)$$

According to Eq. 15.7, then, as more radiant energy is absorbed (that is, as I decreases), the ratio I_0/I increases, as does the absorbance.

Focused Problems

- 15.6 What is the energy of light (in kJ mol^{-1} or kcal mol^{-1}) with a wavelength of
- (a) 450 nm? (b) 250 nm?
- 15.7 (a) What percent of the incident radiation is transmitted by a sample when its absorbance is 1.0? When its absorbance is 0?
- (b) What is the absorbance of a sample that transmits one-half of the incident radiation intensity?
- 15.8 A thin piece of red glass held up to white light appears brighter to the eye than a piece of the same glass that is twice as thick. Which piece has the greater absorbance?

In the UV-vis spectra used in this text, absorbance increases from the bottom to the top of the spectrum. Therefore, absorption maxima occur as high points or peaks in the spectrum. Notice the difference in how UV-vis and IR spectra are presented. (Absorptions in IR spectra increase from top to bottom because IR spectra are conventionally presented as plots of *transmittance*, or percentage of light transmitted; Sec. 13.2A.) In the UV-vis spectrum shown in Fig. 15.5, the absorbance maximum occurs at a wavelength of 222.5 nm. The wavelength at the maximum of an absorption peak is called the λ_{max} (pronounced “lambda-max”). Some compounds have several absorption peaks and a corresponding number of λ_{max} values. Absorption peaks in the UV-vis spectra of compounds in solution are generally quite broad. That is, peak widths span a considerable range of wavelength, typically 50 nm or more. (The reason is discussed in Further Exploration 15.1 in the *Study Guide and Solutions Manual*.)

The absorbance at a given wavelength depends on the number of molecules in the light path. If a sample is contained in a vessel with a thickness along the light path of l cm, and the absorbing



FURTHER EXPLORATION 15.1
More on UV Spectroscopy

compound is present at a concentration of c moles per liter, then the absorbance is proportional to the product lc .

$$A = \epsilon lc \quad (15.8)$$

This equation is called the *Beer–Lambert law* or simply **Beer’s law**. The constant of proportionality ϵ is called the **molar extinction coefficient** or **molar absorptivity**. The units of ϵ are $\text{L mol}^{-1} \text{cm}^{-1}$, or $M^{-1} \text{cm}^{-1}$; these units are sometimes omitted when values of ϵ are cited. Each absorption in a given spectrum has a unique extinction coefficient that depends on wavelength, solvent, and temperature. The larger is ϵ , the greater is the light absorption at a given concentration c and path length l . For example, the extinction coefficient of isoprene (see Fig. 15.5) at its λ_{max} of 222.5 nm is $10,750 M^{-1} \text{cm}^{-1}$ in methanol solvent at 25 °C; its extinction coefficient in alkane solvents is nearly twice as large.

Extinction coefficients of 10^4 – $10^5 M^{-1} \text{cm}^{-1}$ are common for molecules with conjugated π -electron systems. This means that strong absorptions can be obtained from very dilute solutions—solutions with concentrations on the order of 10^{-4} to $10^{-6} M$ with a typical path length of 1 cm. Because of its intrinsic sensitivity and its relatively simple instrumentation, UV–vis spectroscopy was one of the earliest forms of spectroscopy to be used routinely in the laboratory; adequate spectra could be obtained on even the most primitive spectrometers. UV–vis spectroscopy remains an important method for quantitative analysis.

Some UV–vis spectra are presented in abbreviated form by citing the λ_{max} values of their principal peaks, the solvent used, and the extinction coefficients. For example, the spectrum in Fig. 15.5 is summarized as follows:

$$\lambda_{\text{max}}(\text{CH}_3\text{OH}) = 222.5 \text{ nm } (\epsilon = 10,750)$$

or

$$\lambda_{\text{max}}(\text{CH}_3\text{OH}) = 222.5 \text{ nm } (\log \epsilon = 4.03)$$

Focused Problem

- 15.9 (a) From the extinction coefficient of isoprene ($10,750 M^{-1} \text{cm}^{-1}$) and its observed absorbance at 222.5 nm (see Fig. 15.5), calculate the concentration of isoprene in mol L^{-1} (assume a 1 cm light path).
- (b) From the results of part (a) and Fig. 15.5, calculate the extinction coefficient of isoprene at 235 nm.

B. Physical Basis of UV–Vis Spectroscopy

What determines whether an organic compound will absorb UV or visible radiation? Ultraviolet and/or visible radiation is absorbed by the π electrons and, in some cases, by the nonbonding electron pairs in organic compounds. For this reason, UV–vis spectra are sometimes called *electronic spectra*. (The electrons of σ bonds absorb at much shorter wavelengths, in the far ultraviolet.) Absorptions by compounds containing only single bonds and nonbonding electron pairs are generally quite weak (that is, their extinction coefficients are small). However, intense absorption of UV and visible radiation occurs when a compound contains π electrons. The simplest hydrocarbon containing π electrons, ethylene, absorbs UV radiation at $\lambda_{\text{max}} = 165 \text{ nm}$ ($\epsilon = 15,000$). Although this is a strong absorption, the λ_{max} of ethylene and other simple alkenes is below the usual working wavelength range of most conventional UV–vis spectrophotometers; the lower end of this range is about 200 nm. However, molecules with *conjugated* double or triple bonds (for example, isoprene; see Fig. 15.5) have λ_{max} values greater than 200 nm. Therefore, *UV–vis spectroscopy is especially useful for the diagnosis of conjugated double or triple bonds*.



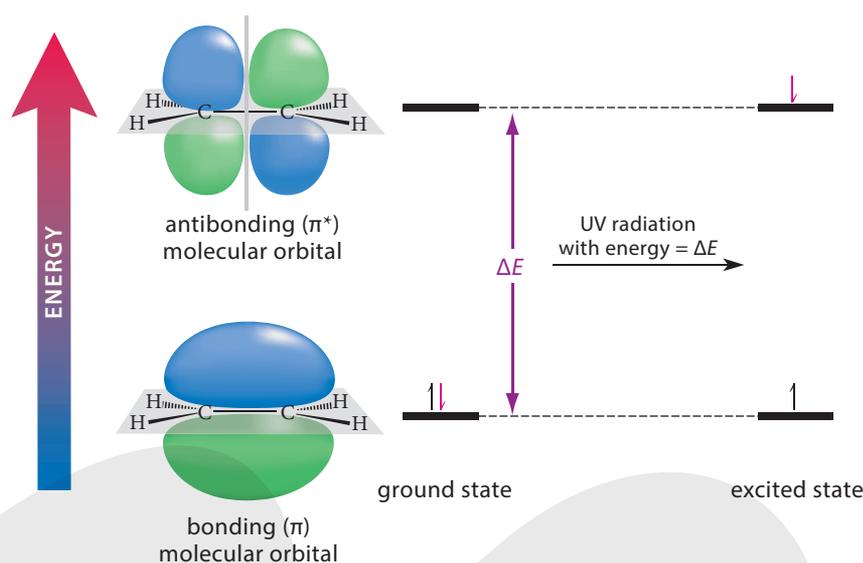
the double bonds are not conjugated;
no λ_{max} above 200 nm



the double bonds are conjugated;
this compound has a λ_{max} above 200 nm:
 $\lambda_{\text{max}} = 227 \text{ nm}$

(15.9)

FIGURE 15.6 Absorption of UV radiation by ethylene. The molecular orbitals of ethylene are shown on the left, and the energy difference between these orbitals is shown as ΔE . In the ground state of ethylene, two electrons of opposite spin occupy the bonding (π) molecular orbital. When ethylene is subjected to UV radiation of energy = ΔE , an electron (shown in red) is promoted from the bonding molecular orbital to the antibonding (π^*) molecular orbital. The product of this energy absorption is an excited state of ethylene.



The structural feature of a molecule responsible for its UV-vis absorption is called a **chromophore**, from Greek words meaning “to bear color.” For example, the chromophore in isoprene (see Fig. 15.5) is the system of conjugated double bonds. Because many important compounds do not contain conjugated double bonds or other chromophores, UV-vis spectroscopy has limited utility in structure determination compared with NMR and IR spectroscopy. However, the technique is widely used for quantitative analysis in both chemistry and biology; and, when compounds do contain conjugated multiple bonds, the UV-vis spectrum can be an important element in a structure proof.

The physical phenomenon responsible for the absorption of energy in the UV-vis spectroscopy experiment can be understood from a consideration of what happens when ethylene absorbs UV-vis radiation at 165 nm. The π -electron structure of ethylene was discussed in Sec. 4.1C and is shown in Fig. 15.6. In the normal state of the ethylene molecule, called the *ground state*, the two π electrons occupy a *bonding* π molecular orbital. When ethylene absorbs energy from light, one π electron is elevated from this bonding molecular orbital to the *antibonding* or π^* molecular orbital. This means that the electron assumes the more energetic wave motion characteristic of the π^* orbital, which includes a node between the two carbon atoms. The resulting state of the ethylene molecule, in which there is one electron in each molecular orbital, is called an *excited state*. The energy required for this absorption must match ΔE , the difference in the energies of the π and π^* orbitals (see Fig. 15.6). As a result, the 165 nm absorption of ethylene is called a $\pi \rightarrow \pi^*$ **transition** (read “pi to pi star”). The UV absorptions of conjugated alkenes are also due to $\pi \rightarrow \pi^*$ transitions.

C. UV-Vis Spectroscopy of Conjugated Alkenes

When UV-vis spectroscopy is used to determine chemical structure, the most important aspect of a spectrum is the λ_{\max} values. The structural feature of a compound that is most important in determining the λ_{\max} is the number of consecutive conjugated double (or triple) bonds. That is, *the more consecutive conjugated multiple bonds there are, the higher the wavelength of the absorption*. Molecular orbital theory provides an explanation for this effect. As shown in Fig. 15.6, the energy of the radiation required for UV-vis absorption is determined by the energy separation between the occupied (bonding) MO and the unoccupied (antibonding) MO. As shown in Sec. 13.1A, this energy is inversely proportional to the wavelength λ :

$$\Delta E = h\nu = \frac{hc}{\lambda} \quad (15.10)$$

where h is Planck's constant, c is the speed of light, and ν is the frequency of the light.

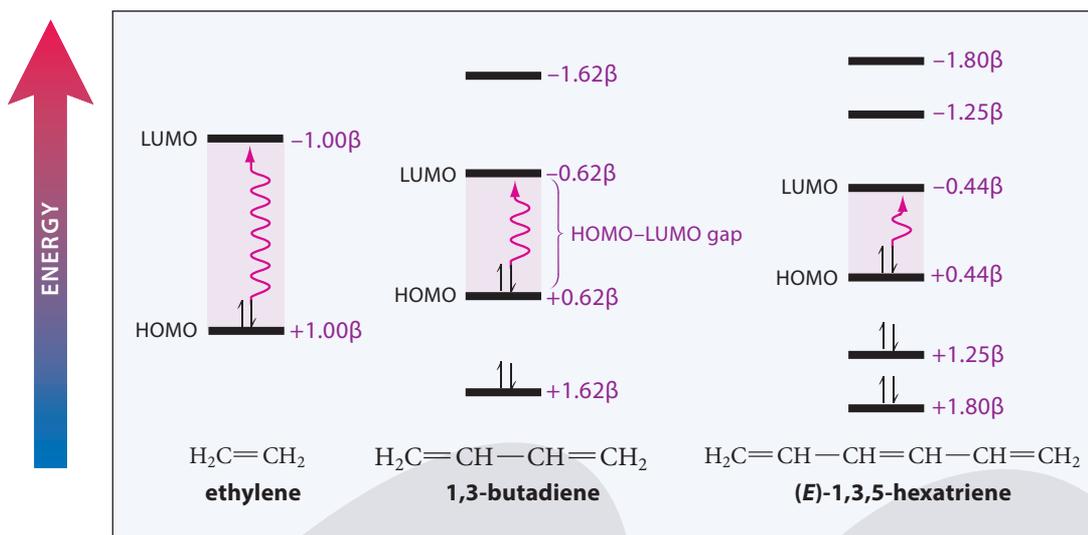


FIGURE 15.7 The relationship of the absorption energy in UV–vis spectroscopy to the number of conjugated double bonds. The energies of the π molecular orbitals for ethylene, 1,3-butadiene, and (*E*)-1,3,5-hexatriene are given in β units. The energy of the UV or visible radiation required for absorption is equal to the gap (lavender shading) between the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO). Absorption (indicated by the red “squiggly arrows”) results in the promotion of an electron from the HOMO to the LUMO. As the number of double bonds increase, the size of the HOMO–LUMO gap decreases and, by Eq. 15.9, the absorption wavelength increases.

A conjugated alkene contains more than one bonding MO and more than one antibonding MO, as shown for 1,3-butadiene (see Fig. 15.1, Sec. 15.1A). In a conjugated diene, the UV–vis absorption at highest wavelength results in promotion of a π electron from the bonding MO of *highest* energy, called the **HOMO** (for “highest occupied molecular orbital”) to the antibonding MO of *lowest* energy, called the **LUMO** (for “lowest unoccupied molecular orbital”). In other words, the HOMO–LUMO energy gap—the energy difference between these two MOs—determines the wavelength of the absorption. The relative energies of the π MOs for ethylene and the first two conjugated alkenes are shown in **Fig. 15.7**. This figure shows that the HOMO–LUMO gap becomes smaller as the number of conjugated double bonds increases. The energy of the radiation required for absorption, then, becomes smaller, and the wavelength greater, as the number of double bonds increases. (Other factors in addition to the HOMO–LUMO gap also contribute to the λ_{\max} ; see Further Exploration 15.1 in the *Study Guide and Solutions Manual*.)

Table 15.2 lists the λ_{\max} values for a series of conjugated alkenes. Notice that λ_{\max} (as well as the extinction coefficient) increases with an increase in the number of conjugated double bonds; each additional conjugated double bond increases λ_{\max} by 30 to 50 nm. Molecules that contain many conjugated double bonds, such as the last one in Table 15.2, generally have several absorption peaks. These result not only from the HOMO–LUMO transition but also from electronic transitions involving other π MOs as well. The λ_{\max} usually quoted for such compounds is the one at highest wavelength, which corresponds to the HOMO–LUMO transition.

If a compound has enough double bonds in conjugation, one or more of its λ_{\max} values will be large enough to fall within the visible region of the electromagnetic spectrum, and the compound will be colored. An example of a conjugated alkene that absorbs visible light is β -carotene, which is found in carrots and is known to be a biological precursor of vitamin A:

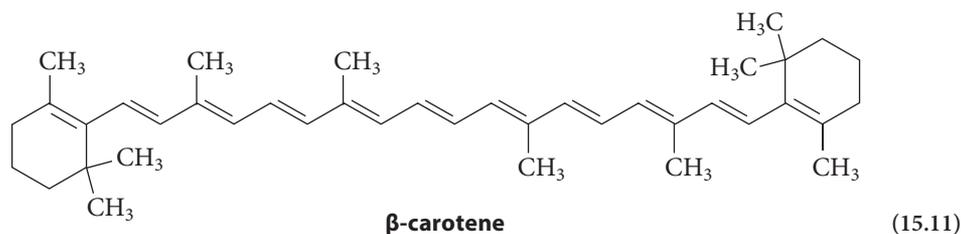
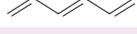
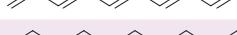


TABLE 15.2 UV Absorptions for Ethylene and Some Conjugated Alkenes

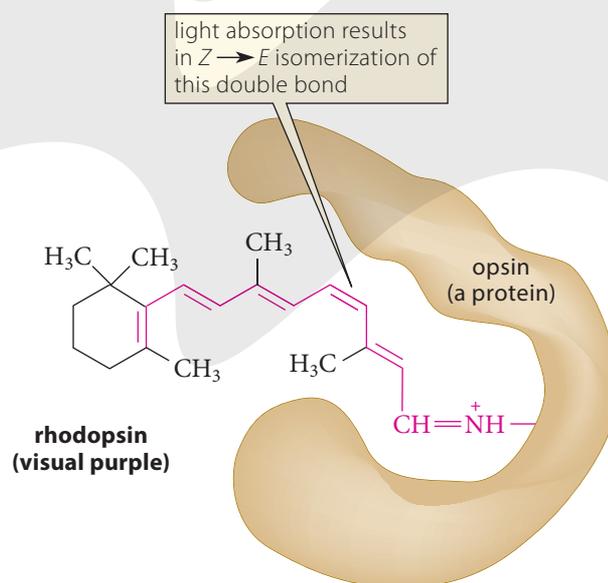
| Alkene | λ_{\max} , nm* | Extinction coefficient (ϵ), $M^{-1} \text{ cm}^{-1}$ |
|---|------------------------|---|
| ethylene | 165 | 15,000 |
|  | 217 | 21,000 |
|  | 268 | 34,600 |
|  | 303 | 53,000 |
|  | 334 | (†) |
|  | 362 | 138,000 |

*The λ_{\max} at longest wavelength (not necessarily the strongest absorption). Solvents are either ethanol, hexane, or cyclohexane; where different solvents were compared for the same alkene, the values were not very solvent-dependent.

†Extinction coefficient not measured.

Because of the large number of conjugated double bonds in β -carotene, it has strong absorption between 400 and 500 nm, which is in the visible (blue-green) part of the electromagnetic spectrum. When a sample of β -carotene is exposed to white light, blue-green light is absorbed, and the eye perceives the *unabsorbed* light, which is red-orange. In fact, β -carotene is responsible for the orange color of carrots. Similarly, flamingos (Fig. 15.8) are red-orange because of the vitamin A in their diets.

The human eye can detect visible light because the eye contains organic compounds that absorb light in the visible region of the electromagnetic spectrum. In fact, light absorption by a pigment, *rhodopsin*, in the rod cells of the eye (as well as a related pigment in the cone cells) is the event that triggers the physiological response that we know as *vision*. The chromophore in rhodopsin is its group of six conjugated double bonds (red in the following structure):



(15.12)

Absorption of a photon by this chromophore results in a $Z \rightarrow E$ isomerization about the double bond indicated in Display 15.12. This isomerization drastically alters the shape of the molecule, and this change of shape, in turn, causes a large change in the conformation of the surrounding protein. These events set off a cascade of molecular signals that culminate in the visual response.

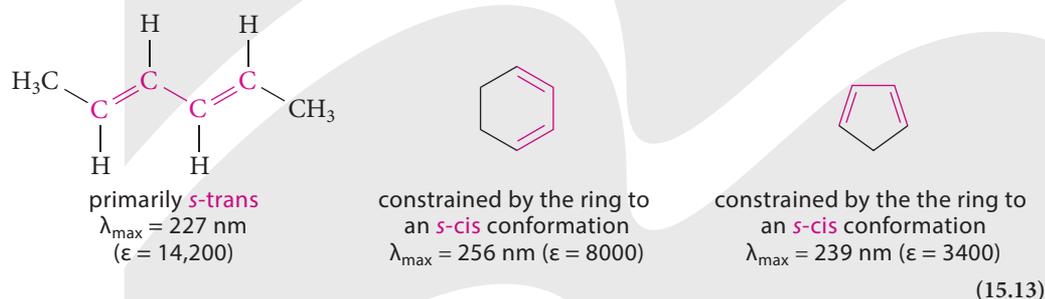
Although the number of double or triple bonds in conjugation is the most important thing that determines the λ_{\max} of an organic compound, other factors are involved. One is *the conformation of a diene unit about its central single bond*—that is, whether the diene is in an *s-cis* or an *s-trans* conformation (Sec. 15.1B). Recall that an acyclic diene assumes the lower energy



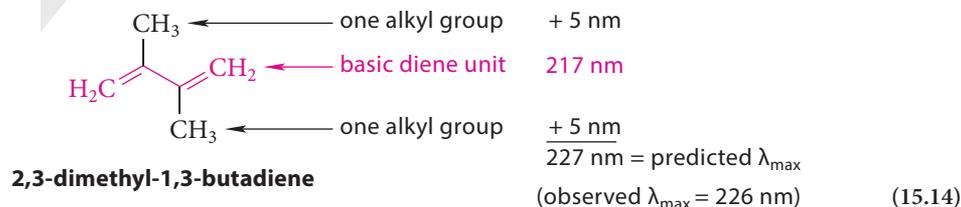
Photo copyright © Marc Loudon

FIGURE 15.8 The bright red-orange color of flamingos is caused by the vitamin A in their diets.

s-trans conformation. However, dienes locked into *s*-cis conformations have *higher* values of λ_{\max} and *lower* extinction coefficients than comparably substituted *s*-trans compounds:



A third variable that affects λ_{\max} in a less dramatic yet predictable way is the presence of substituent groups on the double bond. For example, each alkyl group (regardless of size) on a conjugated double bond adds about 5 nm to the λ_{\max} of a conjugated alkene. The two methyl groups of 2,3-dimethyl-1,3-butadiene therefore add $(2 \times 5) = 10 \text{ nm}$ to the λ_{\max} of 1,3-butadiene, which is 217 nm (see Table 15.2). The predicted λ_{\max} is $(217 + 10) = 227 \text{ nm}$; the observed value is 226 nm.

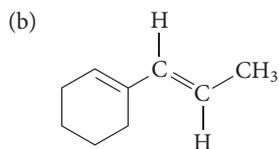
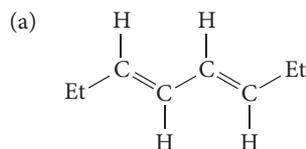


Although other structural features affect the λ_{\max} of a conjugated alkene, here are the two most important points to remember:

1. The λ_{\max} is greater for compounds containing more conjugated double bonds.
2. The λ_{\max} is affected by substituents, conformation, and other structural characteristics of the conjugated π -electron system.

Focused Problem

15.10 Predict λ_{\max} for the UV absorption of each of the following compounds.



Sunscreens



Blend Images/Superstock

Sunscreens and sun-blocks are used to protect the skin from harmful ultraviolet rays of the Sun. The harmful UV radiation of sunlight is often discussed in terms of the parts of the solar spectrum termed “UV-A” and “UV-B.” UV-B rays, which cover roughly the 280–315 nm part of the spectrum, are mostly responsible for sunburn and have long been associated with skin cancer. UV-A rays, which cover the 315–400 nm part of the spectrum, are responsible for wrinkling and aging. Research suggests that UV-A rays can also contribute to skin cancer. Sunscreens, which have a \$400 million market in the United States (part of a \$2 billion annual market for all “sun-care” products), are often characterized by a sun-protection factor (SPF). The SPF typically measures protection from UV-B rays. The most effective sunscreen formulations not only have high SPF numbers but also provide protection from UV-A rays.

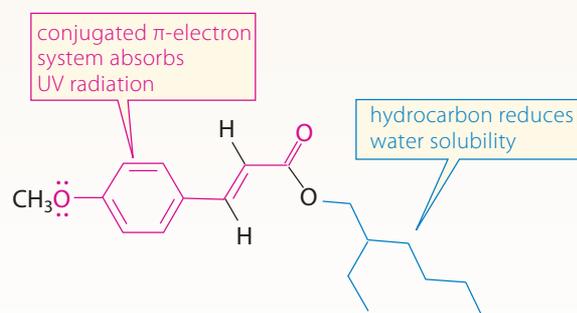
Sunscreens work by absorbing the UV rays of the Sun. Therefore, it should not be surprising that sunscreens have UV–visible spectra, which are direct measures of their UV-absorbing capability. The system of conjugated double

bonds (red) in the structure of a typical sunscreen (shown below) is responsible for the UV absorption.

The UV spectrum of this compound (**Fig. 15.9**) shows that it is an effective absorber of UV-B rays but has only modest absorption in the UV-A region. This is why sunscreen preparations should contain UV-A blockers as well. (Most UV-A blockers also contain conjugated π -electron systems with appropriate UV absorption.)

The long hydrocarbon chain in the ester group (*blue*) reduces the water solubility of the sunscreen. This same hydrocarbon group, however, promotes absorption through the skin. The absorption of sunscreens has been a cause for concern, but their beneficial effect in reducing the incidence of skin cancer seems to outweigh the other risks of their use.

Another, more recent, concern about sunscreens such as the one in Display 15.15 is their harmful effect on coral reefs. This has led the Hawaii legislature to ban this and another ingredient, oxybenzone, in sunscreens sold in Hawaii. (Coral reefs are also threatened by climate change.) Titanium oxide and zinc oxide are mineral-based sunscreens that don't have this problem. They operate by providing a physical barrier to the Sun's rays rather than by absorbing UV radiation. [The National Oceanic and Atmospheric Administration (NOAA) and the National Geographic Society websites have information about sunscreens and their environmental effect.]



2-ethylhexyl *p*-methoxycinnamate
(octinoxate)

(15.15)

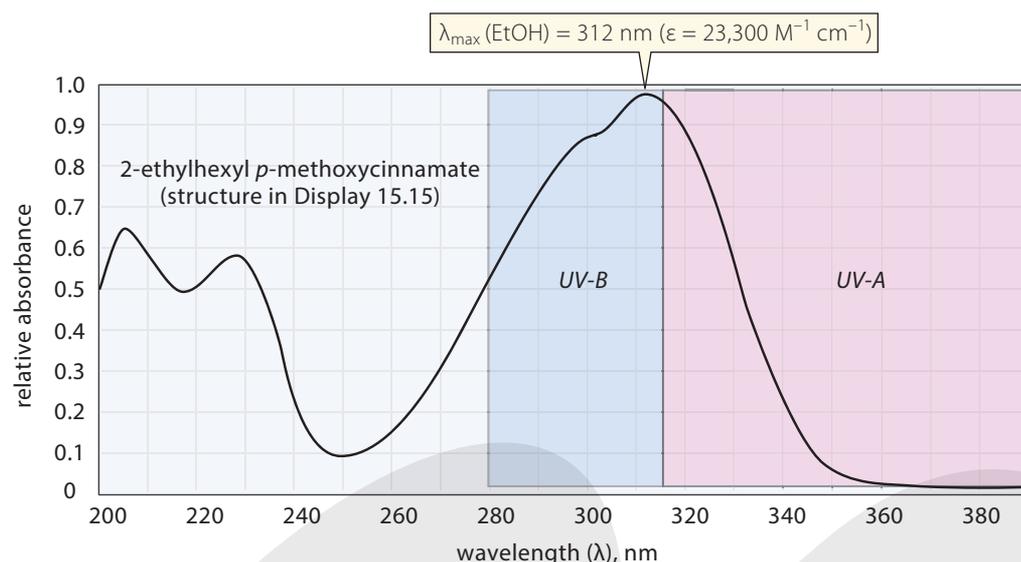
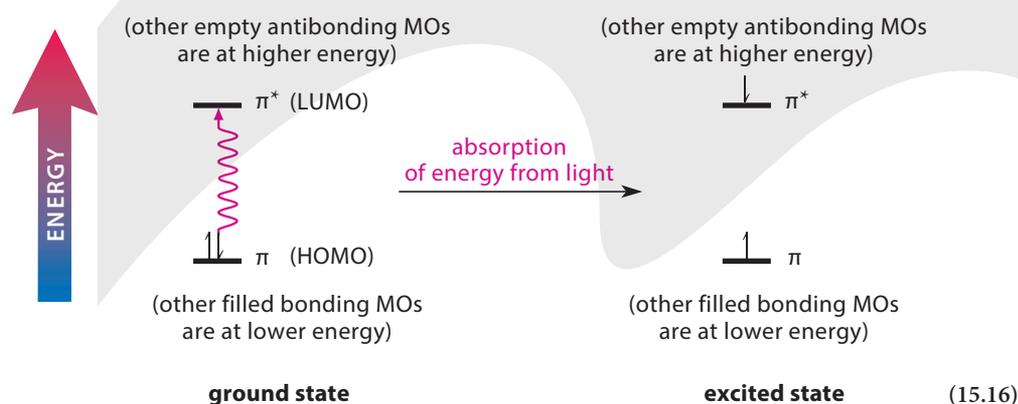


FIGURE 15.9 The UV spectrum of a typical sunscreen, 2-ethylhexyl *p*-methoxycinnamate, in ethanol with the UV-A and UV-B regions indicated.

D. Fluorescence

Most of us have seen objects that “glow” with bright colors under a UV lamp. This glow is caused by the emission of light in the visible region from compounds that absorb ultraviolet light. These compounds are *fluorescent*. The purpose of this section is to explain the origin of fluorescence and why it is important, especially in biology.

To start, we consider the origin of fluorescence by looking more deeply into UV–visible absorption. Recall that when any conjugated molecule absorbs UV or visible radiation, an electron is promoted from the *highest occupied molecular orbital* (HOMO) to the *lowest unoccupied molecular orbital* (LUMO) (see Fig. 15.7). Before absorption, the molecule is said to be in its **ground state**. After absorption, the molecule is said to be in an **excited state**.



The molecule in its excited state now contains energy resulting from light absorption. What happens to that energy? One of the most common outcomes is that the molecule can lose its excess energy by light emission; this light emission is called **fluorescence**. In fluorescence, the electron that was promoted to the LUMO by absorption returns to the HOMO, and the energy that is lost is emitted as light. This simple picture suggests that the light emitted should have the same energy (and therefore the same wavelength) as the light absorbed. Actually, the light emitted occurs at *lower energy*, and therefore *longer wavelength*, than the light absorbed. For example, a molecule that absorbs blue or violet light might emit green fluorescence. The wavelength shift that occurs in fluorescence is called the **Stokes shift**. The Stokes shift is one of the most useful aspects of fluorescence. The Stokes shift is why certain fluorescent objects glow visibly under UV light.

Chemical
Biology
Topic

The origin of the Stokes shift is not apparent from the diagram in Display 15.16. Rather, it originates in the *molecular vibrations* of the molecule. When a molecule absorbs UV or visible radiation, the promotion of the π electron occurs so rapidly that *the bond lengths of the molecule do not change during the absorption*. In the excited state, however, the optimum bond lengths may be different from those in the ground state. For example, the electrons in a conjugated double bond that are delocalized in the ground state may be less delocalized in the excited state because of nodes in LUMO. If the optimum length of this double bond is shorter in the excited state, the bond that had an optimum length in the ground state may be longer than optimum in the excited state. Therefore, absorption produces an excited state that is not only *electronically* excited but also *vibrationally* excited (**Fig. 15.10a**). “Vibrationally excited” means in a mechanical sense that, immediately after absorption, the bonds in the molecule find themselves stretched or compressed relative to their optimum lengths in the excited state. Even though the electronic excited state lasts only 10^{-9} to 10^{-8} seconds, the lifetime of the vibrationally excited state is typically 10^{-11} to 10^{-12} seconds—about 1000 times smaller. Therefore, immediately following absorption, the molecule undergoes vibrational relaxation to the bond lengths that are optimum for the excited state (**Fig. 15.10b**). In this process, some of the energy of the excited state is lost as heat. Eventually, the excited molecule returns to the ground state when the π electron returns to the HOMO from the LUMO, and the loss of energy is seen as fluorescence (**Fig. 15.10c**). Here again, however, the vibrational energy levels come into play. The fluorescence process returns the molecule to a vibrationally excited ground state, from which the remaining excess energy is lost by vibrational relaxation as heat. This description shows that *the energy lost in fluorescence is less than the energy gained in absorption*. Because $E = hc/\lambda$, *the wavelength of the emitted light is greater than that of the absorbed light*. This difference in wavelength between absorbed and emitted light is the Stokes shift.

Fluorescence intensity follows Beer’s law (Eq. 15.8) just as absorption does. Molecules that fluoresce strongly must absorb UV–visible radiation strongly as well—that is, they must have large extinction coefficients for absorption. However, not all strong absorbers produce significant fluorescence because excited states can sometimes undergo reactions, internal rotations, transitions to other types of excited states, and so on—processes that we won’t be concerned with here. The efficiency of fluorescence is determined by the fraction of excited states that return to ground state by fluorescence. This efficiency is called the **quantum yield** of fluorescence. Many compounds commonly used in fluorescence have quantum yields in the 0.8 to 1.0 range.

There aren’t any hard-and-fast rules for determining whether a molecule will have a high quantum yield for fluorescence. To fluoresce strongly, a molecule must have a high absorbance, because fluorescence originates from absorbance. However, a high absorbance is no guarantee that a molecule will have significant fluorescence, because there are other ways besides fluorescence that an excited state can lose energy. Many strongly fluorescent molecules have chromophores consisting of several conjugated double bonds incorporated into rigid polycyclic frameworks. Fluorescent molecules typically don’t contain double bonds that can undergo cis–trans isomerization. Noncarbon atoms such as nitrogen and oxygen are in many cases part of the conjugated system, as we see in the examples later in this section.

The importance of fluorescence as an analytical tool lies in its sensitivity. If fluorescence follows the same concentration dependence as absorption, why is it so sensitive? Recall (Eq. 15.8) that UV–visible absorbance is the logarithm of the *ratio* of the light intensity emerging from the sample to the intensity of the light source; $A = \log(I_0/I)$. (This ratio is usually provided physically by the optics in the spectrophotometer.) In other words, UV absorption requires comparison of the light emerging from the sample with a large background—a small difference between large numbers. In fluorescence, however, we measure the absolute intensity of light emerging from the sample, and the standard of comparison is total darkness. Typically, fluorescence detectors are set up at 90° to the light path so that the exciting light source does not interfere with detection.

An analogy to absorption sensitivity is trying to hear a few people whispering in a room full of people talking loudly. The analogy to fluorescence sensitivity is that if the same people are placed in a totally silent room, their whispering can be heard clearly.

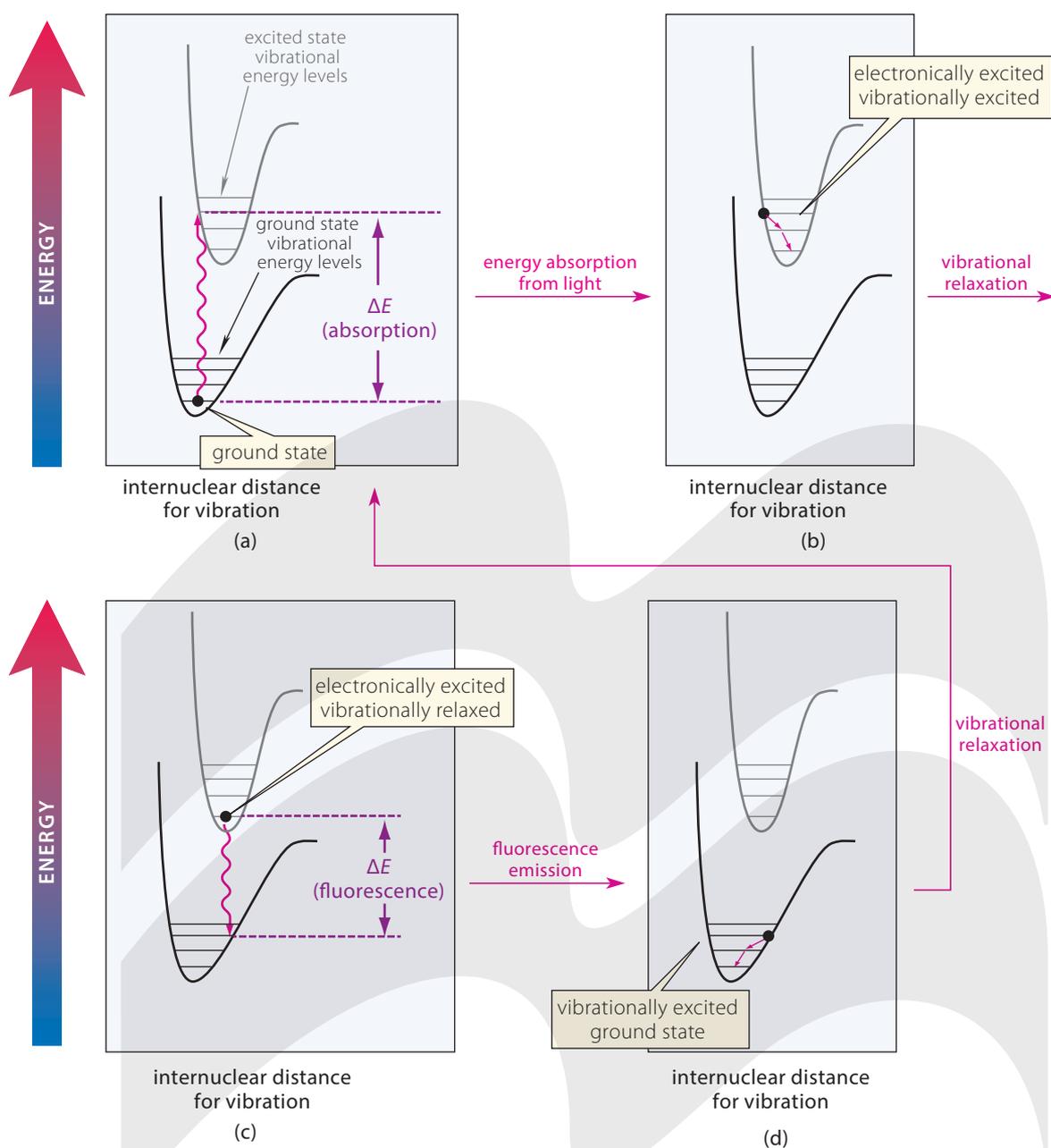


FIGURE 15.10 The absorption and fluorescence process. A molecule in its ground state (a) absorbs energy from light and is promoted to an electronically excited and vibrationally excited state (b). The electronically excited state loses vibrational energy as heat and forms an electronically excited and vibrationally relaxed state (c). This state loses energy by emitting light (fluorescence) to form a vibrationally excited ground state (d). This state then relaxes vibrationally to form the ground state shown in part (a). The energy spacing of the vibrational levels is highly exaggerated for clarity. This process is illustrated for one vibrational mode, but every vibrational mode in the molecule contributes. The energy of the light emitted, ΔE (fluorescence), is less than the energy of the light absorbed, ΔE (absorbance), and for that reason, the wavelength of the emitted light is greater than that of the light absorbed (Stokes shift).

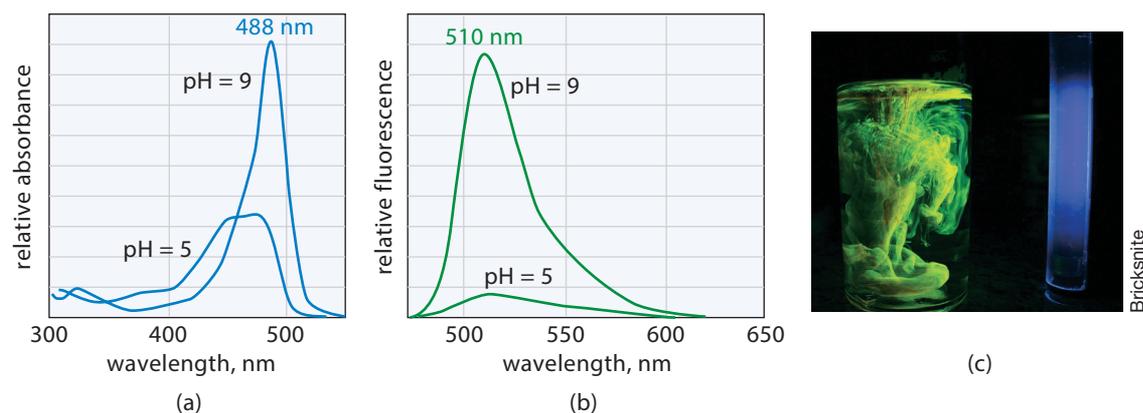
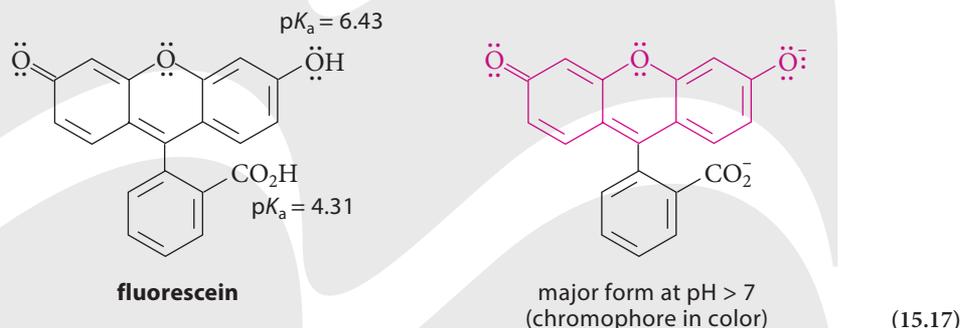


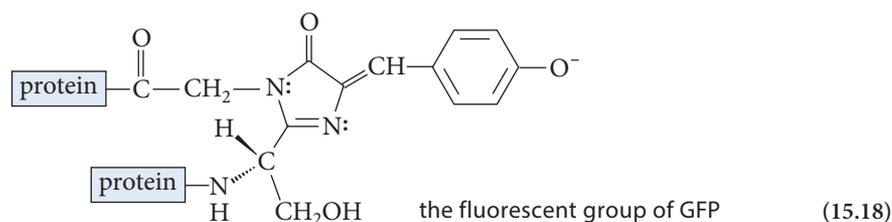
FIGURE 15.11 (a) The UV-visible absorption spectrum of fluorescein at two pH values. (b) The fluorescence emission spectrum of fluorescein at the same two pH values resulting from absorption at the λ_{max} (488 nm). Notice the Stokes shift of fluorescence to a greater wavelength. (c) Fluorescein sprinkled into tap water emits green fluorescence under a handheld UV light.

Fluorescein is a widely used, highly fluorescent compound.



Fluorescein derivatives have been developed that react with other functional groups and can therefore be used as fluorescent “tags.” Fluorescein contains two ionizable groups, and the most fluorescent form, shown in Display 15.17, is the one on the right in which the carboxylic acid ($-\text{CO}_2\text{H}$) and the phenol ($-\text{OH}$) are ionized. Fluorescein has an extended π -electron system, and, as expected, it absorbs UV-visible radiation strongly. The chromophore responsible for the absorption (and the fluorescence) at long wavelengths is relatively rigid; the attached aryl group (black) has only a minor contribution to the absorption at these wavelengths. The nonbonding electron pairs of the ionized phenol oxygen are involved in resonance interaction with the double bonds, and this interaction is an important aspect of the chromophore. (Draw the resonance structures for the delocalization of these electrons.) The absorption and fluorescence spectra of fluorescein are shown in **Figs. 15.11a** and **15.11b**. The fluorescence spectrum is obtained by exciting the molecule at a specific wavelength (in this case, 488 nm, at the λ_{max} for absorption). The peak in the fluorescence emission occurs at 510 nm. Notice the Stokes shift in the fluorescence to higher wavelength. Notice also that the absorption intensity is smaller at lower pH, and so is the fluorescence intensity. **Figure 15.11c** shows the fluorescein fluorescence. In this photo, the electronic absorption is activated by shining a UV light on the sample. We are viewing the fluorescence at a 90° angle to the UV light path.

Fluorescence has revolutionized biology. One of the exciting applications of fluorescence resulted from the discovery of a fluorescent protein in a jellyfish (**Fig. 15.12a**), called *green fluorescent protein* (GFP). The fluorescent group in GFP is “built into” the protein structure:



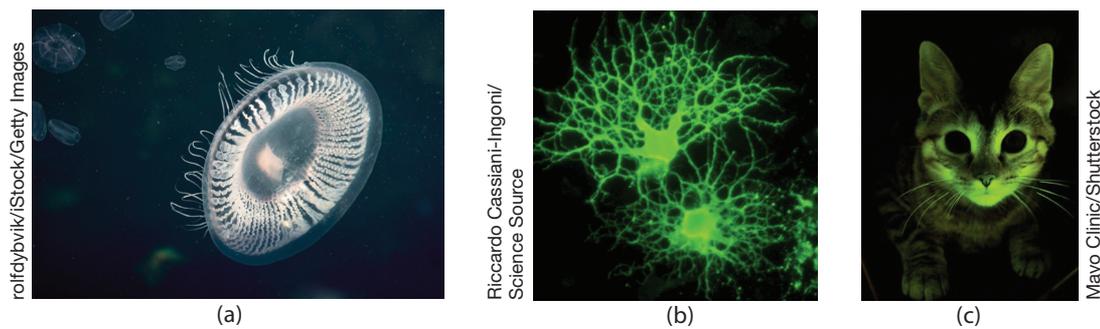


FIGURE 15.12 (a) The fluorescent jellyfish *Aequorea victoria*, source of the green fluorescent protein. (b) A fluorescent light micrograph of GFP-containing oligodendrocytes from a mouse. The gene for a protein localized in the oligodendrocyte was fused with the gene for GFP and the fusion protein was expressed within a genetically engineered mouse in its oligodendrocytes. These cells form the myelin sheath around neurons (nerve cells) in the central nervous system (CNS). (c) Scientists at the Mayo Clinic in Rochester, Minnesota, have produced transgenic cats containing a gene that imparts resistance to feline immunodeficiency virus (FIV, the cat version of HIV). The resistance gene was fused to the GFP gene so that the two genes were incorporated together. Cats containing the resistance gene are readily detected by their fluorescence under blue light.

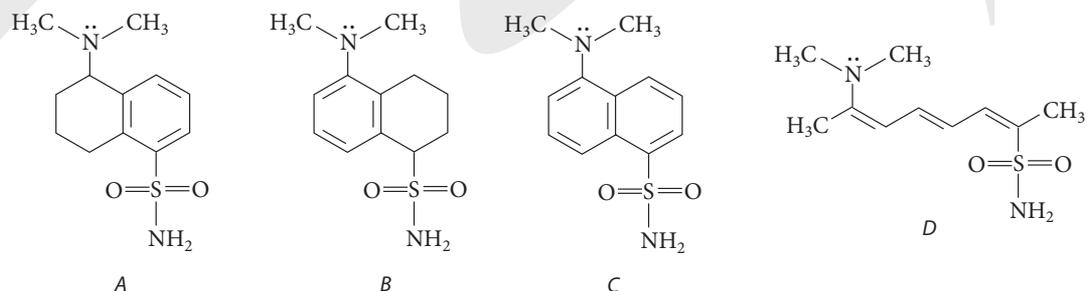
The protein itself wraps around the fluorescent group like a barrel and excludes it from solvent water. When the protein structure is disrupted so that this group can interact with water, its fluorescence quantum yield drops to zero because the energy of the excited state is lost to solvent vibrations rather than by fluorescence.

GFP is a fairly small and relatively stable protein. The gene for GFP can in many cases be joined to the genes of other proteins of interest, and the two proteins can be co-expressed in living organisms as a single “fusion” protein. Essentially, the GFP is carried by the protein of interest as a “molecular flashlight” so that the localization of the protein of interest can be seen by viewing a cell under a fluorescence microscope (Fig. 15.12b). Even genetically modified whole animals carrying GFP have been produced (Fig. 15.12c). It is also possible to produce mutant GFPs that give fluorescence of different colors, such as red and yellow.

The discovery and development of GFP as a biological tool was recognized with the 2008 Nobel Prize in Chemistry, which was awarded to Osamu Shimomura (1928–2018) of the Marine Biological Laboratory in Woods Hole, Massachusetts; Martin Chalfie (b. 1947) of Columbia University; and Roger Y. Tsien (1952–2016) of the University of California, San Diego.

Focused Problems

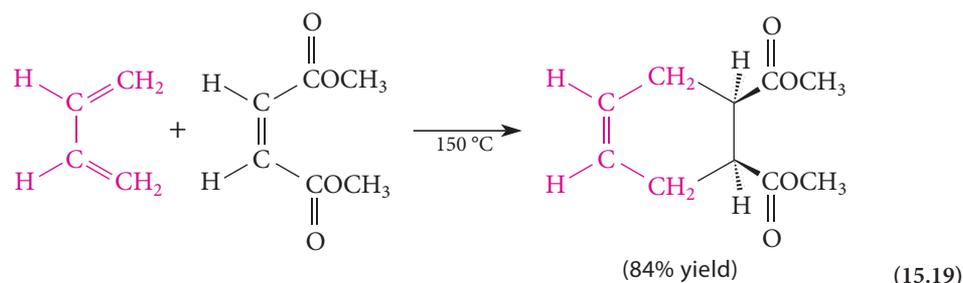
- 15.11 Refer to Fig. 15.11. At what pH does the fluorescence of fluorescein have the greater quantum yield, pH = 9 or pH = 5? How do you know?
- 15.12 One of the following compounds has an intense yellow fluorescence when irradiated with UV light. Which one do you think it is, and why?



15.3 THE DIELS–ALDER REACTION

A. Reaction of Conjugated Dienes with Alkenes

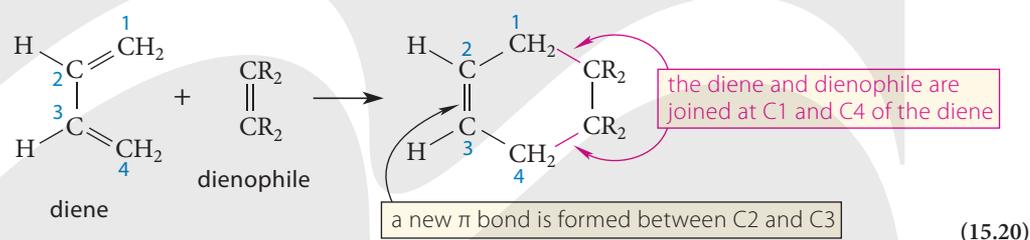
Conjugated dienes undergo several unique reactions. One of these was discovered in 1928, when two German chemists, Otto Diels (1876–1954) and Kurt Alder (1902–1958), showed that many conjugated dienes undergo addition reactions with certain alkenes or alkynes. The following reaction is typical:



This type of reaction between a conjugated diene and an alkene is called the **Diels–Alder reaction**. For their extensive work on this reaction, Diels and Alder shared the 1950 Nobel Prize in Chemistry.

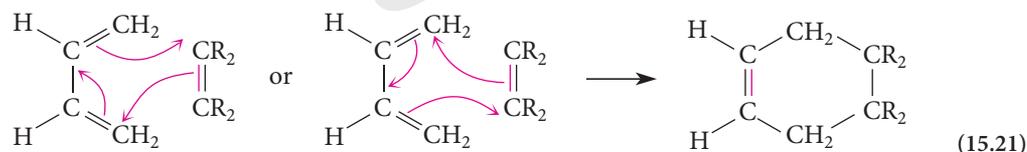
The Diels–Alder reaction is an example of a **cycloaddition reaction**—an addition reaction that results in the formation of a ring. Indeed, *the Diels–Alder reaction is an important method for making rings*, as the example in Eq. 15.19 illustrates.

The Diels–Alder reaction is also an example of a **1,4-addition** or **conjugate addition**. In such a reaction, addition occurs across the outer carbons (carbons 1 and 4) of the diene. *Conjugate addition is a characteristic type of reaction of conjugated dienes*. (Other conjugate additions are described in Secs. 15.4 and 22.9.) In the Diels–Alder reaction, conjugate addition also results in the formation of a double bond between carbons 2 and 3. (The numbers indicate the relative locations of the carbons involved in the addition; they have nothing to do with the numbering of the diene used in its substitutive nomenclature.)



When discussing the reactants in the Diels–Alder reaction, we employ the following terminology, which is illustrated in Eq. 15.20. The conjugated diene reactant is referred to simply as the *diene*, and the alkene with which it reacts is called the **dienophile** (literally, “diene-loving molecule”). 1,3-Butadiene is used as the diene for simplicity in Eq. 15.20, but as we show shortly, a wide variety of dienes can be used in this reaction.

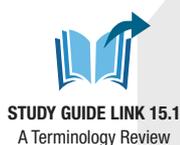
Mechanistically, the Diels–Alder reaction occurs in a single step involving a cyclic flow of electrons. The curved arrows for this mechanism can be drawn in either a clockwise or a counterclockwise direction.

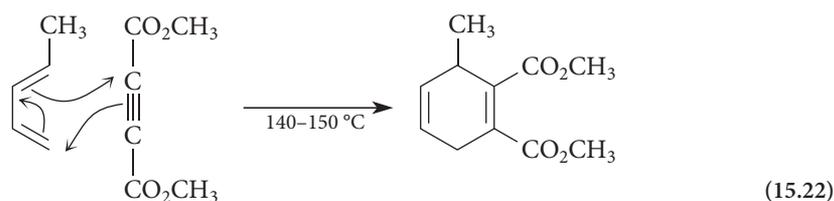


(The best evidence for a concerted rather than a stepwise mechanism for the Diels–Alder reaction comes from the stereochemistry of the reaction, which we discuss in Secs. 15.3B and 15.3C.) A concerted reaction that involves a cyclic flow of electrons is called a **pericyclic reaction**. The Diels–Alder reaction is a pericyclic reaction, as is the hydroboration of alkenes (Sec. 5.6A). However, hydroboration is not a cycloaddition, because no ring is formed.

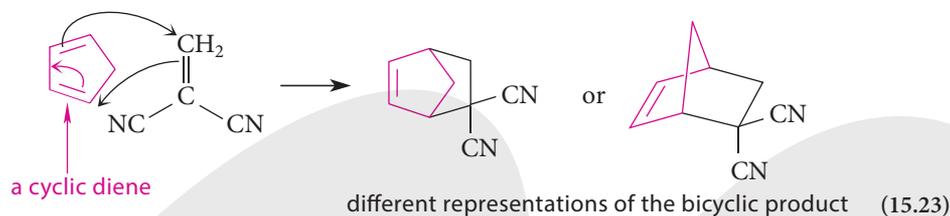
Some of the dienophiles that react most rapidly in the Diels–Alder reaction, as in Eq. 15.19, bear substituent groups such as esters ($-\text{CO}_2\text{R}$), nitriles ($-\text{CN}$), or certain other unsaturated, electronegative groups. However, these substituents are not strictly necessary because the reactions of many other alkenes can be promoted by heat or pressure. Some alkynes can also serve as dienophiles.

Pericyclic reactions as a class are discussed from the perspective of MO theory in Chapter 28.



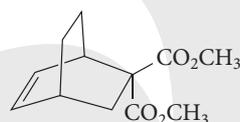


When a simple diene is used in the Diels–Alder reaction, a new ring is formed. When the diene is cyclic, a *second* ring is formed. In other words, the Diels–Alder reaction can be used to prepare certain *bicyclic compounds* (Sec. 7.6A).

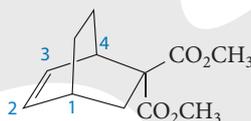


Study Problem 15.1

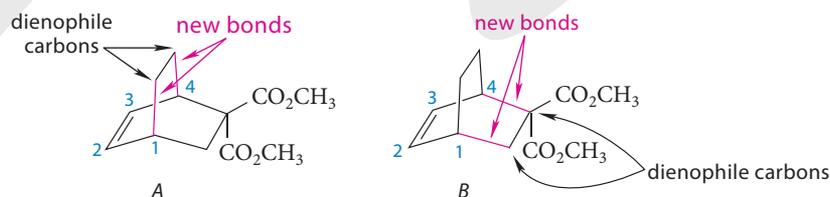
Give the structure of the diene and dienophile that would react in a Diels–Alder reaction to give the following product:



Solution In the product of a Diels–Alder reaction, the two carbons of the double bond and the two *adjacent carbons* originate from the diene. These carbons are numbered 1 through 4 in the following structure:



The two new single bonds formed in the reaction connect carbons 1 and 4 of the diene to the carbons of the dienophile double bond, which (because they are part of the same double bond) must be adjacent in the dienophile. This analysis reveals two possibilities, *A* and *B*, for the bonds formed in the Diels–Alder reaction:

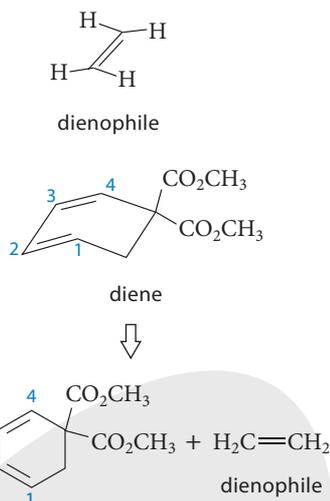


Because the product is bicyclic, the diene in either case is a *cyclic* diene. The double bonds in the diene are between carbons 1 and 2 and between carbons 3 and 4. To derive the starting materials in each case, follow these steps:

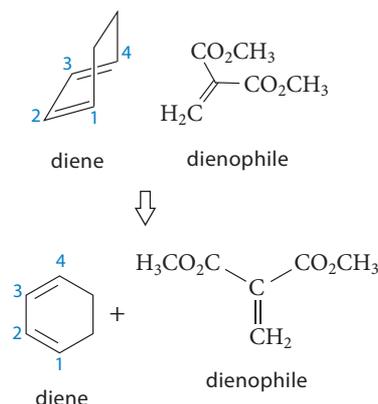
1. Disconnect the bonds between carbons 1 and 4 and their adjacent dienophile carbons.
2. Complete the diene structure by eliminating the double bond between carbons 2 and 3 and by adding the C1–C2 and C3–C4 double bonds.
3. Complete the dienophile structure by adding the double bond between its carbons.

By following these steps we find that the starting materials for possibilities *A* and *B* are as follows. (The carbon skeleton of the diene unit is first drawn exactly as it looks in the product, even though this is a distorted conformation, and then it is drawn in the more conventional way.)

Possibility A:

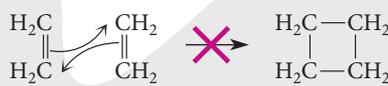


Possibility B:



In principle, either combination *A* or *B* could serve as the starting materials in a Diels–Alder reaction. Recall, however, that dienophiles with ester groups (or other electronegative groups) react faster than those without such groups. For this reason, the reactants in *B* would be preferred.

It might seem that cycloaddition reactions between two alkenes or between two dienes could be possible:

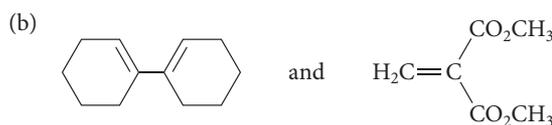
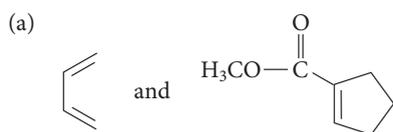


(15.24)

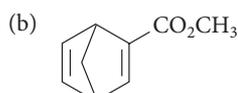
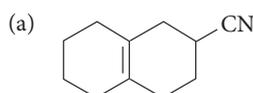
These reactions do *not* occur under the usual conditions. Although we might attribute the failure of the first reaction to ring strain in the product, there is more to it than that. The basis of these observations can be found in the theory of pericyclic reactions, which is the subject of Chapter 28. Be sure you understand that the Diels–Alder reaction is the reaction of a *conjugated diene* with an *alkene*.

Focused Problems

15.13 What products are formed in the Diels–Alder reactions of the following dienes and dienophiles?

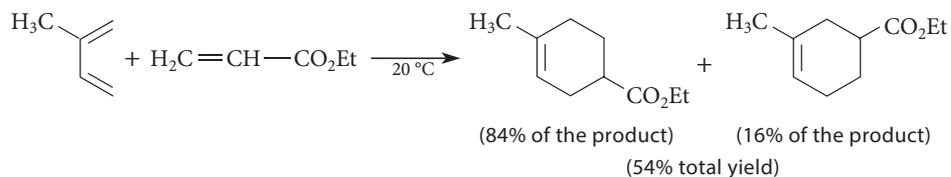


15.14 Give the diene and dienophile that would react in a Diels–Alder reaction to give each of the following products.

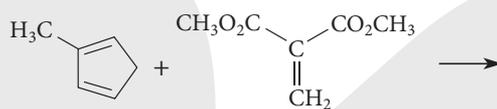


- 15.15 (a) What product would be expected from the Diels–Alder reaction of 1,3-butadiene as the diene and ethylene as the dienophile?
- (b) This product is actually not observed under ordinary conditions because 1,3-butadiene reacts with itself faster than it does with ethylene. In this reaction, one molecule of 1,3-butadiene acts as the diene component and the other as the dienophile. Give the product of this reaction.
- (c) How would you alter the reaction conditions to favor the formation of the product in part (a)?

- 15.16 (a) Explain why two constitutional isomers are formed in the following Diels–Alder reaction:



- (b) What two constitutional isomers could be formed in the following Diels–Alder reaction?



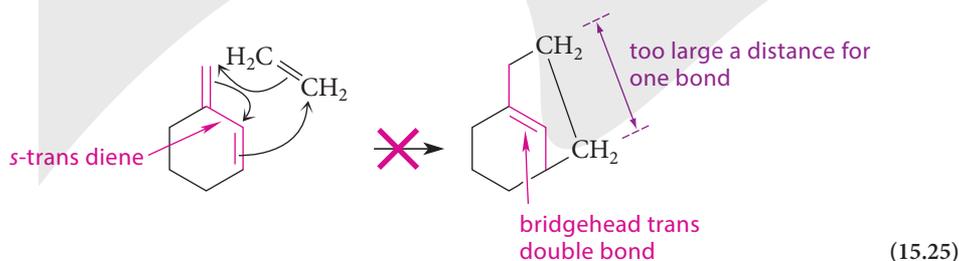
B. Effect of Diene Conformation on the Diels–Alder Reaction

Dienes that are “locked” into *s*-trans conformations are unreactive in Diels–Alder reactions:



“locked” *s*-trans dienes;
unreactive in Diels–Alder reactions

The reason is that if such dienes were to form Diels–Alder products, the *s*-trans single bond of the diene would become a trans double bond in the Diels–Alder product. This means that the Diels–Alder product would contain a trans double bond in a six-membered ring. For example, consider the following reaction:



The product is a bicyclic compound containing a bridgehead double bond. As discussed in Sec. 7.6C, the bridgehead double bond (red in Eq. 15.25) has trans stereochemistry within one of the rings joined at the bridges, and therefore the product violates Bredt’s rule and is too strained to exist. (For a graphic demonstration, try building a model of the product, but don’t break your models.)

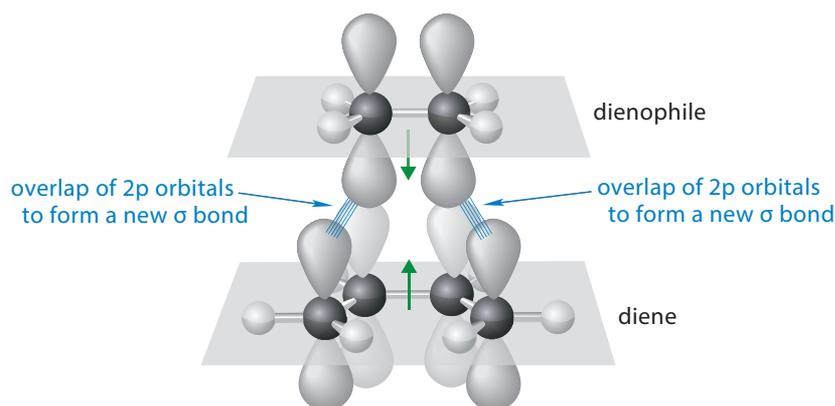
In contrast, dienes locked into *s*-cis conformations are considerably more reactive than the corresponding noncyclic dienes:



all are “locked” *s*-cis dienes;
all are reactive in the Diels–Alder reaction

(15.26)

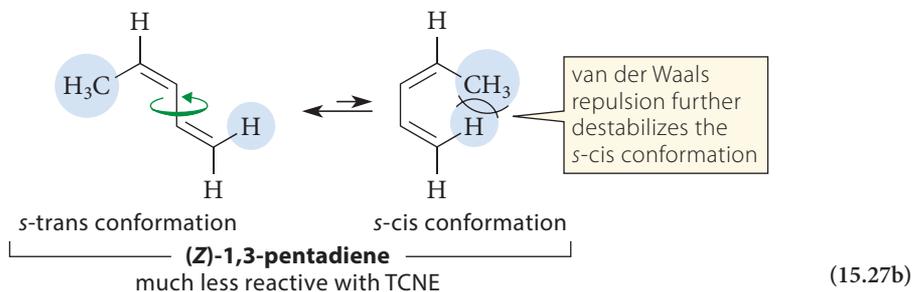
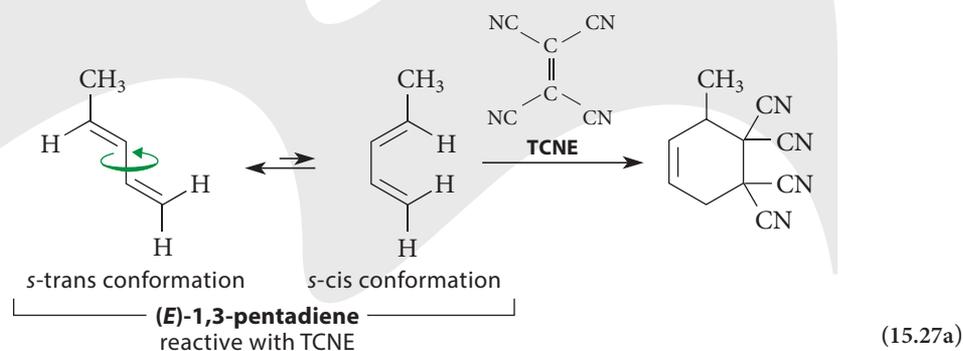
FIGURE 15.13 In the transition state for the Diels–Alder reaction, the diene (1,3-butadiene in this example) and the dienophile (ethylene in this example) approach in parallel planes (as shown by the green arrows) so that the 2p orbitals of the dienophile overlap with the 2p orbitals on carbons 1 and 4 of the diene to form the two new σ bonds. The developing overlap is indicated with blue lines. Notice that the diene is in an *s-cis* conformation.



For example, 1,3-cyclopentadiene, which is locked in an *s-cis* conformation, reacts with typical dienophiles hundreds of times more rapidly than 1,3-butadiene, which exists primarily in the *s-trans* conformation.

These observations are consistent with a transition state in which the diene component of the reaction has assumed an *s-cis* conformation. This transition state is shown in Fig. 15.13 for the reaction of 1,3-butadiene and ethylene. In this transition state, the diene and the dienophile approach in parallel planes. The 2p orbitals on the dienophile interact with the 2p orbitals on the outer carbons of the diene to form the new σ bonds. Because 1,3-butadiene prefers the *s-trans* conformation (see Fig. 15.1, Sec. 15.1B), the energy required for it to assume the *s-cis* conformation in the transition state becomes part of the energy barrier for the reaction. In contrast, a diene that is locked by its structure into an *s-cis* conformation, such as 1,3-cyclopentadiene, does not have this additional energy barrier to climb before it can react; therefore it reacts more rapidly.

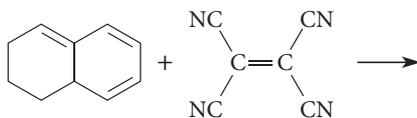
The importance of the *s-cis* diene conformation can have some fairly drastic consequences for the reactivity of some noncyclic dienes. For example, the *E* isomer of 1,3-pentadiene reacts 12,600 times more rapidly than the *Z* isomer of the same diene with tetracyanoethylene (TCNE), a very reactive dienophile:



As Eq. 15.27b shows, the *s-cis* conformation of the *cis* diene is destabilized by a significant van der Waals repulsion between the methyl group and a diene hydrogen. The transition states for the Diels–Alder reactions of this diene, which require an *s-cis* conformation, are destabilized by the same effect. Consequently, the Diels–Alder reactions of (*Z*)-1,3-pentadiene are much slower than the corresponding reactions of (*E*)-1,3-pentadiene, in which the destabilizing repulsion in its *s-cis* conformation is between hydrogens and is much less severe.

Focused Problems

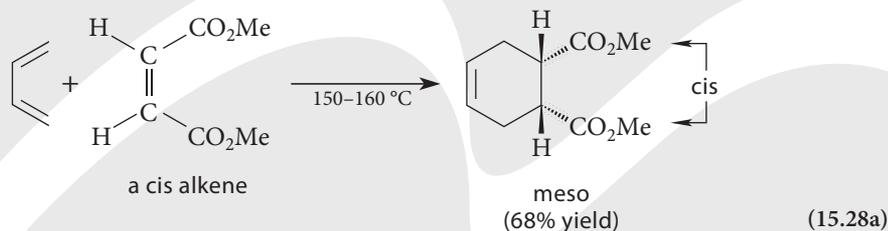
- 15.17 A mixture of 0.1 mol of (2*E*,4*E*)-2,4-hexadiene and 0.1 mol of (2*E*,4*Z*)-2,4-hexadiene was allowed to react with 0.1 mol of TCNE. After the reaction, the unreacted diene was found to consist of only one of the starting 2,4-hexadiene isomers. Which isomer did not react? Explain.
- 15.18 Complete the following Diels–Alder reaction.



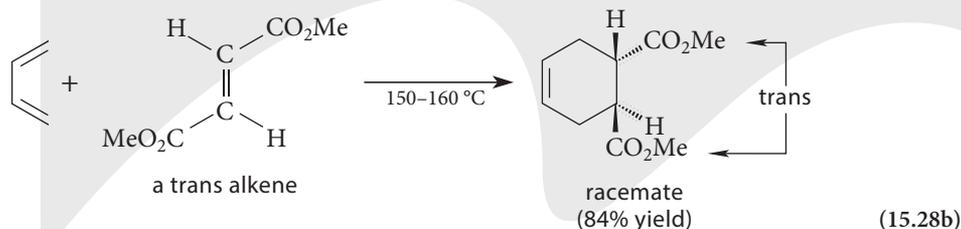
C. Stereochemistry of the Diels–Alder Reaction

If the Diels–Alder reaction takes place in a single step without reactive intermediates, and if the transition-state picture of Fig. 15.13 is correct, then the diene should undergo a syn addition to the dienophile. Likewise, the dienophile should undergo a 1,4-syn addition to the diene. Each component adds to the other at *one face* of the π system.

The stereochemistry of the Diels–Alder reaction is completely consistent with these predictions. If we use a dienophile that is a *cis* alkene, groups that are *cis* in the alkene starting material are also *cis* in the product.

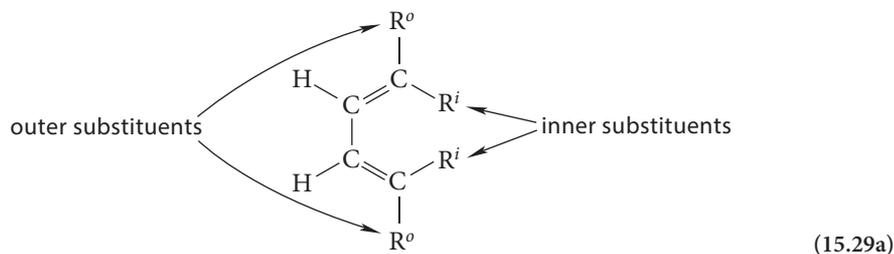


Use of the *trans* isomer of this dienophile gives the complementary result:

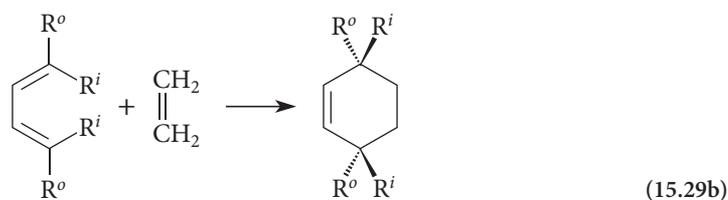


Although one enantiomer of the product is shown in Eq. 15.28b, the product is the racemate, because both starting materials are achiral (Sec. 7.7A).

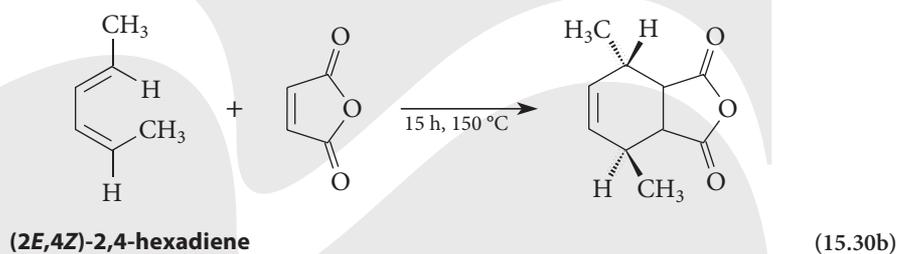
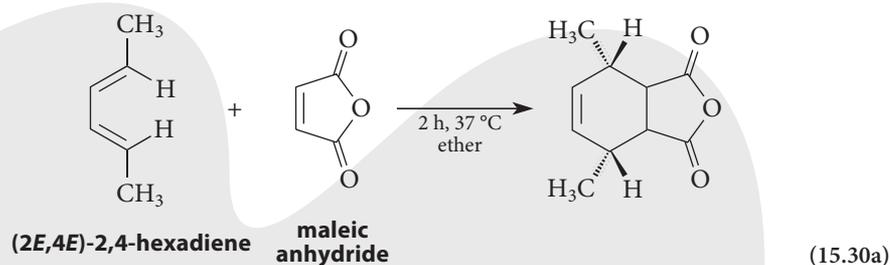
Syn addition to the diene is revealed if the terminal carbons of the diene unit are stereocenters. To assist in the analysis of stereochemistry, we first draw the diene in its *s-cis* conformation and then classify the groups at the terminal carbons as inner substituents (R^i) or outer substituents (R^o):



A syn addition requires that in the Diels–Alder product, the two inner substituents always have a cis relationship; the two outer substituents are also cis; and an inner substituent on one carbon is always trans to an outer substituent on the other.

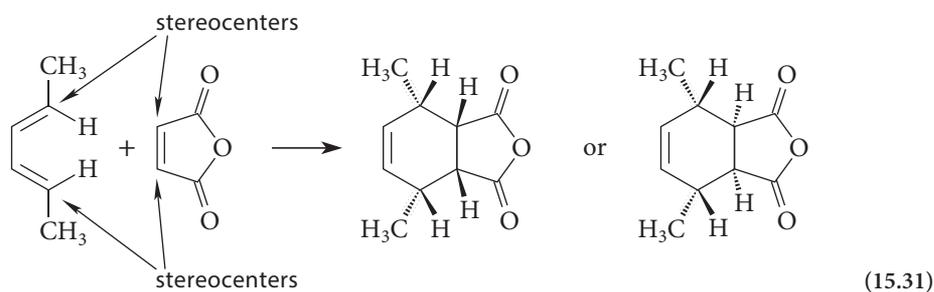


The following reactions of the stereoisomeric 2,4-hexadienes with the dienophile maleic anhydride demonstrate these points.



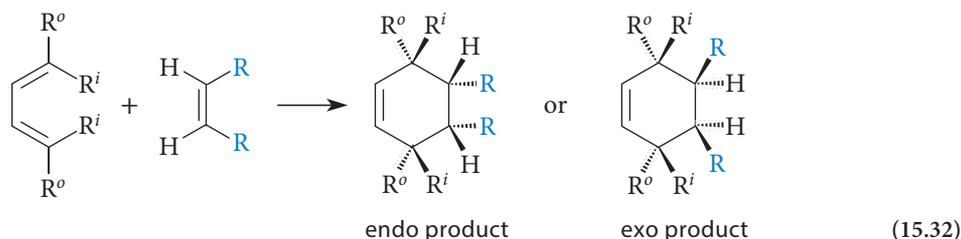
In Eq. 15.30a, the methyl groups in the diene are both outer substituents, and they are cis in the product. In Eq. 15.30b, one methyl group in the diene is outer and the other is inner; consequently, they are trans in the product. (Notice, incidentally, the different reaction conditions required for reactions of the two dienes in Eqs. 15.30a and b. The latter reaction requires *much* more drastic conditions. Why?) (See Eq. 15.27b.)

One other stereochemical issue arises in the reactions of Eqs. 15.27a and b: the stereochemistry at the ring junction. Because maleic anhydride is a cis alkene, and because the Diels–Alder reaction is a syn addition, the stereochemistry at the ring junction must be cis. However, for a given diene and dienophile, two diastereomeric syn-addition products are possible. The reaction of Eq. 15.31 illustrates this point:

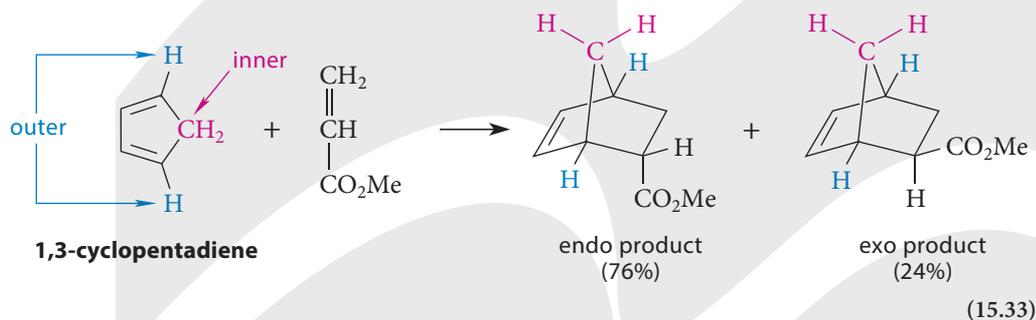


This issue arises when *both* the terminal carbons of the diene *and* the carbons of the dienophile are stereocenters.

We now classify these two possibilities with a more general equation in which a *cis* alkene reacts with a diene:



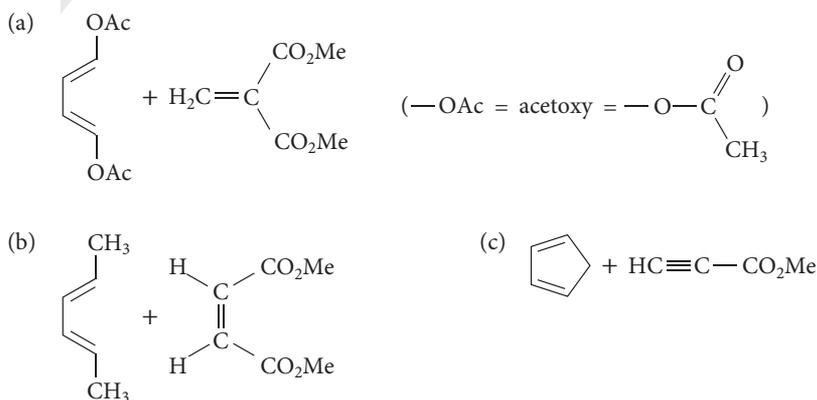
Following the diagram in Eq. 15.29a, we have drawn the diene in its *s-cis* conformation and have labeled the groups at the terminal carbons as outer or inner substituents. The product in which the alkene substituents *R* (shown in blue) are *cis* to the outer diene substituents R^o is said to have **endo** stereochemistry. The product in which the alkene substituents *R* are *trans* to the outer diene substituents R^o is said to have **exo** stereochemistry. (The terms *endo* and *exo* are from Greek roots meaning “inside” and “outside,” respectively.) Because they are diastereomers, the endo and exo products are typically formed in different amounts, as in this example:



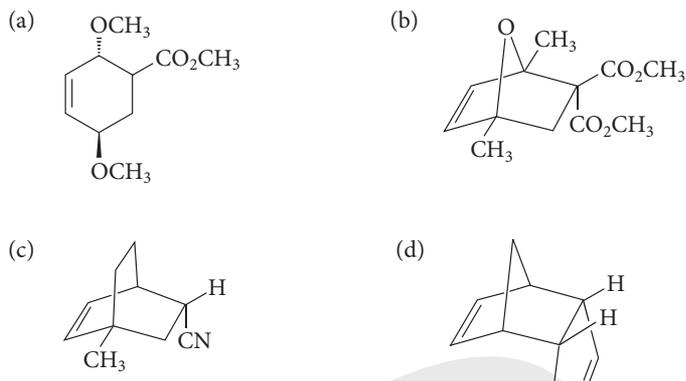
Be sure you see the correspondence between Eq. 15.32 and Eq. 15.33. The CH_2 group of the diene (red) represents the inner groups R^i (tied together in one group as part of the ring); the hydrogens in blue are the outer groups R^o . In the predominant, or endo, product, the $-\text{CO}_2\text{Me}$ group is *cis* to R^o and *trans* to R^i .

Focused Problems

15.19 Give the products formed when each of the following pairs reacts in a Diels–Alder reaction; show the relative stereochemistry of the substituent groups where appropriate. In part (b), show both exo and endo products, and label them.



15.20 Give the structures of the starting materials that would yield each of the following compounds in Diels–Alder reactions. Pay careful attention to stereochemistry, where appropriate.

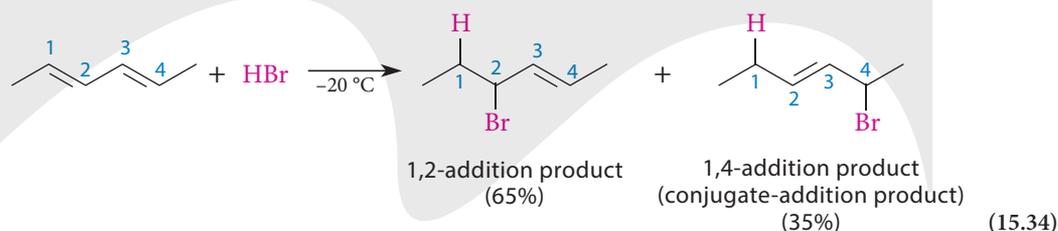


- 15.21 (a) In the products of Eq. 15.30a, the observed stereochemistry at the ring fusion is not specified. Show this stereochemistry, assuming that the Diels–Alder reaction gives the endo product.
- (b) Sketch diagrams like the one in Fig. 15.13 (without the orbitals) that shows the approach of the diene and dienophile leading to both endo and exo products in part (a). Pay careful attention to the relative positions of substituent groups.

15.4 ADDITION OF HYDROGEN HALIDES TO CONJUGATED DIENES

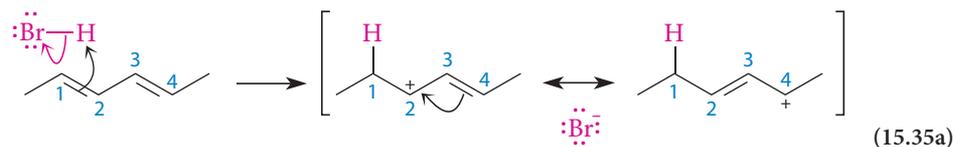
A. 1,2- and 1,4-Additions

Conjugated dienes, like ordinary alkenes (Sec. 4.7), react with hydrogen halides; however, conjugated dienes give two types of addition product. (The numbers are for reference in describing the addition; they are not associated with nomenclature.)

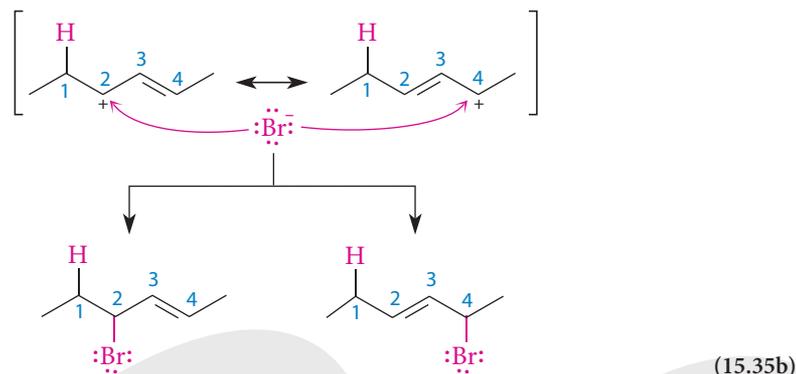


The major product is a *1,2-addition* product. (We address why this is the major product in Sec. 15.4B.) **1,2-Addition** means that addition (of HBr in this case) occurs at adjacent carbons. The minor product results from *1,4-addition*, or *conjugate addition*. In a **1,4-addition**, or **conjugate addition**, addition occurs to carbons that have a 1,4-relationship.

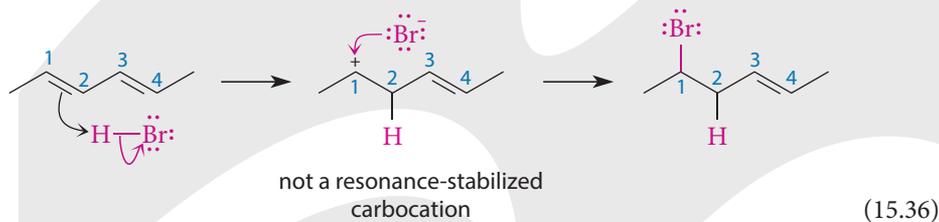
The 1,2-addition reaction is analogous to the reaction of HBr with an ordinary alkene. But how can we account for the conjugate-addition product? As in HBr addition to ordinary alkenes, the first mechanistic step is protonation of a double bond. Protonation of the diene in Eq. 15.34 at either of the equivalent carbons labeled as 1 and 4 gives a resonance-stabilized carbocation:



The resonance structures for this carbocation show that the positive charge in this ion is not localized, but is instead *shared* by two different carbons. *Two constitutional isomers are formed in Eq. 15.34 because the bromide ion can react at either of the electron-deficient carbons:*

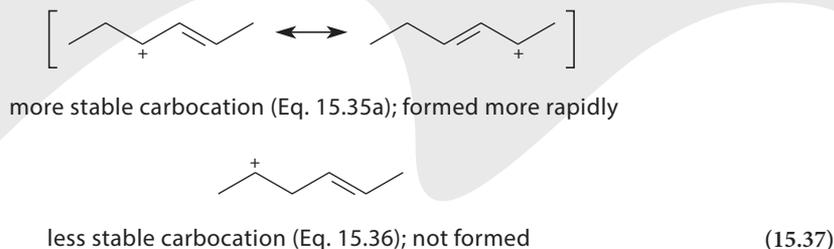


Protonation at carbon-2 of the diene would give a different carbocation, which would react with bromide ion to give an alkyl halide that is different from those obtained experimentally:



(Compare the product of this reaction with the 1,2-addition product in Eq. 15.34 or 15.35.)

The course of addition to conjugated alkenes is suggested by Hammond's postulate (Sec. 4.8D), which predicts that the reaction pathway involving the more stable carbocation occurs more rapidly. Because the carbocation in Eq. 15.35a is more stable, it is formed more rapidly; therefore, the products derived from this carbocation are the ones observed. Although both possible carbocations are secondary, the carbocation in Eq. 15.35a is *resonance-stabilized*, but the carbocation in Eq. 15.36 is not:



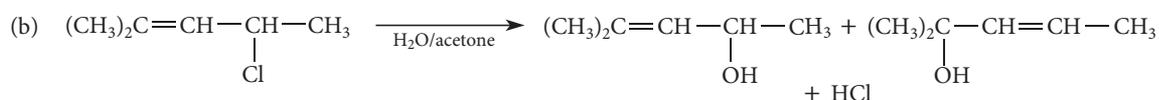
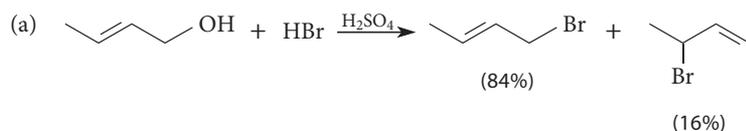
In other words, resonance accounts for the greater stability of the carbocation intermediate that is formed.

Focused Problems

15.22 Use the reaction mechanism, including the resonance structures of the carbocation intermediates, to predict the products of the following reactions.

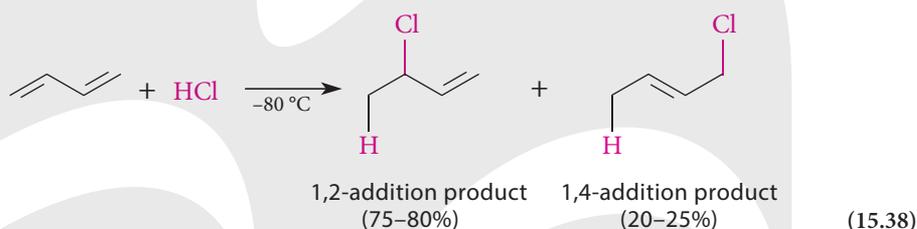
- Addition of HCl to 1,3-butadiene
- S_N1 solvolysis of 3-chloro-1-methylcyclohexene in ethanol

15.23 Suggest a mechanism for each of the following reactions that accounts for both products.

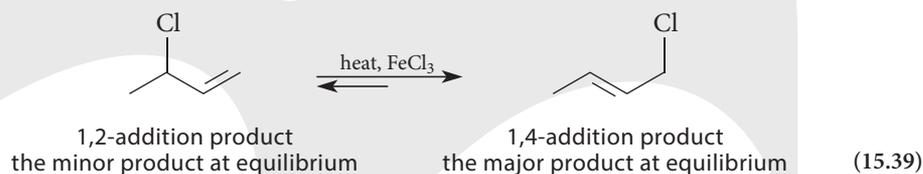


B. Kinetic and Thermodynamic Control

It would be reasonable to expect that when a reaction can give products that differ in stability, the more stable product should be formed in greater amount. However, sometimes the *less* stable product is formed in larger amount. Consider, for example, the addition of hydrogen halides to conjugated dienes. When a conjugated diene reacts with a hydrogen halide to give a mixture of 1,2- and 1,4-addition products, the 1,2-addition product predominates at low temperature:

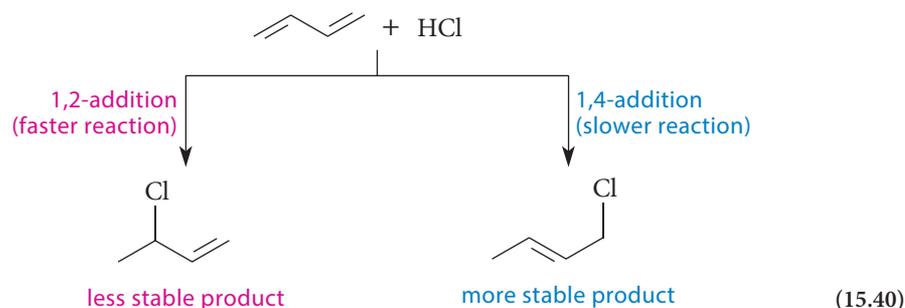


In Sec. 4.5B we showed that alkenes with internal double bonds are more stable than their isomers with terminal double bonds, because the internal double bonds have more alkyl branches. Therefore, in Eq. 15.38, *the major product is the less stable one*. This can be demonstrated experimentally by bringing the two alkyl halide products to equilibrium with heat and Lewis acids:



Because the more stable isomer always predominates in an equilibrium (Sec. 3.5), the result in Eq. 15.39 shows that the 1,4-addition product is more stable than the 1,2-addition product, as expected.

When the less stable product of a reaction is the major product, then two things must be true. First, the less stable product *must form more rapidly* than the other products. As noted in Sec. 4.8, a reaction in which two products form from the same starting material is in reality two competing reactions. Consequently, the reaction that forms the less stable product is faster. Second, the products *must not come to equilibrium* under the reaction conditions, because otherwise the more stable compound would be present in larger amount. So, in the addition of HCl to conjugated dienes, the predominance of the less stable product (Eq. 15.38) shows that 1,2-addition, which gives the less stable product, is faster than 1,4-addition:



When the products of a reaction do not come to equilibrium under the reaction conditions, the reaction is said to be **kinetically controlled**. In a kinetically controlled reaction, the relative proportions of products are controlled solely by the relative rates at which they are formed. Therefore, the addition of hydrogen halides to conjugated dienes is a kinetically controlled reaction. On the other hand, if the products of a reaction come to equilibrium under the reaction conditions, the reaction is said to be **thermodynamically controlled**.

It is possible that a given kinetically controlled reaction might give about the same distribution of products as would be obtained if the products were allowed to come to equilibrium. However, it is *impossible* for a thermodynamically controlled reaction to give a product distribution other than the equilibrium distribution. So, when we obtain a product distribution that is clearly different from that obtained at equilibrium (as occurs in the addition of HCl to conjugated dienes), we know immediately that the reaction must be kinetically controlled.



An Analogy for Kinetic Control



Marius G/Shutterstock

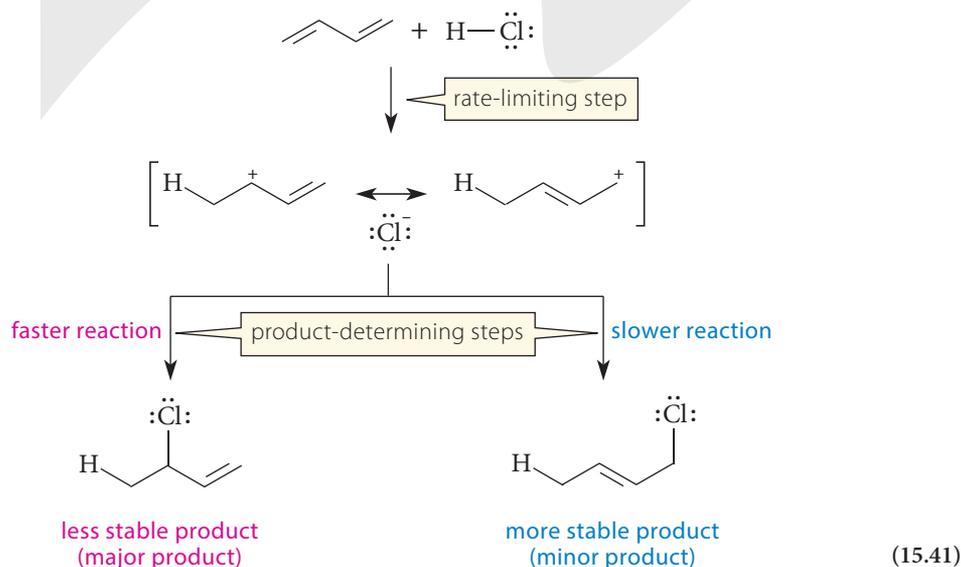
Imagine a very disoriented steer stumbling randomly around a pasture with a shallow watering hole and a deep well with a high fence around it. Where is he likely to end up?

Certainly the deep well is the state of lowest potential energy. However, because of the fence around the well, it is simply less likely that the animal will fall into the well; he is much more likely to wander into the watering hole.

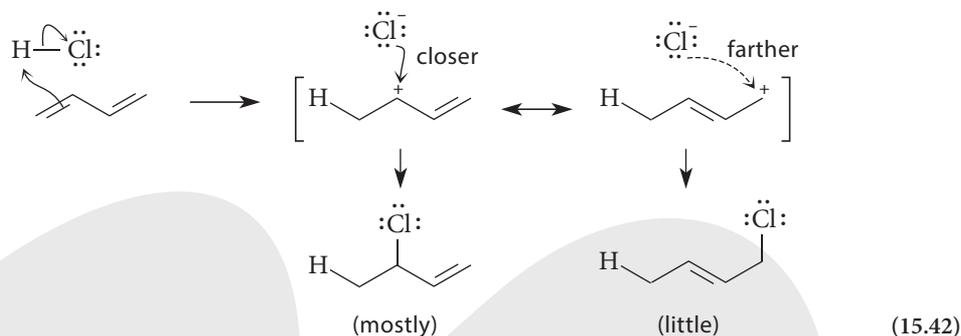
Now, if you imagine a large herd of similarly disoriented steers staggering around the same (very large) pasture, you should get a reasonably good image of kinetic control. Most of the animals wander into the watering hole, even though this is not the state of lowest potential energy.

Likewise with molecules: It is possible for the formation of a more stable product to have a greater standard free energy of activation (a greater energy barrier) than the formation of a less stable product. In such a case, the less stable product forms more rapidly and in greater amount.

In hydrogen halide addition to a conjugated diene, the first and rate-limiting step in the formation of both 1,2- and 1,4-addition products is the same—protonation of the double bond. Consequently, the product distribution must be determined by the relative rates of the *product-determining steps* (Sec. 9.6B): the nucleophilic reaction of the halide ion at one or the other of the electron-deficient carbons of the allylic carbocation intermediate.



Why is the 1,2-addition product formed more rapidly? The reaction is typically carried out in solvents in which the HCl is not dissociated. In other words, the diene reacts with *undissociated* HCl. Consequently, the carbocation and its chloride counter-ion, when first formed, exist as an *ion pair* (see Fig. 8.6, Sec. 8.6F). That is, the chloride ion and the carbocation are closely associated. The chloride ion simply finds itself closer to the positively charged carbon adjacent to the site of protonation than to the other carbon. Addition is completed, therefore, at the nearer site of positive charge, giving the 1,2-addition product.



(The elegant experiment that suggested this explanation is described in Problem 15.74.)

The reason for kinetic control varies from reaction to reaction. Whatever the reason, the relative amounts of products in a kinetically controlled reaction are determined by the relative free energies of the *transition states* for each of the product-determining steps and *not* by the relative free energies of the products.

Focused Problem

- 15.24 (a) Give the structures of the 1,2- and 1,4-addition products that would be formed in the reaction of HBr with (*E*)-3-methyl-1,3-pentadiene? (*Hint*: Which double bond would be protonated more rapidly? Think about carbocation stabilities, and apply Hammond's postulate.)



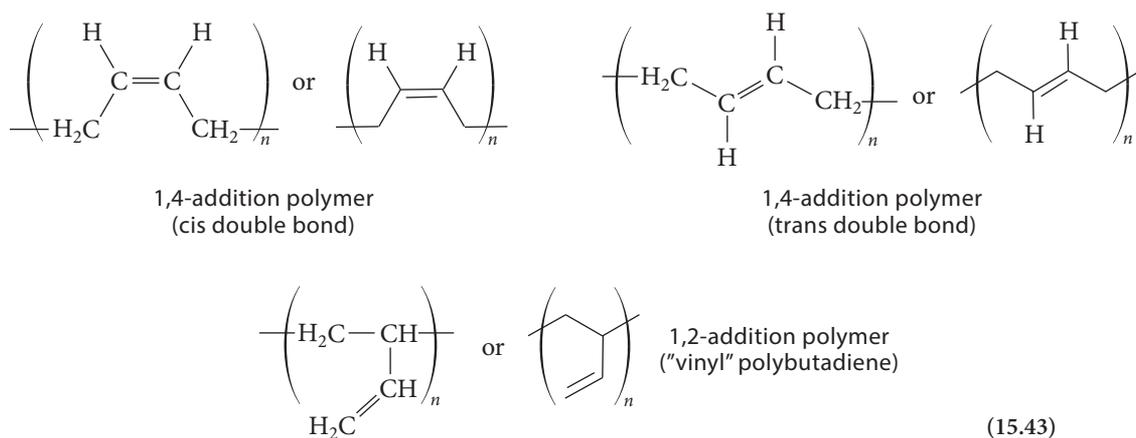
- (b) Which of the alkyl bromide products in part (a) will predominate if they are brought to equilibrium? Why?

Chemistry
in the
Real World

15.5 DIENE POLYMERS

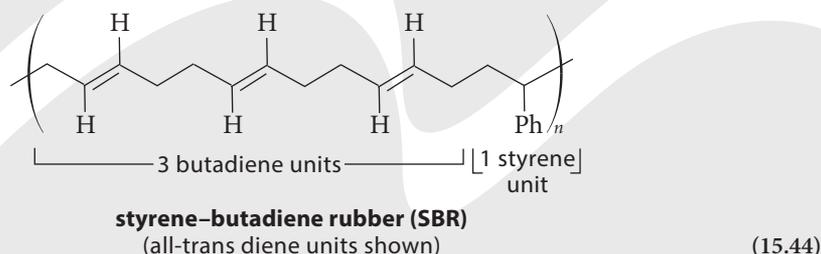
1,3-Butadiene is one of the most important raw materials of the synthetic rubber industry, which includes the production of automobile tires. The annual global production of 1,3-butadiene is about 25 billion pounds. It is also used in the production of nylon.

1,3-Butadiene can be polymerized to give polybutadiene. This polymer can result either from 1,4-addition of butadiene molecules to each other or from 1,2-addition. The 1,4-addition polymers can contain *cis* or *trans* double bonds.



These different types of polymer linkages, although shown separately in the structures in Display 15.43, can be present together in various proportions in a given polymer molecule. The most useful butadiene polymers contain mostly cis double bonds. This type of polymer is produced by the action of transition-metal organometallic catalysts of a type that we present in Sec. 18.5. (The cis double bond is a consequence of the way that the π bonds of the diene interact with the catalyst.) Different types of catalysts can be used to give the different types of diene polymers.

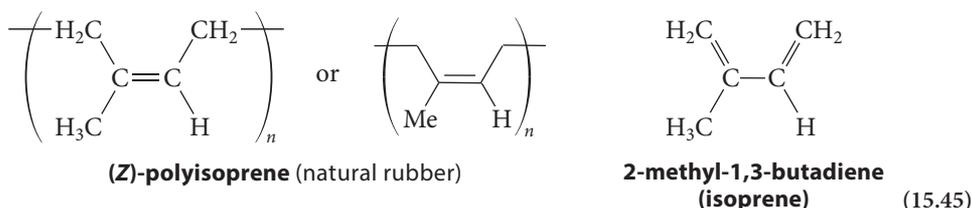
1,3-Butadiene can also be polymerized together with styrene ($\text{H}_2\text{C}=\text{CH}-\text{Ph}$), usually in about a 3:1 ratio, to give another type of synthetic rubber called *styrene-butadiene rubber* (SBR), most of which is used for tires and tread rubber.



As with polybutadiene, the butadiene units in SBR can be polymerized in either a 1,4- or 1,2-addition, and the 1,4-addition polymer can contain cis or trans double-bond stereochemistry. The example here is simplified because it shows an SBR unit with only trans double bonds, which is the predominant type of linkage in commercial SBR. For example, one typical formulation of SBR contains 54.5% trans double bonds in the butadiene units, 9% cis double bonds in the butadiene units, 13% "vinyl" units (resulting from 1,2-addition of butadiene), and 23.5% styrene units. Moreover, the styrene units can occur at random. SBR is produced either by organometallic catalysis or by free-radical polymerization (Sec. 10.3 and Focused Problem 15.25) in an aqueous emulsion.

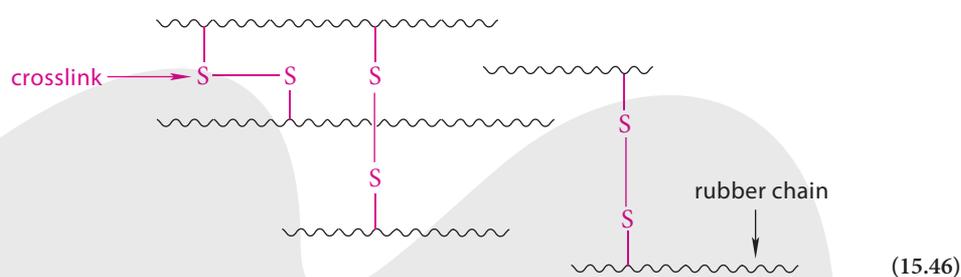
SBR is an example of a **copolymer**: a polymer produced by the simultaneous polymerization of two or more monomers. The annual global demand for styrene-butadiene copolymers is more than 15 billion pounds and is growing rapidly as the demand for automobiles increases around the globe.

Natural rubber is (*Z*)-polyisoprene, another diene polymer:



Although it is conceptually a diene polymer, natural rubber is not made in nature from isoprene. (The biosynthesis of naturally occurring isoprene derivatives is discussed in Sec. 17.6B.) Rubber hydrocarbon (polyisoprene) is obtained as a 40% aqueous emulsion from the rubber tree. Although polyisoprene can be made synthetically, the natural material is generally preferred for economic reasons. Chemists and botanists are investigating the possibility of cultivating other hydrocarbon-producing plants that could become hydrocarbon sources of the future.

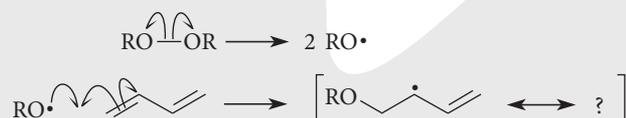
Crude natural rubber, SBR, and other diene polymers do not have adequate mechanical durability for their commercial applications. For this reason, they are subjected to a process called *vulcanization*. In this process, discovered in 1840 by Charles Goodyear (1800–1860), the rubber is kneaded and heated with sulfur. The sulfur forms disulfide crosslinks between the polymer chains, which can be represented schematically as follows:



The crosslinks increase the rigidity and strength of the polymer at the cost of some flexibility.

Focused Problem

- 15.25 An initiation step (Eq. 10.8, Sec. 10.1C) in the free-radical co-polymerization of styrene and 1,3-butadiene is the free-radical addition of a peroxide-derived radical to a double bond of 1,3-butadiene:

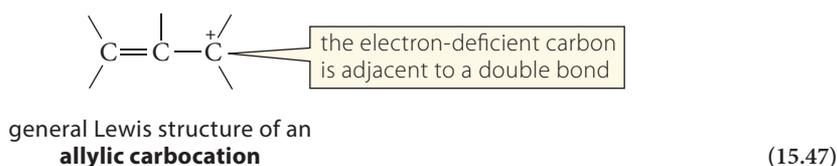


- Use the fishhook curved-arrow notation to derive the missing resonance structure.
- Use this resonance structure as part of a fishhook mechanism for free-radical co-polymerization to form SBR. (Show the incorporation of one diene unit in a 1,4-addition, one diene unit in a 1,2-addition, and one styrene unit.)
- Suggest a reason that the diene part of the polymer has mostly *trans* double-bond stereochemistry.

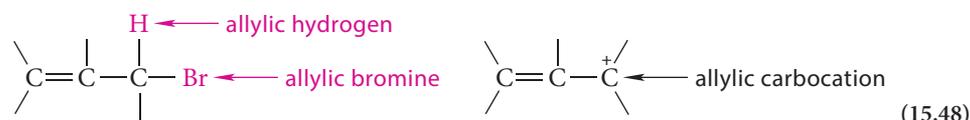
15.6 THE CONNECTION BETWEEN RESONANCE AND STABILITY

In Sec. 1.5, we stated that resonance is a stabilizing effect. We've shown other examples in which the resonance stabilization of a carbocation intermediate determines the course of the reaction. (See, for example, Eq. 15.35a, Sec. 15.4A.) Now we delve more deeply into the question of resonance stabilization: What is it about electron delocalization that lowers the energy of a molecule, radical, or ion?

To explore the connection between resonance and stability, we use a carbocation similar to the one involved in HBr addition to conjugated alkenes (Eq. 15.35a). This is an example of an **allylic carbocation**: a carbocation in which the positively charged, electron-deficient carbon is adjacent to a double bond.

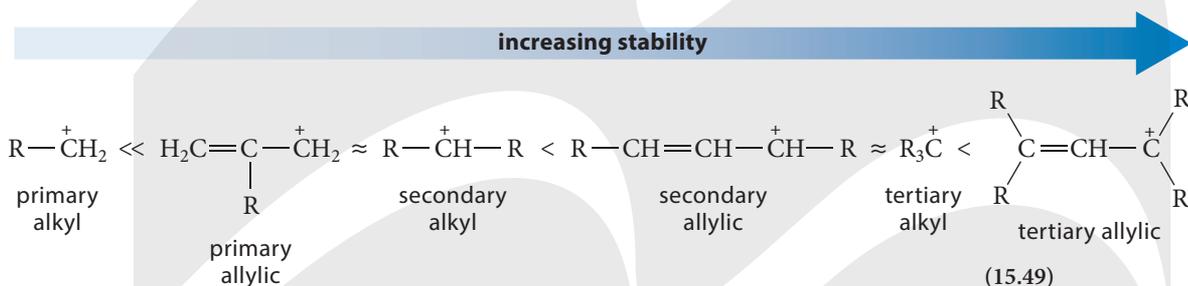


The word *allylic* is a generic term applied to any functional group at a carbon adjacent to a double bond.



Allylic carbocations are more stable than comparably branched nonallylic alkyl carbocations. Roughly speaking, an allylic carbocation is about as stable as a nonallylic alkyl carbocation with one additional alkyl branch. For example, a secondary allylic carbocation is about as stable as a tertiary nonallylic one. To summarize:

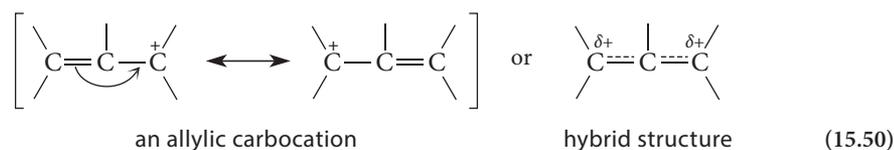
Stability of carbocations:



The stability of allylic carbocations lies in their electronic structures, which we now explore using molecular orbital (MO) theory. The π -electron structure of the allyl cation, $\text{H}_2\text{C}=\text{CH}-\text{CH}_2^+$ (the simplest allylic cation), is shown in **Fig. 15.14**. The electron-deficient carbon and the carbons of the double bond are all sp^2 -hybridized; each carbon has a 2p orbital (Fig. 15.14a). The overlap of these three 2p orbitals results in three π molecular orbitals. The MO of lowest energy, π_1 , is bonding with an energy of $+1.41\beta$, and it has no nodes. (Remember that β is a negative number.) The next MO, π_2 , has the same energy as an isolated 2p orbital (0β). An MO that has the same energy as an isolated 2p orbital is called a **nonbonding MO (NBMO)**. This MO has one node. Because nodes must be placed symmetrically, this node goes through the central carbon. The position of this node determines the location of the positive charge, as we'll see shortly. The MO of highest energy, π_3^* , is antibonding. It has two nodes—one between each carbon.

The allyl cation has two electrons; both reside in π_1 . Each π electron contributes $+1.41\beta$ to the energy of the molecule, for a total of $+2.82\beta$. The *delocalization energy* (Sec. 15.1A) of the allyl cation is the difference between this energy and the sum of the energies of an isolated ethylene ($+2.00\beta$) and an isolated 2p orbital (0β). The allyl cation, then, has a delocalization energy of 0.82β . Because the source of this stabilization is the “nodeless” π_1 MO, *the stabilization of the allyl cation arises from the delocalization of π electrons across the entire molecule.* This delocalization, then, is a source of *additional bonding* in the allyl cation that would not be present if the alkene π bond and the carbocation could not interact.

What is the connection between molecular stability and resonance? *Resonance structures provide a symbolic way to show electron delocalization in the low-energy bonding MOs with Lewis structures.* For example, allylic cations have two equivalent resonance structures.



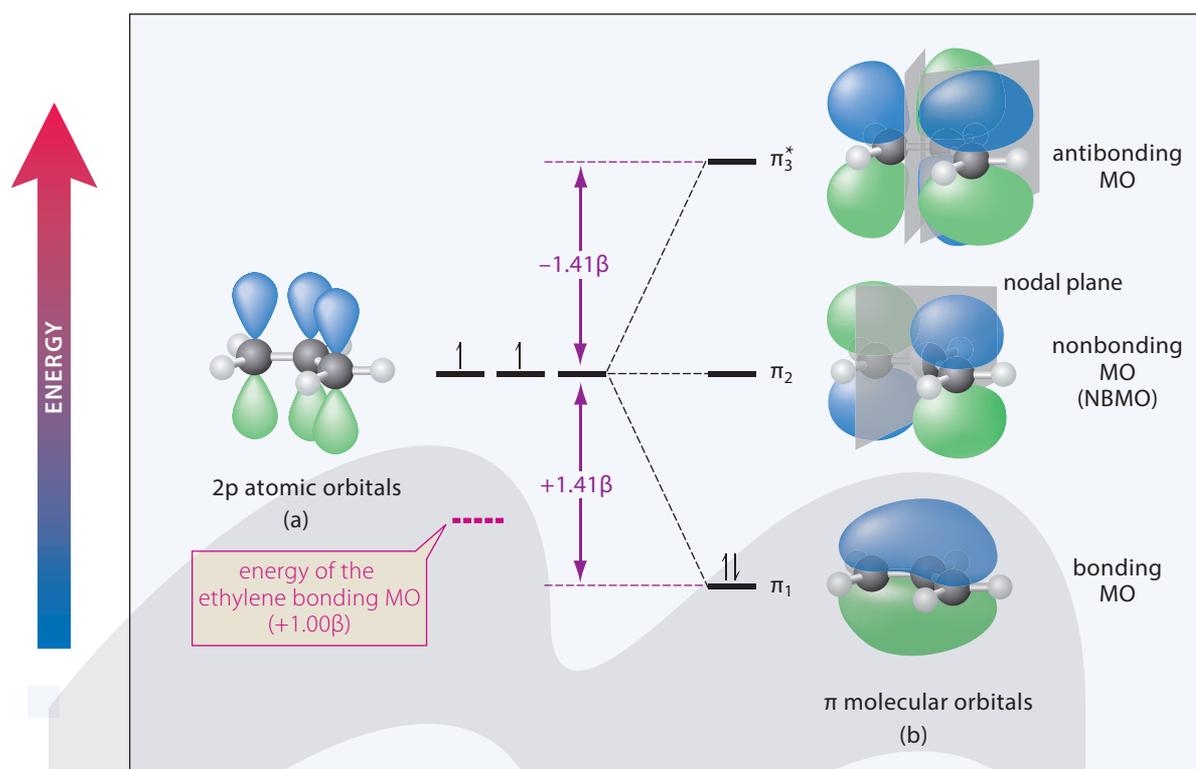


FIGURE 15.14 (a) An orbital interaction diagram that shows the arrangement of 2p orbitals in the allyl cation, the simplest allylic carbocation. The axes of the 2p orbitals are parallel and thus properly aligned for overlap. (b) Interaction of the three 2p orbitals (dashed lines) gives three π MOs. Nodal planes are shown in gray. The two 2p electrons both go into π_1 , the bonding MO. The violet arrows and numbers show the relative energies of the MOs in β units, and the relative energy of the ethylene bonding MO is shown in red. The absence of electrons in π_2 accounts for the positive charge. The nodal plane in π_2 cuts through the central carbon; as a result, there is no positive charge on this carbon.

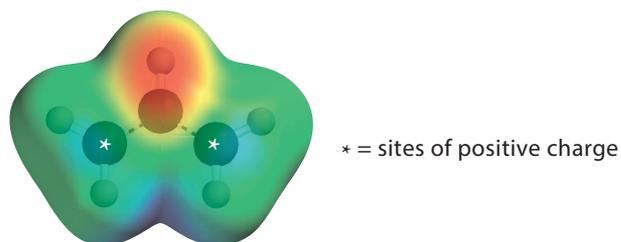
The two structures show the sharing of π -electron density and charge—in other words, electron delocalization. The hybrid structure shows the same delocalization with dashed bonds and partial charges. In summary, the logic of resonance stabilization is as follows:

1. Resonance structures symbolize electron delocalization.
2. Electron delocalization is stabilizing because it results in additional bonding associated with the formation of low-energy bonding MOs.
3. Resonance, therefore, is a stabilizing effect.

Because resonance describes electron delocalization, *delocalization energy* (Sec. 15.1B), the energetic advantage of electron delocalization, is also referred to as **resonance energy**. Section 1.4 explained that resonance-stabilized molecules are more stable than any of their fictional contributors. Resonance energy is a quantitative measure of this additional stability.

One other important aspect of resonance structures emerges from a consideration of the positive-charge distribution in the allyl cation. Notice in the resonance structures that, although the π electrons are delocalized across the entire molecule, the positive charge resides on only two of the three carbons; *there is no positive charge on the central carbon of an allylic cation*. This charge distribution is consistent with the molecular orbital description of the cation, shown in Fig. 15.14b. The charge is due to the absence of a third π electron. If a third π electron were present, it would occupy the NBMO π_2 . In other words, the picture of π_2 describes the distribution of the “missing electron”—the positive charge. Because π_2 has a node on the central carbon, this carbon bears no charge. This charge distribution is shown graphically in the EPM of

the allyl cation, which is calculated from MO theory. The terminal carbons have more positive charge (*blue*) than the central carbon (*red*):



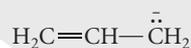
EPM of the allyl cation

(15.51)

Resonance structures are useful because they give us the qualitative results of MO theory without any calculations!

Focused Problems

- 15.26 (a) The allyl anion has a nonbonding electron pair on the allylic carbon:

**allyl anion**

This anion has two more π electrons than the allyl cation. Use the molecular orbital diagram in Fig. 15.14b to decide which molecular orbital these “extra electrons” occupy.

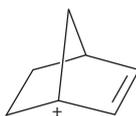
- (b) According to the molecular orbital description, which carbons of the allyl anion bear the negative charge?
- (c) Show that the same conclusion can be reached by drawing resonance structures of the allyl anion. Use the curved-arrow notation.
- 15.27 (a) The allyl radical has an unpaired electron on the allylic carbon:

**allyl radical**

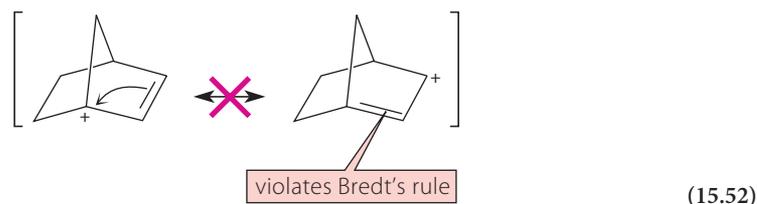
- (b) According to the molecular orbital description, which carbons of the allyl anion share the unpaired electron?
- (c) Show that the same conclusion can be reached by drawing resonance structures of the allyl radical. Use the fishhook notation.

The discussion in this section shows that the phenomenon of resonance is a *symbolic depiction of orbital overlap*. Section 3.3B presented the guidelines for drawing resonance structures. To these rules we now add one more: *Do not draw resonance structures if the corresponding orbital overlap is impossible*.

As an example, consider the following carbocation in which the cationic carbon is a bridgehead carbon of a bicyclic structure:

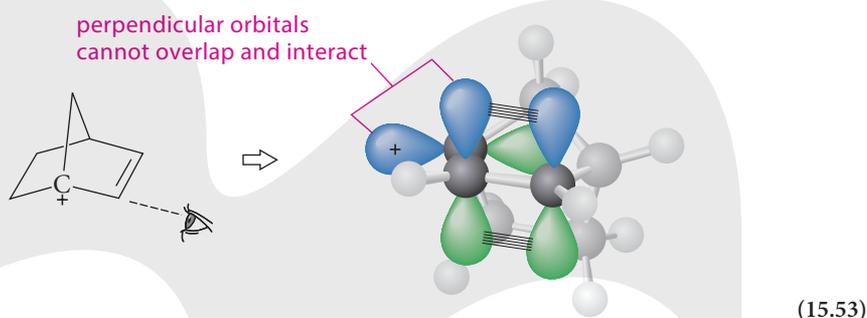


This carbocation is formally allylic, but it is very unstable. Our first indication of this instability is that the resonance structure of this carbocation violates Bredt's rule (Sec. 7.6C) because it contains a bridgehead double bond.



Another source of the instability of this carbocation is the requirement that the optimum geometry required by its sp^2 hybridization should be trigonal-planar. The cationic carbon is constrained by the ring to a somewhat pyramidal geometry, and it cannot become planar without introducing intense ring strain. However, we focus here on the absence of orbital overlap, which makes the situation that much worse.

The fundamental reason for this instability (and for Bredt's rule) is that the 2p orbitals of the double bond are perpendicular to the empty 2p orbital of the cation and therefore cannot provide the orbital overlap necessary for stabilization.



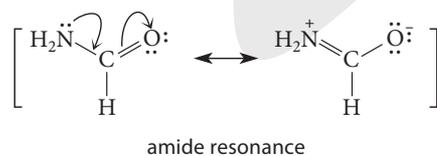
Moreover, the electronegativity of the sp^2 -hybridized carbons of the double bond further destabilizes the positive charge.

To the rules in Sec. 3.3C for determining the importance of resonance structures, we add one more:

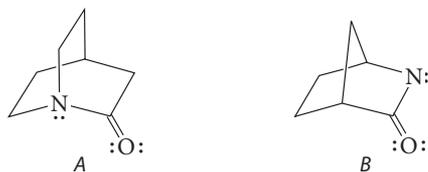
If the orbital overlap symbolized by a resonance structure does not occur, the resonance structure is not important.

Focused Problem

15.28 Most amides are stabilized by a resonance interaction between the nitrogen and the double bond of the carbonyl group:

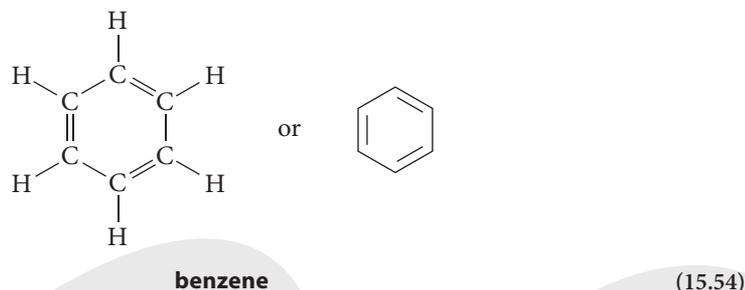


Is this resonance interaction possible in each of the following bicyclic amides? Why or why not?

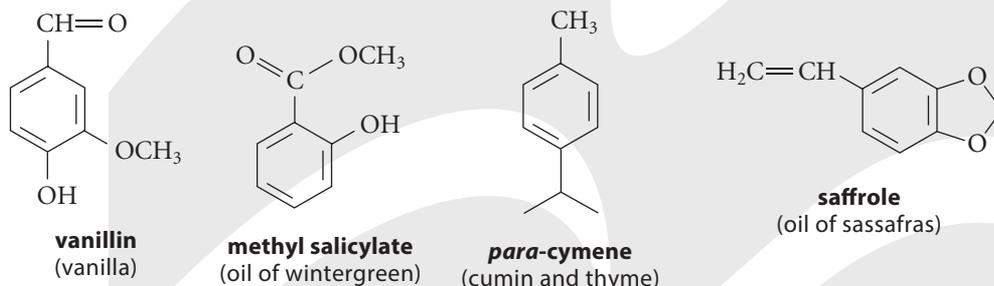


15.7 INTRODUCTION TO AROMATIC COMPOUNDS

The term *aromatic*, as we show in this section, is a precisely defined *structural* term that applies to cyclic conjugated molecules that meet certain criteria. Benzene and its derivatives are the best-known examples of aromatic compounds.



The origin of the term *aromatic* is historical: many fragrant compounds known from earliest times, such as the following ones, proved to be derivatives of benzene.

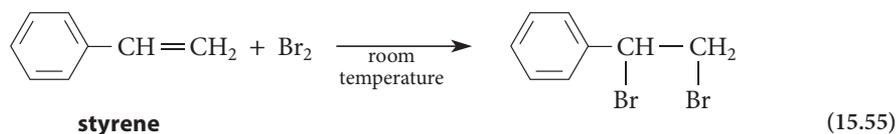


Although it is known today that benzene derivatives are not distinguished by unique odors, the term *aromatic*—which has nothing to do with odor—has stuck, and it is now a class name for benzene, its derivatives, and a number of other organic compounds.

Development of the theory of aromaticity was a major theoretical advance in organic chemistry because it solved a number of intriguing problems that centered on the structure and reactivity of benzene. Before considering this theory, let's see what some of these problems were.

A. Benzene, a Puzzling “Alkene”

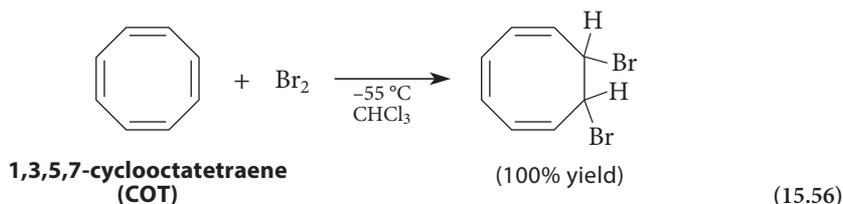
The structure used today for benzene was proposed in 1865 by August Kekulé, who claimed later that it came to him in a dream. The Kekulé structure portrays benzene as a cyclic conjugated triene. Yet benzene does not undergo any of the addition reactions that are associated with either conjugated dienes or ordinary alkenes. Benzene itself, as well as benzene rings in other compounds, are inert to the usual conditions of alkene addition reactions. This property of the benzene ring is illustrated by the addition of bromine to styrene, a compound that contains both a benzene ring and one additional double bond:



The noncyclic double bond in styrene rapidly adds bromine, but the benzene ring remains unaffected, even if excess bromine is used. To early chemists, *this lack of alkenelike reactivity defined the uniqueness of benzene and its derivatives.*

Does benzene's lack of reactivity have something to do with its cyclic structure? Cyclohexene adds bromine readily. Perhaps, then, it is the cyclic structure and the conjugated double bonds

that *together* account for the unusual behavior of benzene. However, 1,3,5,7-cyclooctatetraene (abbreviated in this text as COT) adds bromine smoothly even at low temperature.



These examples illustrate the difficulties that the Kekulé structure could not easily explain away. To account for the resistance of benzene to addition reactions, Albert Ladenburg in 1869 proposed a structure for benzene called *Ladenburg benzene* or *prismane*:



Although Ladenburg benzene is recognized today as a highly strained and unstable molecule (it has been described as a “caged tiger”), an attractive feature of this structure to nineteenth-century chemists that seemed to explain its lack of reactivity was the absence of double bonds.

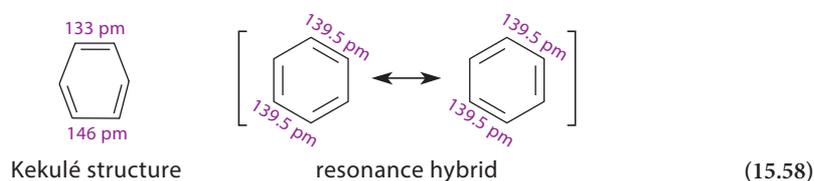
Several facts, however, ultimately led to the adoption of the Kekulé structure. One of the most compelling arguments was that all efforts to prepare the alkene 1,3,5-cyclohexatriene using standard alkene syntheses led to benzene. The argument was, then, that benzene and 1,3,5-cyclohexatriene must be one and the same compound. The reactions used in these routes received additional credibility because they were also used to prepare COT, which, as Eq. 15.56 illustrates, has the reactivity of an ordinary alkene.

Although the Ladenburg benzene structure had been discarded for all practical purposes decades earlier, its final refutation came in 1973 with its synthesis by Professor Thomas J. Katz and his colleagues at Columbia University. These chemists found that Ladenburg benzene is an explosive liquid with properties that are quite different from those of benzene.

How, then, can the Kekulé “cyclic triene” structure for benzene be reconciled with the fact that benzene is inert to the usual reactions of alkenes? The answer to this question will occupy our attention in the next three parts of this section.

B. The Structure of Benzene

The structure of benzene is given in **Fig. 15.15a**. This structure shows that benzene has *one* type of carbon–carbon bond with a bond length (139.5 pm) that is the average of the lengths of sp²–sp² single bonds (146 pm) and double bonds (133 pm, **Fig. 15.15c**). All atoms in the benzene molecule lie in one plane. The Kekulé structure for benzene shows *two* types of carbon–carbon bond: single bonds and double bonds. This inadequacy of the Kekulé structure can be remedied, however, by depicting benzene as *the hybrid of two equally contributing resonance structures*:



Benzene is an average of the two resonance contributors; it is *one* compound with *one* type of carbon–carbon bond with a bond order of 1.5—neither a single bond nor a double bond, but a

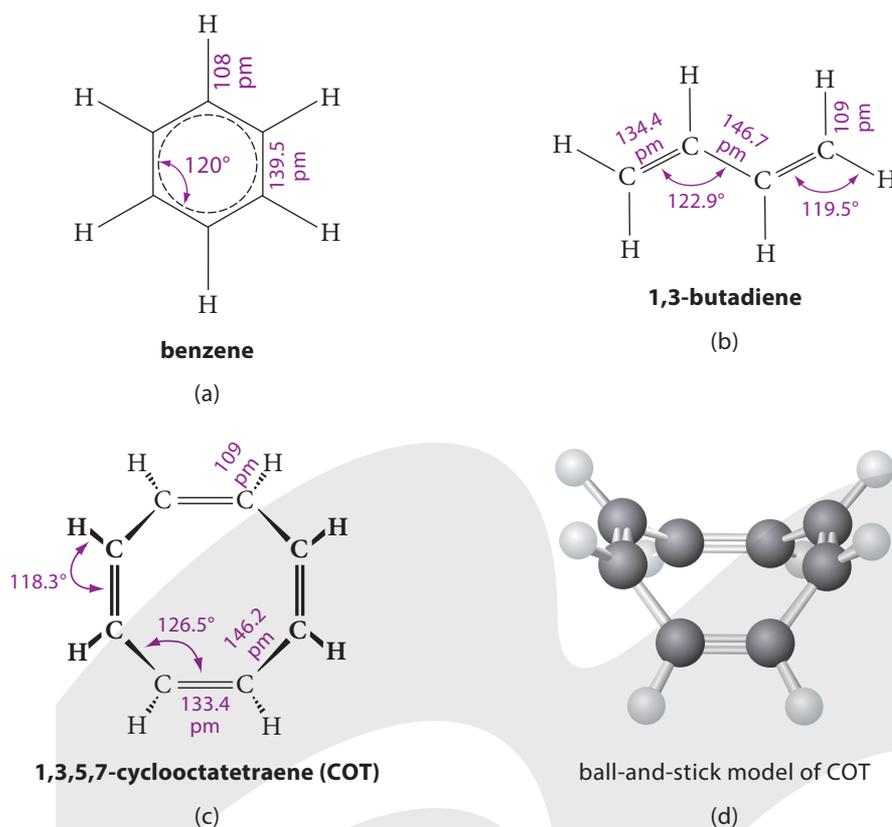
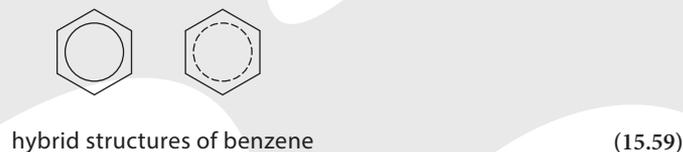


FIGURE 15.15 Comparison of the structures of benzene, 1,3-butadiene, and COT. (a) The structure of benzene. (The hybrid structure is shown.) (b) The structure of 1,3-butadiene, a conjugated diene. (c) The structure of 1,3,5,7-cyclooctatetraene (COT). (d) A ball-and-stick model of COT. The carbon skeleton of benzene is a planar hexagon, and all of the carbon-carbon bonds are equivalent with a bond length that is the average of the lengths of carbon-carbon single and double bonds in COT. In contrast, COT has distinct single and double bonds with lengths that are almost the same as those in 1,3-butadiene, and COT is tub-shaped rather than planar.

bond that is halfway in between. A benzene ring is often represented with either of the following hybrid structures, which are meant to suggest the “smearing out” of double-bond character:



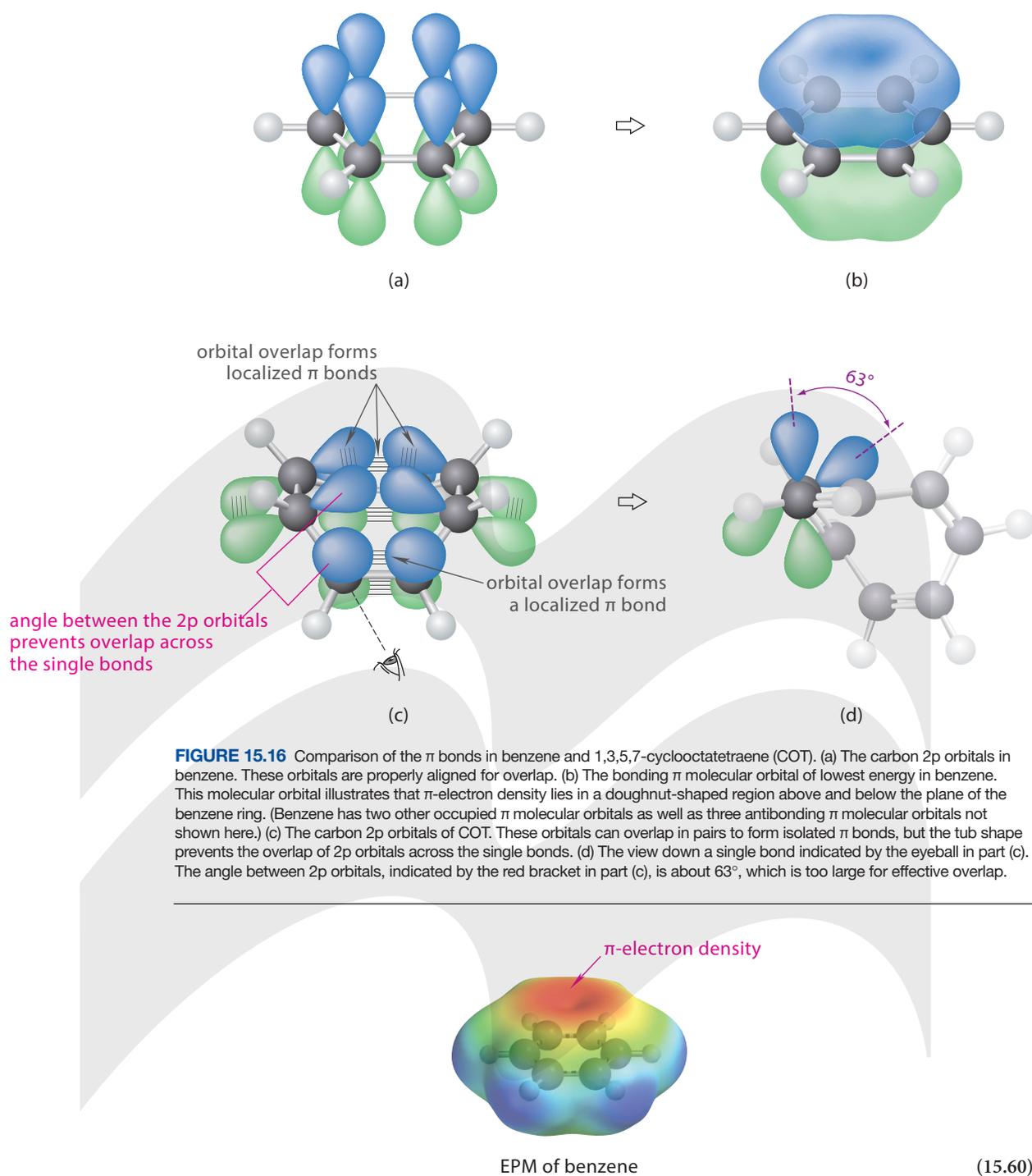
As with other resonance-stabilized molecules, we continue to represent benzene as either one of its resonance contributors because the curved-arrow notation and electronic bookkeeping devices are easier to apply to structures with fixed bonds.

It is interesting to compare the structures of benzene and 1,3,5,7-cyclooctatetraene (COT) in view of their greatly different chemical reactivities (Eqs. 15.55 and 15.56). Their structures are remarkably different (see Fig. 15.15). First, although benzene has a single type of carbon-carbon bond, COT has alternating single and double bonds, which have almost the same lengths as the single and double bonds in 1,3-butadiene. Second, COT is not planar like benzene, but instead is tub-shaped.

The π bonds of benzene and COT are also different (**Fig. 15.16**). The Kekulé structures for benzene suggest that each carbon atom should be trigonal-planar, and therefore sp^2 -hybridized. This means each carbon atom has a 2p orbital (Fig. 15.16a). Because the benzene molecule is planar, and the axes of all six 2p orbitals of benzene are parallel, these 2p orbitals can overlap to form six π molecular orbitals. The bonding π molecular orbital of lowest energy is shown in Fig. 15.16b. (The other five π molecular orbitals of benzene are shown in Further Exploration 15.2 in the *Study Guide and Solutions Manual*.) This molecular orbital shows that π -electron density in benzene lies in doughnut-shaped regions both above and below the plane of the ring. *This overlap is symbolized by the resonance structures of benzene.* The π -electron overlap above and below the plane of the benzene ring is also reflected in the EPM of benzene, which shows a concentration of negative potential in these regions.



FURTHER EXPLORATION 15.2
The π Molecular Orbitals of Benzene



In contrast, the carbon atoms of COT are not all coplanar, but they are nevertheless all trigonal. This means that there is a 2p orbital on each carbon atom of COT (Fig. 15.16c). The tub shape of COT forces the 2p orbitals on the ends of each single bond to be oriented at a 63° angle, which is too far from coplanarity for effective interaction and overlap (Fig. 15.16d). Consequently, the 2p orbitals in COT cannot form a continuous π molecular orbital analogous to the one in benzene. Instead, COT contains four π -electron systems of two carbons each. As far as the π electrons are concerned, *COT looks like four isolated ethylene molecules*. Because there is no electronic overlap between the π orbitals of adjacent double bonds, *COT does not have resonance structures analogous to those of benzene*. (See the additional guideline for resonance structures in Sec. 15.6.)



To summarize: resonance structures can be written for benzene, because the carbon 2p orbitals of benzene can overlap to provide the additional bonding and additional stability associated with *filled bonding molecular orbitals*. Resonance structures *cannot* be written for COT because there is no overlap between 2p orbitals on adjacent double bonds.

Why doesn't COT flatten itself to allow overlap of all its 2p orbitals? We return to this point in Sec. 15.7E.

C. The Stability of Benzene

As mentioned earlier in this section, chemists of the nineteenth century considered benzene to be unusually stable because it is inert to reagents that react with ordinary alkenes. However, chemical reactivity (or the lack of it) is not the way that we measure energy content. We have shown that the more precise way to relate molecular energies is by their *standard heats of formation* ΔH_f° . Because benzene and COT have the same empirical formula (CH), we can compare their heats of formation per CH group. The ΔH_f° of benzene is $82.93 \text{ kJ mol}^{-1}$ or $82.93/6 = 13.8 \text{ kJ mol}^{-1}$ per CH group. The ΔH_f° of COT is $298.0 \text{ kJ mol}^{-1}$ or $298.0/8 = 37.3 \text{ kJ mol}^{-1}$ per CH group. Therefore, benzene, per CH group, is $(37.3 - 13.8) = 23.5 \text{ kJ mol}^{-1}$ more stable than COT. It follows that benzene is $23.5 \times 6 = 141 \text{ kJ mol}^{-1}$ ($33.6 \text{ kcal mol}^{-1}$) more stable than a hypothetical six-carbon cyclic conjugated triene with the same stability as COT.

This energy difference of about 141 kJ mol^{-1} or 34 kcal mol^{-1} is called the **empirical resonance energy** of benzene. The empirical resonance energy is an experimental estimate of just how much special stability is implied by the resonance structures for benzene—thus the name “resonance energy.”

D. Aromaticity and the Hückel $4n + 2$ Rule

We've shown that benzene is unusually stable, and that this stability is correlated with the overlap of its carbon 2p orbitals to form π molecular orbitals. In 1931, Erich Hückel (1896–1980), a German chemical physicist, elucidated with molecular orbital arguments the criteria for this sort of stability, which has come to be called *aromaticity*. Using Hückel's criteria, we can define aromaticity more precisely. (Remember again that aromaticity in this context has nothing to do with odor.) This definition has allowed chemists to recognize the aromaticity of many compounds in addition to benzene.

A compound is said to be **aromatic** when it meets *all* of the following criteria.

Criteria for aromaticity:

1. Aromatic compounds contain one or more rings that have a cyclic arrangement of p orbitals. Thus, aromaticity is a property of certain *cyclic* compounds.
2. *Every* atom of an aromatic ring has a p orbital.
3. Aromatic rings are *planar*.
4. The cyclic arrangement of p orbitals in an aromatic compound must contain $4n + 2$ π electrons, where n is any positive integer (0, 1, 2, ...). In other words, an aromatic ring must contain 2, 6, 10, ... π electrons.

These criteria are often called collectively the **Hückel $4n + 2$ rule** or simply the **$4n + 2$ rule**.

The basis of the $4n + 2$ rule lies in the molecular orbital theory of *cyclic* π -electron systems. The theory holds that aromatic stability is observed only with *continuous cycles* of p orbitals—criteria 1 and 2. The theory also requires that the p orbitals must overlap to form π molecular orbitals. This overlap requires that an aromatic ring must be planar; p orbitals cannot overlap in rings significantly distorted from planarity—criterion 3. The last criterion has to do with the number of π molecular orbitals and the number of electrons they contain. Therefore, to understand criterion 4, we need to know the energies and electron occupancies of the various π molecular orbitals. Two Northwestern University physical chemists, A. A. Frost and

The resonance energy is the energy by which benzene is *stabilized*; it is therefore an energy that benzene *doesn't have*. The empirical resonance energy of benzene has been estimated in several different ways; these estimates range from 126 to 172 kJ mol^{-1} (30 to 41 kcal mol^{-1}). (Another estimate is discussed in Sec. 16.6.) The important point, however, is not the exact value of this number, but the fact that it is *large*.

Boris Musulin, described in 1953 a simple graphical method for deriving the π -molecular orbital energies of cyclic π -electron systems without resorting to any of the mathematics of quantum theory. This method has come to be known as the **Frost circle**. The steps used in constructing a Frost circle follow, and they are illustrated in Study Problem 15.2.

Steps for constructing a Frost circle:

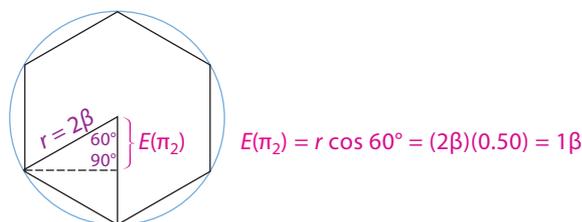
1. For a cyclic conjugated hydrocarbon or ion with j sides (and therefore j overlapping 2p orbitals), inscribe a regular polygon of j sides within a circle of radius 2β with one vertex of the polygon “pointing down” (in the lowest vertical position). (Remember from Sec. 15.1B that β is an energy unit used with molecular orbitals.)
2. Place one MO energy level at each vertex of the polygon. Because there are j vertices, there will be j MOs.
3. Draw a horizontal line that bisects the polygon. All MOs below the line are bonding, all MOs above the line are antibonding, and any MOs on the line are nonbonding (that is, they have the same energy as the isolated 2p orbital).
4. The lowest energy level must lie at 2β because it is at the lowest vertex, which is at the end of the vertical radius. The energies of the other levels are calculated by determining their positions along the vertical radius by trigonometry.
5. Add the π electrons to the energy levels in accordance with the Pauli principle and Hund’s rules.

Study Problem 15.2 illustrates the application of the Frost circle to benzene.

Study Problem 15.2

Use the Frost circle to determine the energy levels and electron occupancies for the π MOs of benzene.

- Step 1.** For benzene, $j = 6$. Therefore, we inscribe a regular hexagon into a Frost circle of radius 2β with one vertex pointing down (**Fig. 15.17a**).
- Step 2.** Place an energy level at each vertex. This gives six energy levels.
- Step 3.** The horizontal dashed line in Fig. 15.17a bisects the polygon. The three MOs below the dashed line are bonding, and the three MOs above the dashed line are antibonding. There are no nonbonding MOs. (In **Fig. 15.7b**, the two MOs on the line are nonbonding.)
- Step 4.** Calculate the energies. The energies of π_1 and π_6^* equal the radius of the circle, so their energies must be 2β and -2β , respectively. (Remember that β is a negative number.) Then draw a perpendicular from the π_2 (or π_3) vertex to the vertical radius and calculate $E(\pi_2)$, the energy of π_2 , as follows:



From this calculation, the energies of π_2 and π_3 , which are identical, equal $+1.0\beta$. By symmetry, the energies of π_4^* and π_5^* are -1.0β .

- Step 5.** Add the π electrons to the energy levels. Benzene has six π electrons. Because each bonding MO can accommodate two electrons, the available electrons exactly fill the bonding MOs.

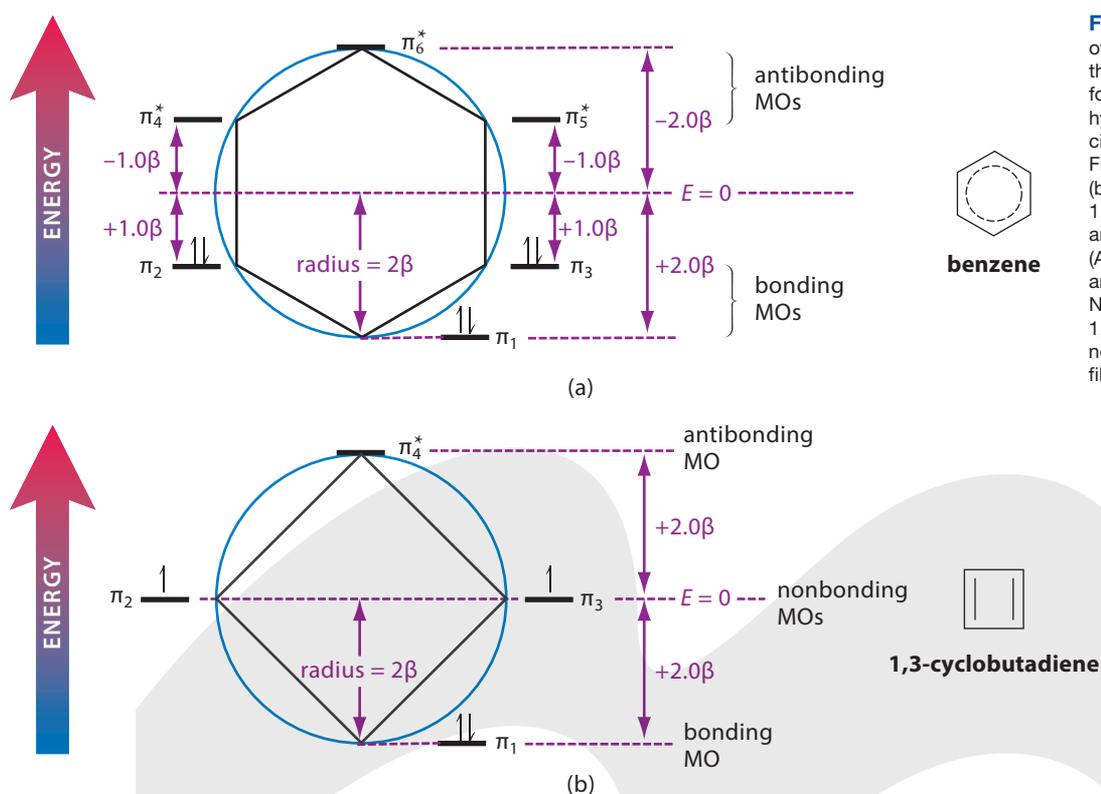


FIGURE 15.17 Application of the Frost circle to find the MOs and their energies for cyclic conjugated hydrocarbons. The Frost circle is in blue. (a) The Frost circle for benzene. (b) The Frost circle for 1,3-cyclobutadiene, an antiaromatic compound. (Antiaromatic compounds are discussed in Sec. 15.7E.) Notice that π_2 and π_3 in 1,3-cyclobutadiene are nonbonding and are only half filled.

This method shows that benzene has six MOs. (Remember, a system of j overlapping 2p orbitals forms j MOs; in this case, $j = 6$.) But it also shows that two bonding MOs, π_2 and π_3 , have identical energies, and two antibonding MOs, π_4^* and π_5^* , also have identical energies. When orbitals have the same energy, they are said to be **degenerate**. Therefore π_2 and π_3 are degenerate MOs, and π_4^* and π_5^* are degenerate MOs.

The π -electron energy of benzene is 8.0β . The π -electron energy of three isolated ethylenes (with a bonding-MO energy of 1.0β) is 6.0β . The delocalization energy, or resonance energy, of benzene is then 2.0β . If we equate this to the empirical resonance energy of benzene (Sec. 15.7C), which is $141\text{--}150\text{ kJ mol}^{-1}$ or $34\text{--}36\text{ kcal mol}^{-1}$, we find that $\beta = 70\text{--}75\text{ kJ mol}^{-1}$ ($17\text{--}18\text{ kcal mol}^{-1}$). The resonance energy is a consequence of the very low-lying π_1 MO; the other bonding MOs, π_2 and π_3 , have the same energy (1.0β) as the bonding MO of ethylene. The π_1 MO, shown in Fig. 15.16b, has no nodes, and it most closely corresponds to the resonance-hybrid structure of benzene, which shows the π electrons spread evenly around the entire molecule.

Focused Problems

- 15.29** Use a Frost circle to determine the π -electron structure of the cyclopentadienyl anion, which has a planar structure and six π electrons.



cyclopentadienyl anion

- 15.30** (a) How many bonding MOs are there in a planar, cyclic, conjugated hydrocarbon that contains a ring of 10 carbon atoms?
 (b) How many π electrons does it have?
 (c) How many of the π electrons can be accommodated in the bonding MOs?

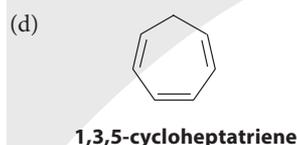
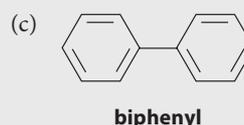
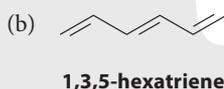
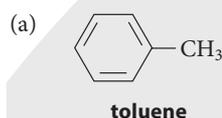
Compounds (and ions) with $4n + 2$ π electrons contain exactly the number of electrons required to fill the bonding MOs. Benzene has six π electrons ($4n + 2 = 6$ for $n = 1$); as Study Problem 15.2 shows, these exactly fill the bonding MOs of benzene. A planar, cyclic conjugated hydrocarbon with 10 π electrons (see Focused Problem 15.30) has five bonding MOs, which can accommodate all 10 electrons ($4n + 2 = 10$ for $n = 2$). A molecule that contains *more* than $4n + 2$ π electrons, even if it could meet all of the other criteria for aromaticity, must have one or more electrons in nonbonding or antibonding MOs. If a molecule contains fewer than $4n + 2$ electrons, its bonding molecular orbitals are not fully populated, and its resonance energy (delocalization energy) is reduced. But there's more to aromaticity than just fully occupied bonding MOs; after all, 1,3-butadiene and other conjugated *acyclic* hydrocarbons also have fully occupied bonding MOs (see Fig. 15.1, Sec. 15.1A). *The bonding molecular orbitals in aromatic compounds have particularly low energy*, especially the MO at $E = 2.0\beta$. The resonance energy of benzene is 2.0β , but the resonance energy of (*E*)-1,3,5-hexatriene, the acyclic conjugated triene, is 1.0β (Focused Problem 15.2, Sec. 15.1A, or Fig. 15.7, Sec. 15.2C). Moreover, the magnitude of β for acyclic conjugated hydrocarbons (-50 kJ mol^{-1}) is only two-thirds of that for cyclic conjugated hydrocarbons. (Simple MO theory does not account for this difference, but more advanced theories do.) This difference further increases the energetic advantage of aromaticity. To summarize the basis of the $4n + 2$ rule:

1. Cyclic conjugated molecules and ions with $4n + 2$ π electrons (that is, aromatic molecules and ions) have exactly the right number of π electrons to fill the bonding MOs.
2. The bonding MOs in aromatic molecules and ions, especially the bonding MO of lowest energy, have a very low energy. For this reason, aromatic molecules and ions have a large resonance energy.

Recognizing aromatic compounds is a matter of applying the four criteria for aromaticity. This objective is addressed in Study Problem 15.3 and the discussion that follows it.

Study Problem 15.3

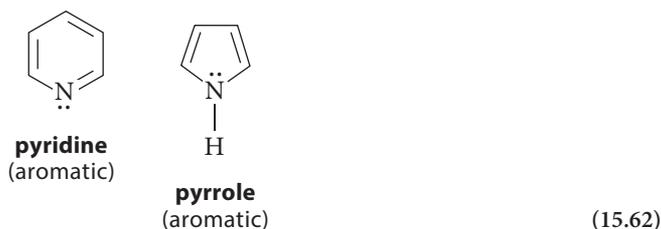
Decide whether each of the following compounds is aromatic. Explain your reasoning.



Solution In each example, first count the π electrons by applying the following rule: *Each double bond contributes two π electrons.* Then apply *all* of the criteria for aromaticity.

- The ring in toluene, like the ring in benzene, is a continuous planar cycle of six π electrons, so the ring in toluene is aromatic. The methyl group is a substituent group on the ring and is not part of the ring system. Because toluene contains an aromatic ring, it is considered to be an aromatic compound. This example shows that *parts of molecules* can be aromatic or, equivalently, that aromatic rings can have nonaromatic substituents.
- Although 1,3,5-hexatriene contains six π electrons, it is not aromatic, because it fails criterion 1 for aromaticity: *it is not cyclic.* Aromatic species must be cyclic.
- Biphenyl has two rings, each of which is separately aromatic, so biphenyl is an aromatic compound.
- Although 1,3,5-cycloheptatriene has six π electrons, it is not aromatic, because it fails criterion 2 for aromaticity: one carbon of the ring does not have a p orbital. In other words, the π -electron system is not continuous, but is interrupted by the sp^3 -hybridized carbon of the CH_2 group.
- 1,3-Cyclobutadiene is not aromatic. Even though it is a continuous cyclic system of 2p orbitals, it fails criterion 4 for aromaticity: it does not have $4n + 2$ π electrons. (We consider the case of 1,3-cyclobutadiene in Sec. 15.7E.)

Aromatic Heterocycles Aromaticity is not confined solely to hydrocarbons. Some *heterocyclic compounds* (Sec. 8.2C) are aromatic; for example, pyridine and pyrrole are both aromatic nitrogen-containing heterocycles.



Except for the nitrogen in the ring, the structure of pyridine closely resembles that of benzene. Each atom in the ring, including the nitrogen, is part of a double bond and therefore contributes one π electron. How does the electron pair on nitrogen figure in the π -electron count? This electron pair resides in an sp^2 orbital in the plane of the ring (see Fig. 15.18a). (It has the same relationship to the pyridine ring that any one of the C—H bonds has.) Because the nitrogen nonbonding pair does not overlap with the ring's π -electron system, it is not included in the π -electron count. Therefore, *vinylc electrons (electrons on doubly bonded atoms) are not counted as π electrons.*

In pyrrole, the electron pair on nitrogen is *allylic*—that is, on an atom *adjacent* to a double bond (Fig. 15.18b). This situation is much like that on the nitrogen in an amide. In Sec. 1.6C (Eq. 1.47) and Sec. 1.7E (Eq. 1.79) we showed that if a nitrogen can participate in resonance with adjoining π bonds, it is sp^2 -hybridized. Therefore, this nitrogen in pyrrole has trigonal-planar geometry and sp^2 hybridization that allow its electron pair to occupy a 2p orbital and contribute to the π -electron count. The N—H hydrogen lies in the plane of the ring. In general, *allylic electrons are counted as π electrons when they reside in orbitals that are properly situated for overlap with the other 2p orbitals in the molecule.* Therefore, pyrrole has six π electrons—four from the double bonds and two from the nitrogen—and it is aromatic.

Notice the different ways in which we handle the electron pairs on the nitrogens of pyridine and pyrrole. The nitrogen in pyridine is part of a double bond, and the electron pair *is not* part of the π -electron system. The nitrogen in pyrrole is allylic, and its electron pair *is* part of the π -electron system.

Aromatic Ions Aromaticity is not restricted to neutral molecules; a number of ions are aromatic. One of the best characterized aromatic ions is the cyclopentadienyl anion:

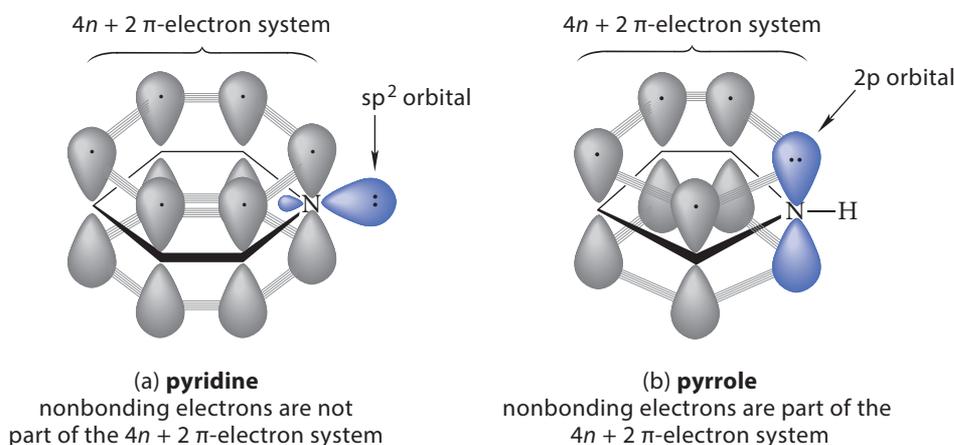
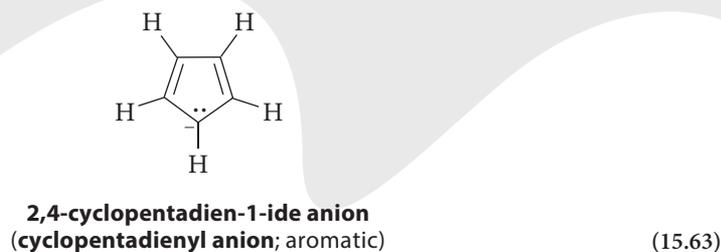
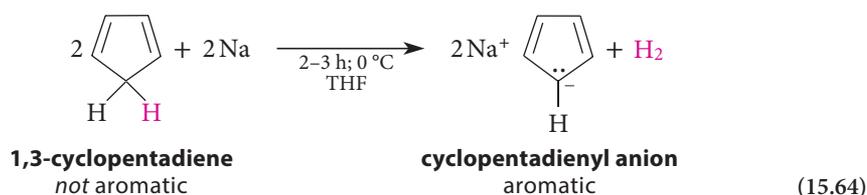
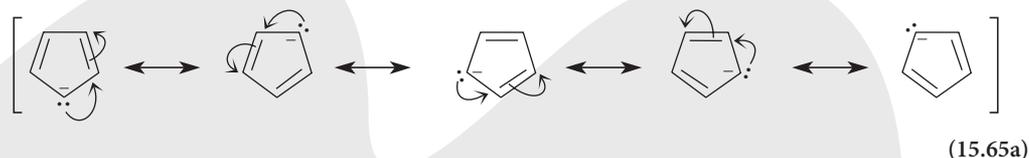


FIGURE 15.18 The 2p orbitals in pyridine and pyrrole. The gray lines represent orbital overlap. (a) The nonbonding electron pair in pyridine is vinylc and is therefore in an sp^2 orbital (blue) and is not part of the aromatic π -electron system. (b) The nonbonding electron pair in pyrrole is allylic and can occupy a 2p orbital (blue) that is part of the aromatic π -electron system.

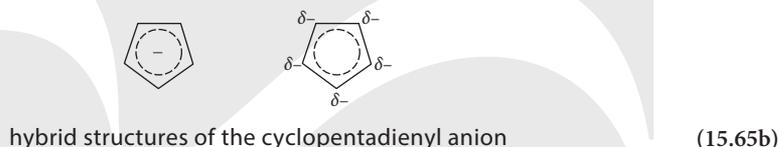
(The Frost circle for this ion was considered in Focused Problem 15.29a.) The cyclopentadienyl anion resembles pyrrole; however, because the atom bearing the allylic electron pair is carbon rather than nitrogen, its charge is -1 . One way to form this ion is by the reaction of sodium with the conjugate acid hydrocarbon, 1,3-cyclopentadiene; notice the analogy to the reaction of Na with H_2O .



The cyclopentadienyl anion has five equivalent resonance structures; the negative charge can be delocalized to each carbon atom:

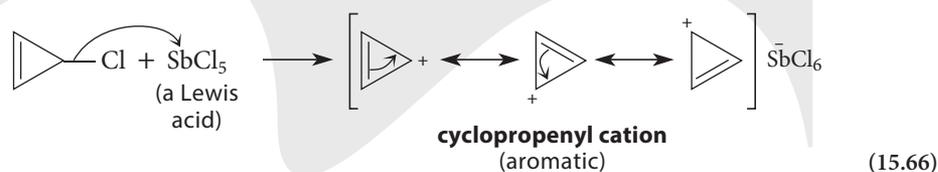


These structures show that all carbon atoms of the cyclopentadienyl anion are equivalent. For this reason, the cyclopentadienyl anion is sometimes represented as a hybrid structure:



Because of the stability of this anion, its conjugate acid, 1,3-cyclopentadiene, is an unusually strong hydrocarbon acid. (Remember: The more stable the conjugate base, the more acidic is the conjugate acid; see Fig. 3.3, Sec. 3.7E.) With a $\text{p}K_a$ of 15, this compound is 10^{10} times more acidic than a 1-alkyne, and almost as acidic as water!

Cations, too, may be aromatic. (See Focused Problem 15.33b.)

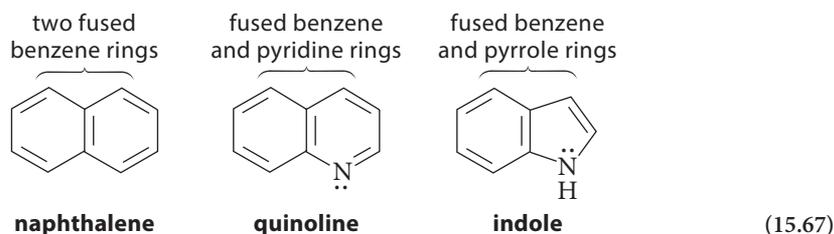


This example illustrates another point about counting electrons for aromaticity: *atoms with empty p orbitals are part of the π -electron system, but they contribute no electrons to the π -electron count.* Because this cation has two π electrons, it is aromatic ($4n + 2 = 2$ for $n = 0$). The stability of the cyclopropenyl cation, despite its considerable angle strain, is a particularly strong testament to the stabilizing effect of aromaticity.

Counting π electrons accurately is crucial for successfully applying the $4n + 2$ rule. We summarize the rules for π -electron counting:

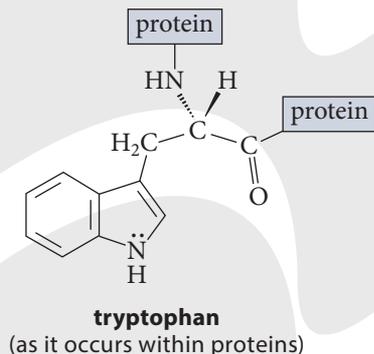
1. Each atom that is part of a double bond contributes one π electron.
2. Vinylic nonbonding electron pairs do not contribute to the π -electron count.
3. Allylic nonbonding electron pairs contribute two electrons to the π -electron count if they occupy an orbital that is oriented so as to overlap with the other p orbitals in the molecule.
4. An atom with an empty p orbital can be part of a continuous aromatic π -electron system, but it contributes no π electrons.

Aromatic Polycyclic Compounds The Hückel $4n + 2$ rule applies strictly to single rings. However, a number of common fused bicyclic and polycyclic compounds, such as naphthalene, quinoline, and indole, are also aromatic:



Although rules have been devised to predict the aromaticity of fused-ring compounds, these rules are rather complex, and we need not be concerned with them. However, it shouldn't be difficult to see the resemblance of these compounds to monocyclic aromatic compounds—naphthalene to benzene, quinoline to benzene and pyridine, and indole to benzene and pyrrole.

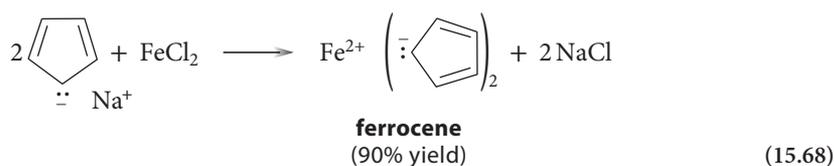
Indole is particularly important in biology because of its presence in proteins within the structure of the amino acid *tryptophan*.



Fused-ring aromatic hydrocarbons with more than two rings are well known. Some of these are shown in Fig. 15.19a. Two of the most spectacular examples of fused-ring aromatic compounds are graphite (Fig. 15.19b) and buckminsterfullerene (Fig. 15.19c). *Graphite* is a form of elemental carbon that consists of layers of fused benzene rings. The softness of graphite and its ability to act as a lubricant can be attributed to the ease with which the layers slide past one another. Even though graphite is not an ionic compound, it is an excellent electrical conductor because its π electrons can be delocalized across its structure. Graphite is used in arc-welding electrodes and in lithium-ion and nickel–metal–hydride batteries. Single layers of graphite (called *graphene*) have been isolated and studied. (You have probably produced graphene when you have written with a lead pencil on paper. Pencil “lead” is actually graphite.)

Buckminsterfullerene was discovered as one component of soot and interstellar gas. The structure, which corresponds to the seams on a modern soccer ball, was proposed in 1985 by Sir Harold W. Kroto (1939–2016) of the University of Sussex, Brighton, United Kingdom, along with Richard E. Smalley (1943–2005) and Robert F. Curl (b. 1933) of Rice University. All 60 of the carbons in buckminsterfullerene are equivalent, as its single ^{13}C -NMR resonance at δ 143 shows.

Aromatic Organometallic Compounds Some remarkable organometallic compounds have aromatic character. For example, the cyclopentadienyl anion, discussed previously in this section as one example of an aromatic anion, forms stable complexes with a number of transition-metal cations. One of the best known of these complexes is *ferrocene*, which is synthesized by the reaction of two equivalents of cyclopentadienyl anion with one equivalent of ferrous ion (Fe^{2+}).



The 2010 Nobel Prize in Physics was awarded to Andre Geim (b. 1958) and Konstantin Novoselov (b. 1974) of the University of Manchester, United Kingdom, for their experiments that characterized graphene.

The intriguing name, “buckminsterfullerene” (also sometimes nicknamed “buckyball”), came from its resemblance to the geodesic dome designed by American architect Buckminster Fuller (1895–1983). Since the discovery of buckminsterfullerene, a variety of related “buckyballs” and “buckytubes” have been discovered. Kroto, Smalley, and Curl were recognized for this and related discoveries with the 1996 Nobel Prize in Chemistry.

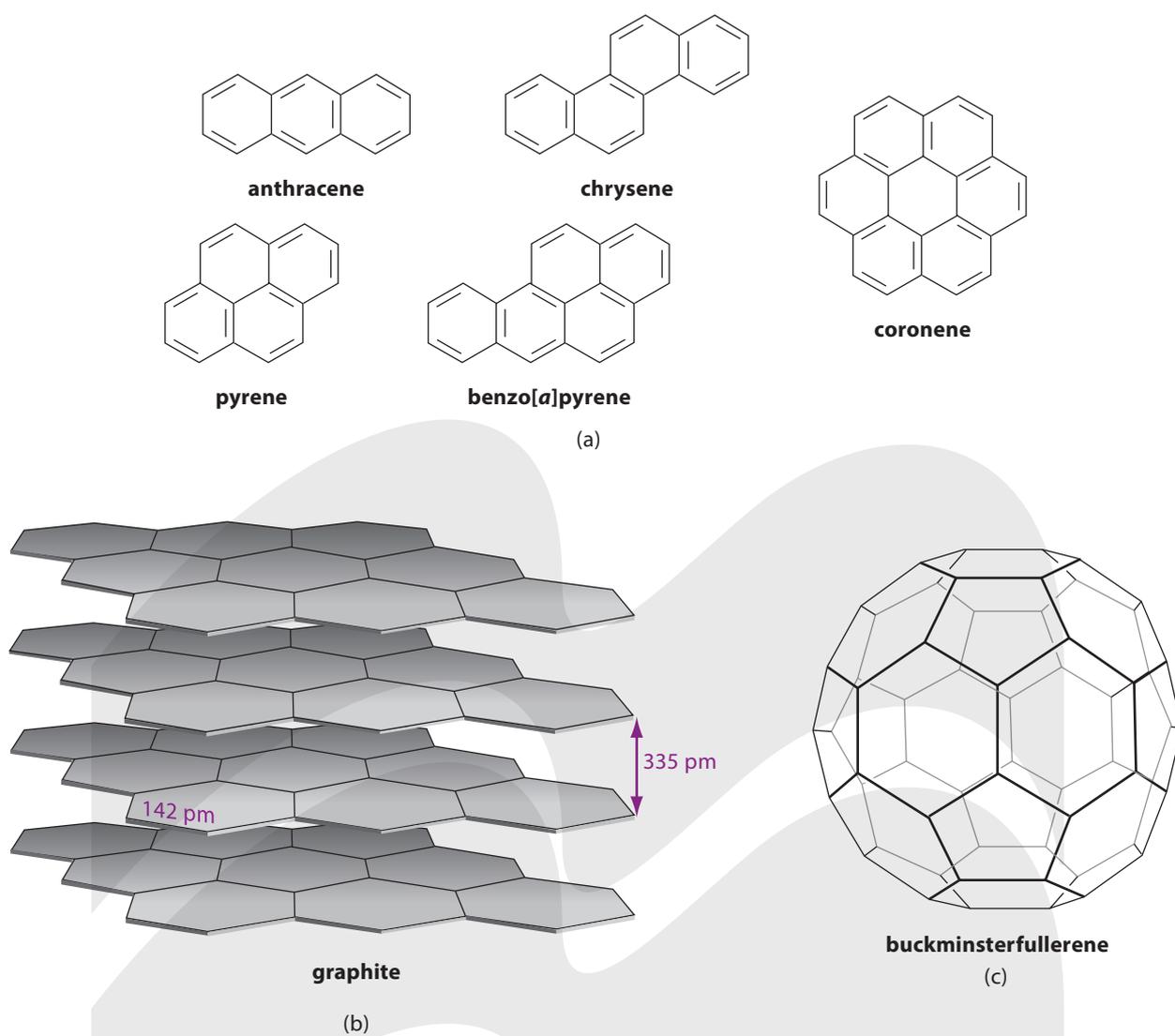
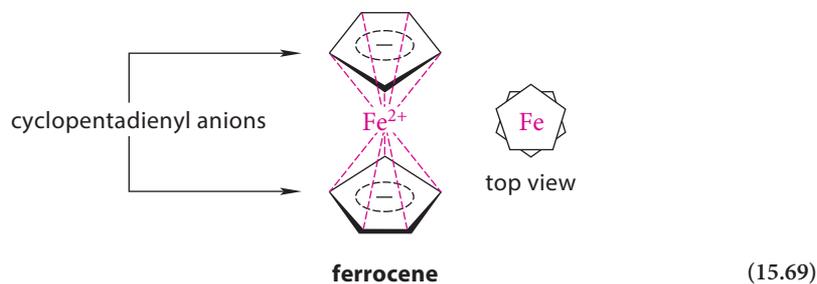


FIGURE 15.19 Some fused-ring aromatic compounds. (a) Some common fused-ring aromatic hydrocarbons containing more than two rings. (The role of benzo[a]pyrene in cancer is discussed in Sec. 16.7.) (b) Graphite. In this structure, the delocalized double bonds are not shown. Notice that the carbon-carbon bond length is very similar to that in benzene. (c) Buckminsterfullerene (C_{60}). In this structure the delocalized double bonds are not shown.

Although this synthesis resembles a metathesis (exchange) reaction in which two salts are formed from two other salts, ferrocene is not a salt but is a remarkable “molecular sandwich” in which a ferrous ion is imbedded between two cyclopentadienyl anions.



The red dashed lines mean that the electrons of the cyclopentadienyl anions are shared not only by the ring carbons but also by the ferrous ion; each carbon is bonded equally to the iron.

Let's now return to the question posed near the beginning of this section: Why is benzene inert in the usual reactions of alkenes? The *aromaticity* of benzene is responsible for its unique chemical behavior. If benzene were to undergo the addition reactions typical of alkenes, its continuous cycle of $4n + 2$ π electrons would be broken; it would lose its aromatic character and much of its stability.

This is not to say, however, that benzene is unreactive under all conditions. Indeed, benzene and many other aromatic compounds undergo a number of characteristic reactions that are presented in Chapter 16. However, the conditions required for these reactions are typically much harsher than those used with alkenes, precisely because benzene is so stable. As you will also see, the reactions of benzene give very different kinds of products from the reactions of alkenes.

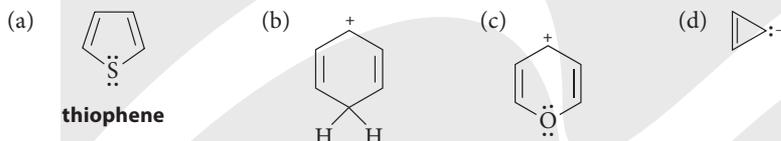
Focused Problems

15.31 Furan is an aromatic compound. Discuss the hybridization of its oxygen and the geometry of its two electron pairs.



15.32 Do you think it would be possible to have an aromatic free radical? Why or why not?

15.33 Which of the following species should be aromatic by the Hückel $4n + 2$ rule?



E. Antiaromatic Compounds

Compounds that contain *planar*, continuous rings of $4n$ π electrons, in stark contrast to aromatic compounds, are especially *unstable*; such compounds are said to be **antiaromatic**. 1,3-Cyclobutadiene (which we'll call simply cyclobutadiene) is such a compound; its small ring size and the sp^2 hybridization of its carbon atoms constrain it to planarity. This compound is so unstable that it can only be isolated at very low temperature, 4 K.

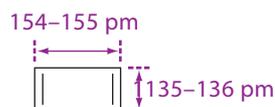


1,3-cyclobutadiene

(15.70)

The Frost circle for 1,3-cyclobutadiene is shown in Fig. 15.17b. Two of the π MOs, π_2 and π_3 , lie at $E = 0$. The π -electron energy of cyclobutadiene is 4.0β , which is *the same* as the π -electron energy of two isolated ethylenes. In other words, *cyclobutadiene has no resonance energy*. Moreover, Hund's rules require that the two degenerate MOs, π_2 and π_3 , be half occupied. This means that cyclobutadiene has two unpaired electrons and is therefore a double free radical! Finally, cyclobutadiene has considerable angle strain.

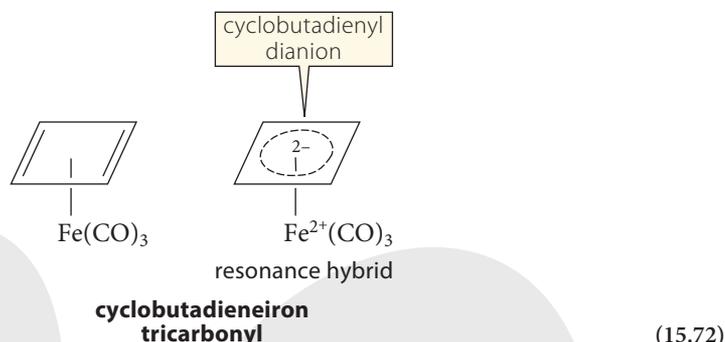
The overlap of 2p orbitals in molecules with cyclic arrays of $4n$ π electrons is a *destabilizing* effect. (It could be said that antiaromatic molecules are "destabilized by resonance.") More advanced MO calculations show that cyclobutadiene, in an effort to escape this high-energy situation, distorts by lengthening its single bonds and shortening its double bonds:



(15.71)

As a result of this distortion, the degeneracy of π_2 and π_3 is removed; so, one MO lies at slightly lower energy than the other and is doubly occupied. Cyclobutadiene, in effect, contains *localized* double bonds. This distortion, while minimizing antiaromatic overlap, introduces even more strain than the molecule would contain otherwise. The molecule can't win; it is too unstable to exist under normal circumstances.

Although cyclobutadiene is itself very unstable, it forms a very stable complex with Fe(0):



(In this structure, the CO groups are neutral carbon monoxide ligands.) 1,3-Cyclobutadiene has four π electrons and is therefore two electrons short of the number (six) required for aromatic stability. These two missing electrons are provided by the iron. As the resonance hybrid structure on the right in Display 15.72 suggests, this complex in effect consists of a 1,3-cyclobutadiene with two additional electrons—a cyclobutadienyl *dianion*, a six π -electron aromatic system—combined with an iron minus two electrons—that is, Fe^{2+} . In effect, the iron stabilizes the antiaromatic diene by donating two electrons, thus making it aromatic.

This section began with a comparison of the stabilities of benzene and 1,3,5,7-cyclooctatetraene (COT). We can now recognize that COT contains a continuous cycle of $4n$ π electrons.



1,3,5,7-cyclooctatetraene (COT)

Is COT antiaromatic? It would be if it were planar. COT is large and flexible enough, however, that it can escape unfavorable antiaromatic overlap by folding into a tub conformation, as shown in Figs. 15.15d and 15.16c. It is believed that *planar* cyclooctatetraene, which *is* antiaromatic, is more than 58 kJ mol^{-1} (14 kcal mol^{-1}) less stable than the tub conformation.

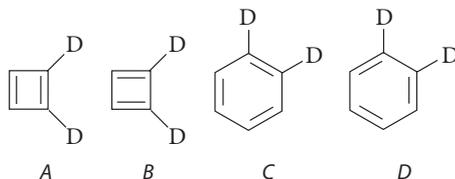
F. Aromaticity and Resonance

This discussion of aromaticity provides our final caveats about the use of resonance structures:

1. Resonance structures are appropriate for aromatic systems. We can draw resonance structures for systems of $4n + 2$ π electrons, such as benzene and its derivatives, or other polycyclic aromatic compounds such as naphthalene.
2. Compounds with planar, cyclic arrangements of $4n$ π electrons are antiaromatic and are destabilized by resonance. Resonance structures should *not* be drawn for such compounds.
3. If compounds with $4n$ π electrons can distort from planarity, then they do so; the π orbitals of their double bonds are thus isolated from each other and do not interact. COT is an example. Because resonance structures can only be used to symbolize the stabilizing interaction of p or π orbitals, resonance structures are not appropriate for these compounds.

Focused Problems

15.34 Using the theory of aromaticity, explain the finding that *A* and *B* are different compounds, but *C* and *D* are identical. (That *A* and *B* are different molecules was established by Professor Barry Carpenter and his students at Cornell University in 1980.)



15.35 Which of the compounds or ions in Focused Problem 15.33 (Sec. 15.7D), if any, are likely to be antiaromatic and therefore very unstable? Explain.

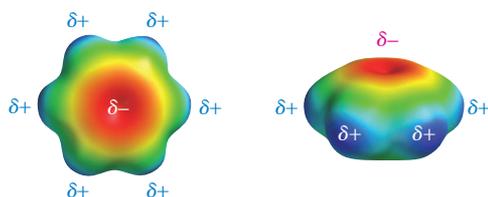
15.8 NONCOVALENT INTERACTIONS OF AROMATIC RINGS

In Secs. 8.5–8.8 we described a number of noncovalent interactions:

1. Van der Waals interactions: interactions between fluctuating dipoles and interactions between dipoles and induced dipoles
2. Electrostatic interactions: charge–charge interactions, charge–dipole interactions, and dipole–dipole interactions
3. Hydrogen bonding: the association of an O—H or N—H donor with a Lewis-base acceptor
4. “Hydrophobic bonding”: the association of nonpolar groups driven by entropy changes in water

Benzene and its derivatives can interact noncovalently with other compounds. Two noncovalent interactions of aromatic rings are rather unique, and they are very important in many biomolecules and in their interactions with drug molecules. The first is the noncovalent interaction of aromatic rings with each other. The second is the noncovalent interaction of aromatic rings with cations. This section describes these noncovalent interactions and provides examples of each.

The basis of both types of interaction is the charge distribution in aromatic compounds, which we illustrate with benzene. Although benzene, because of its symmetry, has an overall zero dipole moment, it does have local regions of positive and negative charge. As we’ve shown in Sec. 15.7, the π electrons in benzene and other aromatic compounds are concentrated above and below the ring plane in the bonding π molecular orbitals. Associated with this π -electron density is a localized partial negative charge in these regions, illustrated by the electrostatic potential maps (EPMs) that follow. The red color is associated with regions of partial negative charge.



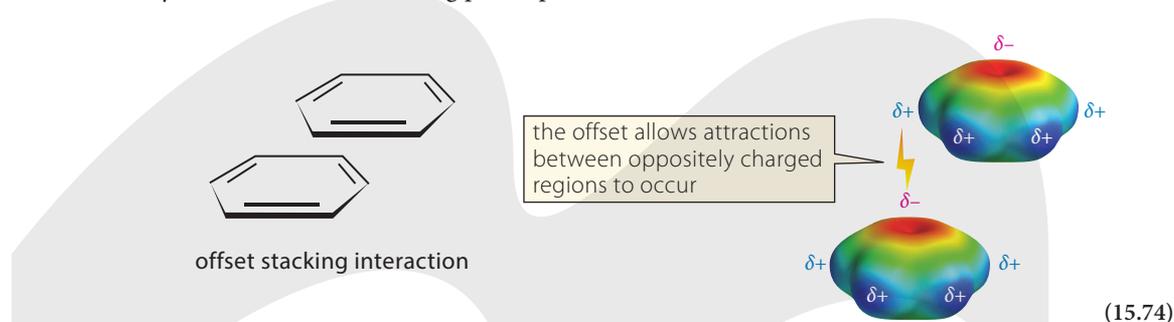
EPMs of benzene illustrating regions of partial positive and partial negative charge

(15.73)

Benzene is a neutral molecule; so, corresponding to the localized partial negative charge, there must be regions of localized partial positive charge. These positively charged regions occur around the periphery of the ring, as shown by the blue areas in the EPMS. Because the π electrons are concentrated *above and below* the ring plane, the compensating partial positive charges are concentrated *in* the ring plane. This occurs because the positive charge of the carbon nucleus is screened from outside groups *in the ring plane* by the carbon sp^2 electrons but not by the π electrons. This effect was also discussed in Sec. 3.7C, which explains why sp^2 -hybridized carbons (including those of aromatic rings) are electronegative and the attached hydrogens are relatively positive.

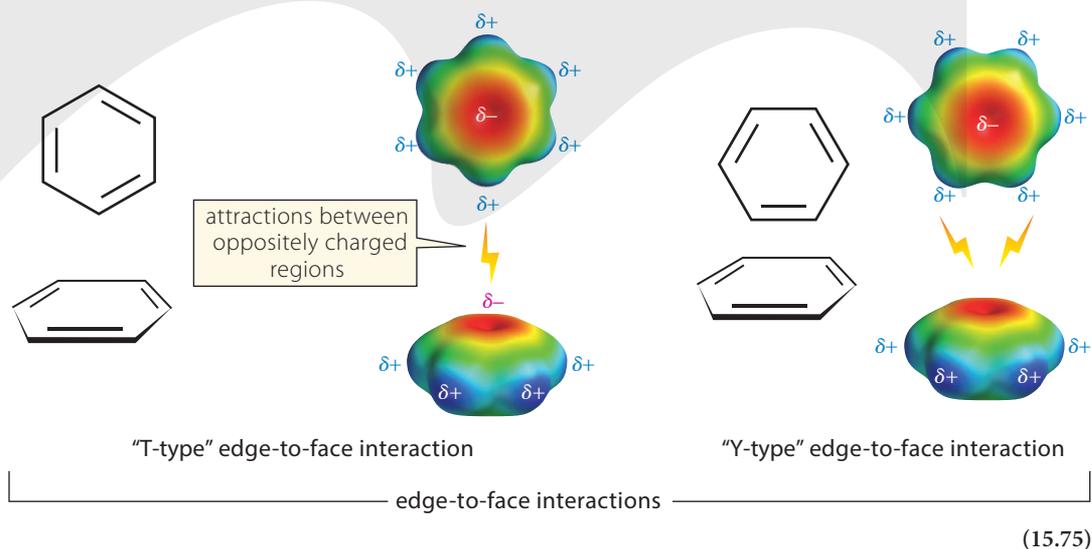
A. Noncovalent Interactions between Aromatic Rings

Aromatic rings can interact noncovalently with each other in two major ways. The first is that they can “stack” with their ring planes parallel.



The centers of the rings involved in a stacking interaction are offset to avoid the juxtaposition of like charges in the two interacting rings. The offset also allows the positively charged region of one ring to interact attractively with the negatively charged region of the other. This type of interaction is called **offset stacking**.

In the second type of interaction between rings, the planes of the two interacting rings are perpendicular. This orientation also allows the positively charged region of one ring to interact attractively with the negatively charged region of the other. This type of interaction is called an **edge-to-face** ring interaction.



As the diagram shows, the edge-to-face interaction can occur in two ways; one is called a “T interaction” and the other is called a “Y interaction.” Opinions differ as to the relative importance of these two orientations.

Both physical calculations and experimental evidence support the idea that the edge-to-face interaction is the more stable of the two attractions. However, there are many examples of both offset stacking and edge-to-face interactions in chemistry and biology; so, both are important.

The interactions depicted in Displays 15.74 and 15.75 are somewhat different from the “hydrophobic bonds” discussed in Sec. 8.6D, which are driven largely by a favorable entropy change associated with the solvent organization. Although an entropic component is present when two aromatic rings come together in water, a negative enthalpy change ΔH° also drives the association. The negative enthalpy is caused, at least in part, by a significant attraction between the rings, which is described in the foregoing discussion.

Aromatic rings can also interact with other polarizable but nonpolar groups (for example, alkyl groups) in conventional van der Waals attractions. Examples are known in which an alkyl group lies in the face of the ring, close to the π electrons, and other examples are known in which the hydrocarbon group lies along the edge of the ring. In either case, the localized charge in the aromatic ring induces a temporary dipole in the alkyl group, and, as a result, an attractive interaction develops between the two groups.

B. Noncovalent Interaction of Aromatic Rings with Cations

Once we understand the nature of the charge distribution in aromatic rings, we can understand that an aromatic ring can interact favorably with cations. This type of noncovalent interaction is called a **pi-cation interaction** (Fig. 15.20). As we have shown (Display 15.73), the π -electron cloud of a benzene ring or other aromatic ring results in a region of local negative charge on the two faces of the ring. The pi-cation interaction is an electrostatic attraction of the positive cation with this region of local negative charge (Fig. 15.20a). This attraction was first discovered in a study of gas-phase interactions. In the gas phase, one or more benzene molecules can interact attractively with a potassium ion. Complexes of one to four benzene molecules with a potassium ion in the gas phase are known. Figure 15.20b shows the gas-phase pi-cation interaction of four benzene rings with a potassium ion. The formation of the complex between a potassium ion and a single benzene molecule in the gas phase has a large favorable ΔG° value of $-48.5 \text{ kJ mol}^{-1}$ ($-11.6 \text{ kcal mol}^{-1}$), which includes the loss of entropy that typically accompanies an association reaction. The interaction energy, which has the unfavorable entropy removed, is approximated by the ΔH° value of $-76.6 \text{ kJ mol}^{-1}$ ($-18.3 \text{ kcal mol}^{-1}$).

C. Noncovalent Interactions of Aromatic Rings in Biology

Offset stacking, edge-to-face attractions, and pi-cation attractions are all very important in biology. These interactions provide mechanisms that stabilize protein structures and contribute to the formation of stable complexes between proteins (enzymes, receptors) and small molecules (substrates, inhibitors). Formation of such complexes between enzymes and substrates is an

Chemical
Biology
Topic

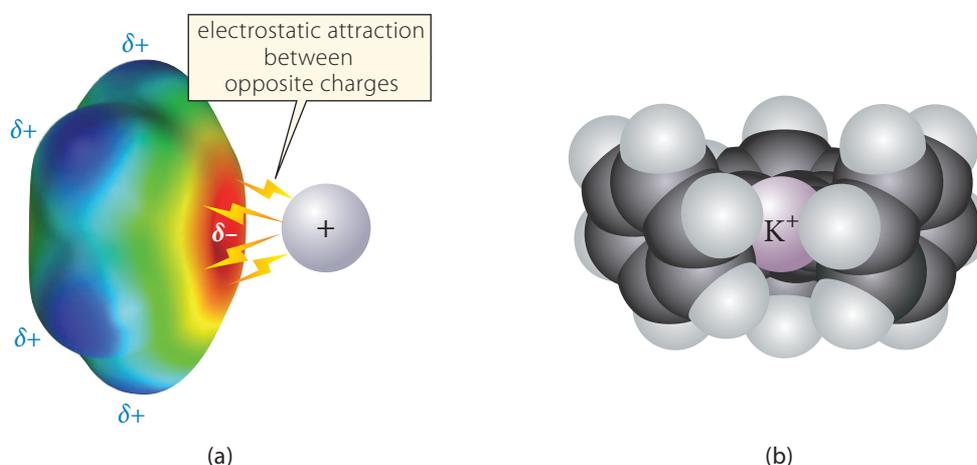
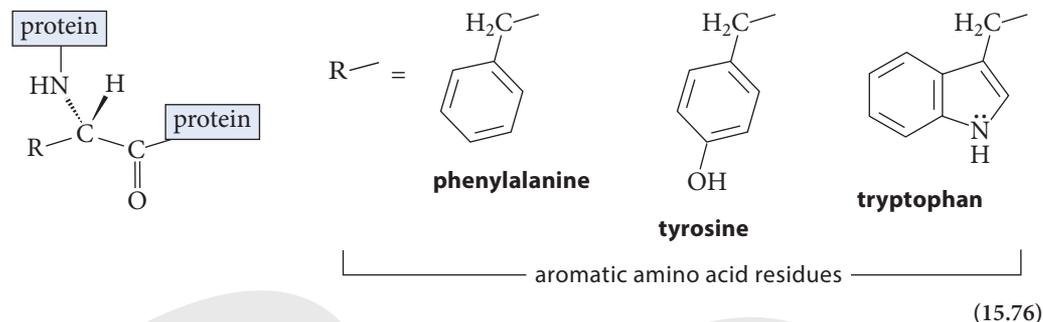


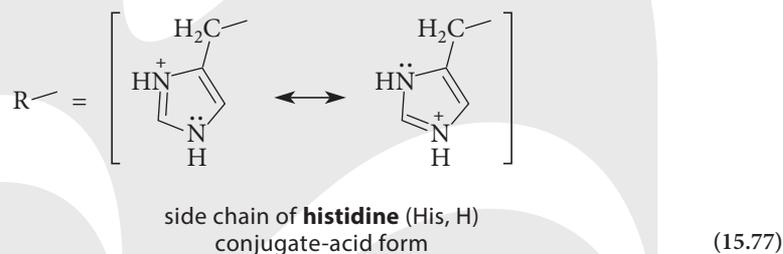
FIGURE 15.20 Pi-cation interactions. (a) The potassium ion interacts electrostatically with the region of local negative charge caused by the π electrons of a benzene ring. (b) A space-filling model showing the interaction of four benzene molecules with a potassium cation in the gas phase. In both, the cation is centered on the face of an aromatic ring.

essential prelude to catalysis, as discussed in Sec. 12.8E. This section provides a few biological examples of these interactions.

The aromatic rings in proteins are the groups in the side chains of the amino acid residues phenylalanine, tyrosine, and tryptophan.



The amino acid histidine also has an aromatic imidazole ring in its side chain, but this ring (which is often found as its conjugate-acid cation) more often serves an acid–base role than a source of aromatic-ring interactions.



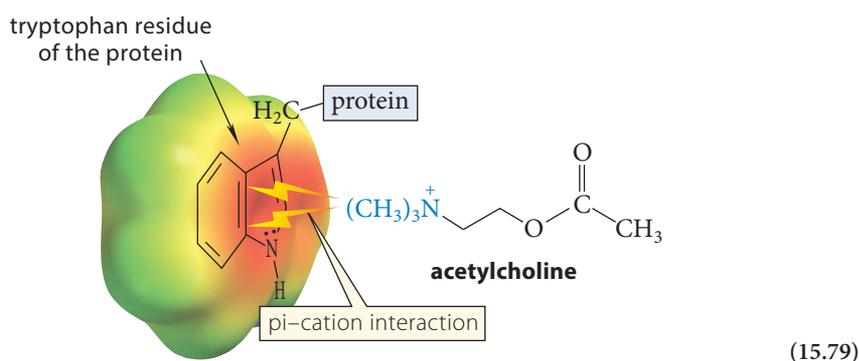
Double-helical DNA provides a spectacular example of offset stacking. If you are familiar with the double-helical structure of DNA, you know that the bases in each strand are “stacked” perpendicular to the axis of the double helix. (The double-helical structure of DNA is shown in Fig. 26.5, Sec. 26.5B.) These bases are aromatic compounds. Their stacking is offset by the turn in the helix. The favorable interaction between the aromatic rings is an important element—possibly the *most important* element—that stabilizes the helical structure.

The structures of many proteins also contain stabilizing interactions between the rings of aromatic amino acid residues.

An important biological example of a pi–cation interaction occurs in the binding of the cationic molecule acetylcholine to the *acetylcholine receptor* (AcChR). One important form of AcChR is a large protein associated with cell membranes at the neuromuscular junction and elsewhere. Acetylcholine is a cationic molecule.



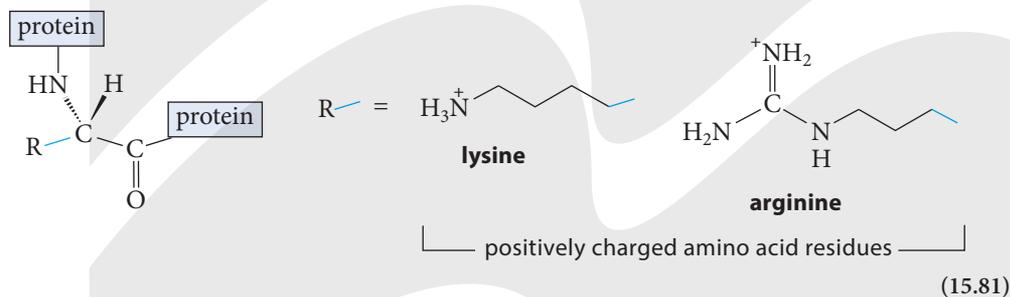
The binding of acetylcholine to the AcChR causes a large conformational change in the protein that opens a pore in the protein and allows sodium and potassium ions to flow through the cell membrane. At the neuromuscular junction, this ion transmission potentiates muscle contraction. A major attractive interaction between acetylcholine and the receptor is a pi–cation interaction between the cationic group of acetylcholine and a tryptophan residue on the protein, shown with the EPM of the indole ring:



Binding of nicotine in its cationic, conjugate-acid form at the acetylcholine site in the AcChR of the brain is involved in the mechanism of nicotine addiction.



Many protein structures also contain stabilizing pi-cation interactions of the aromatic amino acid rings with the positively charged amino acid side chains of lysine and arginine.



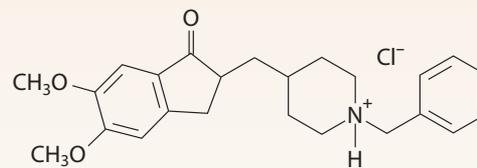
Aricept: Drug Therapy for Alzheimer's Disease



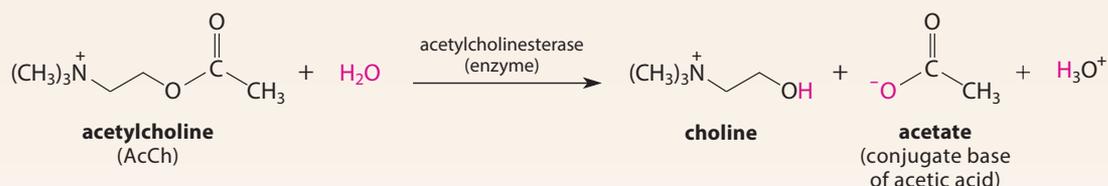
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Alzheimer's disease (AD) is a condition in which a progressive and ultimately severe dementia is caused by protein misaggregation in the brain. Although largely a disease of the elderly, it can also occur in younger adults. Although much current research is focused on the prevention of AD, current drug therapy is focused largely on delaying the onset of cognitive impairment associated with the disease. One of the most widely used drugs for this purpose is

donepezil, marketed as its hydrochloride salt under the trade name Aricept.



The biological target of donepezil is the brain enzyme *acetylcholinesterase*. The normal function of this enzyme is to catalyze the hydrolysis of acetylcholine, an important neurotransmitter.



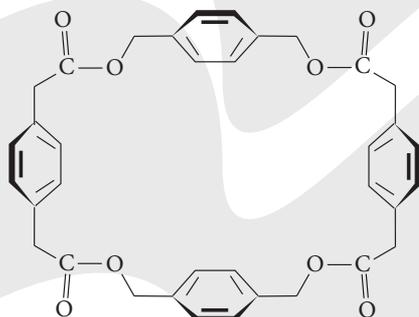
This hydrolysis terminates nerve transmission mediated by AcCh. Donepezil binds to acetylcholinesterase near its active site and thereby prevents the enzyme from binding AcCh. The inhibition of acetylcholine hydrolysis is believed to intensify neural activity in the brain.

As in all enzyme-catalyzed reactions, the hydrolysis reaction is preceded by binding of the substrate to the enzyme. Because donepezil binds close to the AcCh site in the enzyme, it blocks the binding of AcCh to the enzyme and thereby inhibits the hydrolysis of the

neurotransmitter. The binding of donepezil to acetylcholinesterase is shown in **Fig. 15.21**. This binding involves several examples of the interactions discussed in this section. The drug molecule is shown in green, and various aromatic amino-acid side chains (identified by their three-letter abbreviations) are in gray. Identifiable offset stacking and pi-cation interactions are indicated. An edge-to-face interaction and offset interactions of groups on the enzyme with each other are also present; can you find them?

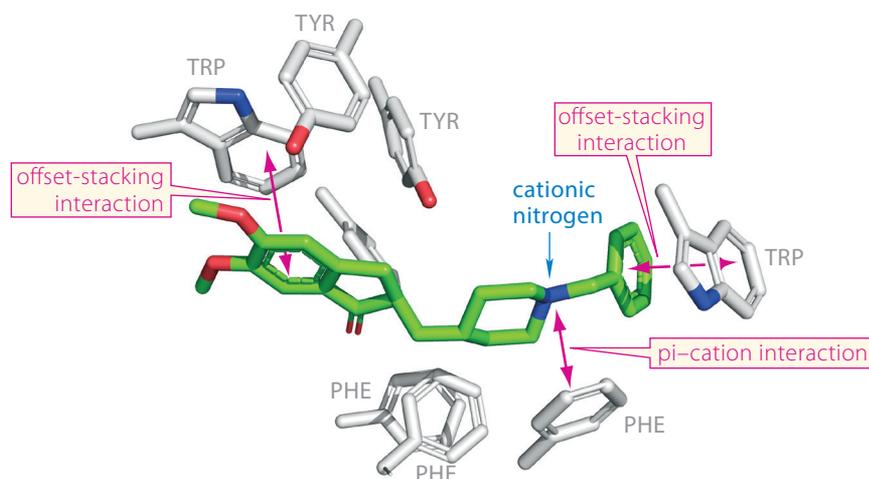
Focused Problem

- 15.36 The following molecule has a barrel shape (in which the benzene rings are the walls of the barrel). It forms a noncovalent complex with the iodide salt of acetylcholine in chloroform solvent.



Describe the orientation of the acetylcholine molecule within the complex.

FIGURE 15.21 The binding of Aricept (donepezil, green) within the active site of the enzyme acetylcholinesterase is stabilized by both offset stacking and pi-cation interactions. Aromatic side chains of the enzyme are shown in gray. Several interactions of aromatic rings within the enzyme structure are also shown; can you identify some of them?





CHAPTER SUMMARY For a summary of the chapter, see Chapter 15 in the Study Guide and Solutions Manual.

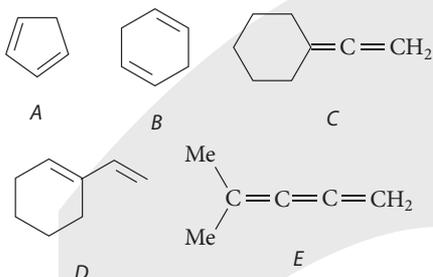


REACTION REVIEW For a summary of reactions discussed in this chapter, see the Reaction Review section of Chapter 15 in the Study Guide and Solutions Manual.

SKILLS OBJECTIVES WITH PROBLEMS

• Recognize conjugated and cumulated dienes. **15.1**

15.37 Specify which (if any) of the following compounds are conjugated alkenes and which are cumulated alkenes.



• Draw resonance structures for a conjugated alkene, ion, or radical, and use an MO diagram to relate the source of resonance energy to its resonance structures. **15.1A, 15.6**

15.38 (a) Derive resonance structures for the 2,4-pentadien-yl cation by using the curved-arrow notation. (*Hint:* You should have three structures, including the following one.)



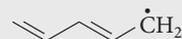
2,4-pentadien-1-yl cation diagram for part (c)

- (b) This cation has five π molecular orbitals with energies 1.73β , 1.0β , 0β , -1.0β , and -1.73β . (Remember that β is by definition a negative number.) Sketch a molecular orbital energy diagram with the energy levels arranged vertically. Add arrows into each MO to indicate electron occupancy.
- (c) Represent the cation schematically as five black circles on a horizontal line (corresponding to the five carbons) next to each MO (as shown previously), and indicate the position of each node in each MO with a vertical line. (*Hint:* The nodes are placed symmetrically; the MO of lowest energy (π_1) has no nodes, and each higher-energy orbital has one additional node; the nodes for the π_2 , π_3 , and π_4^* MOs go through carbon atoms.)
- (d) Classify each MO as bonding, antibonding, or nonbonding.

(e) Calculate the resonance energy (delocalization energy) for this cation.

(f) Explain why the MO diagram of this cation predicts the same distribution of positive charge as the resonance structures you drew in part (a).

15.39 (a) Derive resonance structures for the 2,4-pentadien-1-yl radical using the fishhook notation.

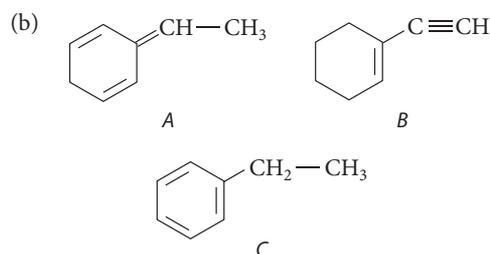
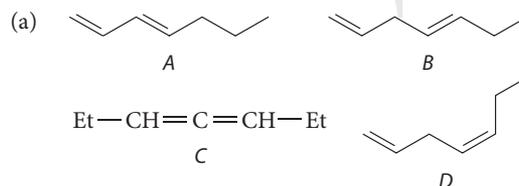


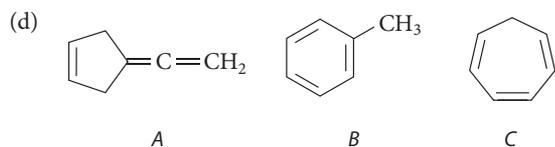
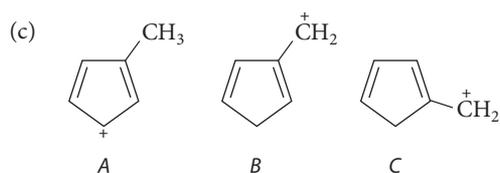
2,4-pentadien-1-yl radical

- (b) The MOs of this radical are, to a useful approximation, the same as those for the cation in Problem 15.38. Populate these MOs with electrons.
- (c) Calculate the resonance energy for this radical.
- (d) Explain why the MO diagram of this radical predicts the same distribution of unpaired-electron character as the resonance structures you drew in part (a).

• Given their structures, predict qualitatively the relative stability of a series of alkenes, free radicals, or ions. **15.1B,C; 15.6; 15.7D,E**

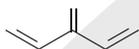
15.40 Rank the isomers within each set in order of increasing heat of formation (lowest first).





• Explain the physical basis of UV-visible spectra. **15.2B**

- 15.41 (a) The molecular orbitals of 3-methylene-1,4-pentadiene occur at the following energies: 1.932β , 1β , 0.517β , -0.517β , -1β , and -1.932β .



3-methylene-1,4-pentadiene

Sketch an energy diagram of these MOs, and add electrons to your diagram. Between which two MOs does the electronic transition occur when UV light is absorbed?

- (b) Which has a UV absorption at higher wavelength: this compound or (*E*)-1,3,5-hexatriene? [Hint: See Fig. 15.7, Sec. 15.2C, for the MO energies of (*E*)-1,3,5-hexatriene.]

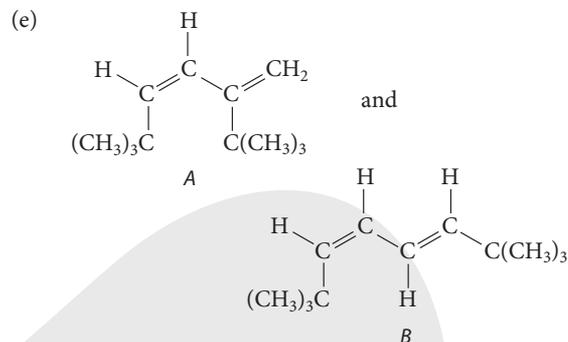
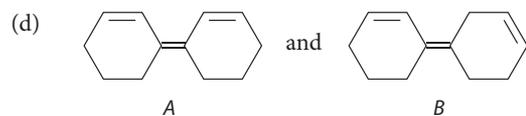
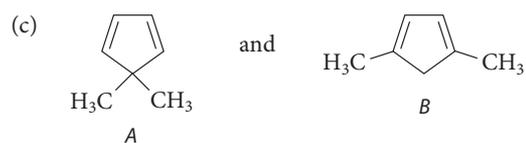
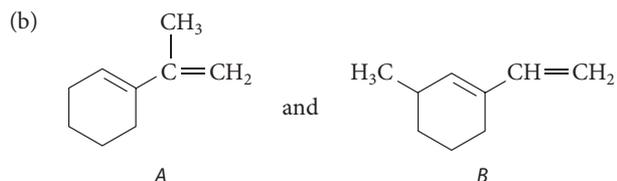
• Apply the Beer-Lambert law to determine the concentration of a compound from its UV spectrum. **15.2A**

- 15.42 A colleague, Ima Hack, has subjected isoprene (see Fig. 15.5, Sec. 15.2A) to catalytic hydrogenation to give isopentane. Hack has inadvertently stopped the hydrogenation prematurely and wants to know how much unreacted isoprene remains in the sample. The mixture of isoprene and 2-methylbutane (75 mg total) is diluted to 1 liter with pure methanol and found to have an absorption at 222.5 nm (1 cm path length) of 0.356. Given an extinction coefficient of 10,750 at this wavelength, what mass percent of the sample is unreacted isoprene?

• Predict qualitatively the relative λ_{\max} of a series of alkenes. **15.2C**

- 15.43 Assume you have unlabeled samples of the compounds within each of the following sets. Explain how UV-vis spectroscopy could be used to distinguish each of the compounds from the others.

- (a) 1,4-cyclohexadiene and 1,3-cyclohexadiene



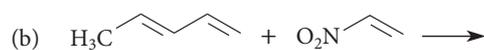
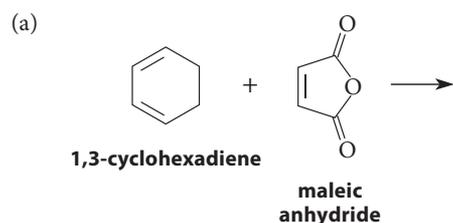
• Explain the physical basis of fluorescence, including the origin of the Stokes shift. **15.2D**

- 15.44 Complete the following statements about fluorescence by making the proper choice between the given alternatives or by completing the sentence in the blank.

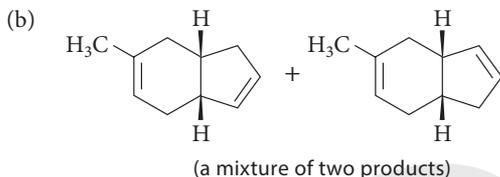
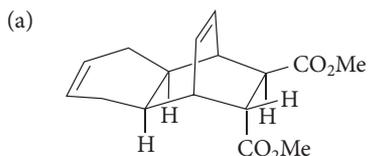
- (a) The fluorescence wavelength is (greater than, the same as, less than) the absorption wavelength.
- (b) Fluorescence involves (the same, different) electronic energy levels than absorption.
- (c) The quantum yield of fluorescence is the ratio of _____.
- (d) Fluorescence involves (the same, different) vibrational energy levels than absorption.
- (e) Fluorescence spectroscopy is a more sensitive technique than absorption spectroscopy because _____.

• Given the starting materials, give the products of a Diels-Alder reaction; given the products, give the structure of the dienophile and diene starting materials, including stereochemistry. **15.3**

- 15.45 Complete the following Diels-Alder reactions, including the stereochemistry. If endo and exo products are possible, show both and label them.

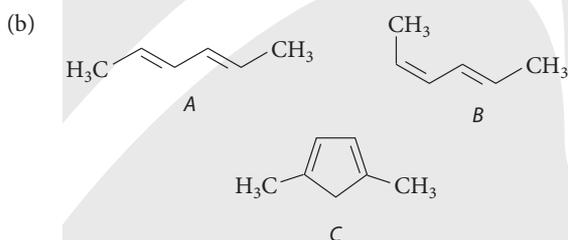
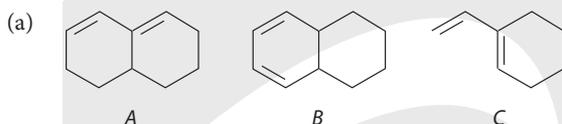


15.46 In each part, provide the structures of the starting materials that would give the product(s) shown.



• Use their reacting conformations to predict the relative reactivity of a series of conjugated dienes in the Diels–Alder reaction. **15.3A,C**

15.47 In each part, rank the dienes in order of increasing Diels–Alder reactivity with a dienophile. Explain your choices.



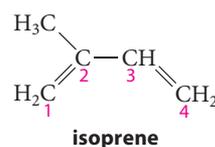
15.48 The following natural product readily gives a Diels–Alder adduct with maleic anhydride (structure in Problem 15.45a) under mild conditions. What is the most likely configuration of the two double bonds (cis or trans)? Explain.



15.49 Explain why 4-methyl-1,3-pentadiene is much less reactive as a diene in Diels–Alder reactions than (*E*)-1,3-pentadiene, but its reactivity is similar to that of (*Z*)-1,3-pentadiene.

• Give the 1,4- and 1,2-addition products for the addition reaction of a conjugated diene. Give the curved-arrow or fishhook mechanism for each addition. **15.4A**

15.50 (a) Which carbocation is more stable: the one formed by protonation of isoprene at carbon-1 or the one formed by protonation of isoprene at carbon-4? Explain.



(b) Predict the products expected from the addition of one equivalent of HBr to isoprene; explain your reasoning.

(c) Which is likely to be the major kinetically controlled product? Explain.

15.51 (a) Use mechanistic reasoning to predict the products expected from the addition of one equivalent of HBr to (*E*)-1,3,5-hexatriene; explain your reasoning.

(b) Which of the products in part (a) is likely to be the major kinetically controlled product?

15.52 The addition of HBr to 1,3-butadiene in the presence of peroxides gives mostly 1,4-addition product and a small amount of 1,2-addition product. Using the fishhook notation, show the initiation and propagation steps of this reaction that lead to both products.

• Recognize whether the product of a reaction results from kinetic control or thermodynamic control. **15.4B**

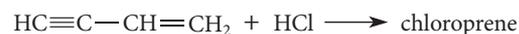
15.53 When 1,3-cyclopentadiene and maleic anhydride (structure in Problem 15.45a) are allowed to react at room temperature, a Diels–Alder reaction takes place in which the endo product is formed as the major product. When this product is heated above its melting point of 165 °C, it is transformed into an equilibrium mixture that contains about 57% of the exo stereoisomer and 43% of the endo stereoisomer. (The equilibrium constant for interconversion of the two stereoisomers probably does not vary greatly with temperature.)

(a) Show these transformations with equations, including the structures of all compounds.

(b) According to these observations, is the Diels–Alder reaction of maleic anhydride and 1,3-cyclopentadiene at room temperature a kinetically controlled or a thermodynamically controlled reaction?

• Given the structure of a conjugated diene, draw structures for the polymer resulting from 1,4-addition polymerization; draw free-radical mechanisms for the reaction using the fishhook notation. **15.5**

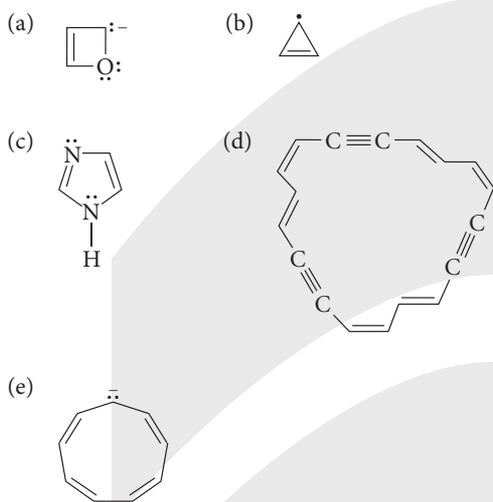
15.54 (a) When HCl and 1-buten-3-yne react, HCl adds to the triple bond to form a diene called *chloroprene*. Give the structure of chloroprene along with a curved-arrow mechanism for the reaction.



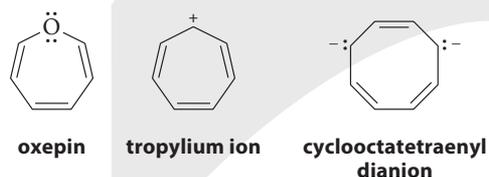
- (b) The free-radical polymerization of chloroprene gives (mostly) a 1,4-addition polymer called *neoprene*, which is used as a synthetic rubber in applications such as wet suits and boots. Use the fishhook mechanism for the polymerization to derive the structure of neoprene.

• By applying the $4n + 2$ rule, recognize from its structure whether a compound is likely to be aromatic, antiaromatic, or neither. **15.7D,E**

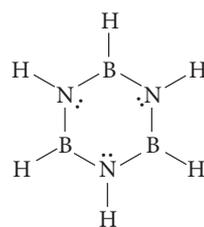
- 15.55 Using the Hückel $4n + 2$ rule, determine whether each of the following compounds is likely to be aromatic. Explain how you arrived at the π -electron count in each case.



- 15.56 Which of the following molecules is likely to be planar and which nonplanar? Explain.



- 15.57 Explain why borazole (sometimes called *inorganic benzene*) is a very stable compound.



borazole

• Apply the Frost circle to determining the molecular orbitals of a cyclic conjugated system. **15.7D**

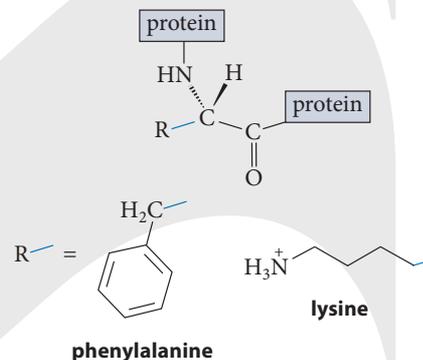
- 15.58 Use a Frost circle to determine the π -electron structure of the cyclopropenyl cation, which has a planar structure and two π electrons.



cyclopropenyl cation

• Draw the relative orientation of an aromatic compound and cation, or two aromatic compounds, poised for noncovalent attraction. **15.8**

- 15.59 (a) If a lysine residue and a phenylalanine residue are located close to each other in a protein structure, describe how you would expect them to be oriented for the most energetically favorable interaction.



- (b) If two phenylalanine residues (see the previous part) are located close to each other in a protein structure, describe how you would expect them to be oriented for the most energetically favorable interaction.

INTEGRATED PROBLEMS

- 15.60 Give the principal product(s) expected, if any, when *trans*-1,3-pentadiene reacts under the following conditions. Assume one equivalent of each reagent reacts unless noted otherwise.

- (a) Br_2 (dark) in CH_2Cl_2
 (b) HBr

- (c) H_2 (two molar equivalents), Pd/C
 (d) H_2O , H_3O^+
 (e) Na^+ EtO^- in EtOH
 (f) Maleic anhydride (structure in Problem 15.45a), heat

15.61 Explain each of the following observations.

- (a) The allene 2,3-heptadiene can be resolved into enantiomers, but the cumulene 2,3,4-heptatriene cannot.
- (b) The cumulene in part (a) can exist as diastereomers, but the allene in part (a) cannot.

15.62 What six-carbon conjugated diene would give the same single product from either 1,2- or 1,4-addition of HBr?

15.63 Predict the products of addition of HBr to 4-methyl-1,3-pentadiene in the presence of peroxides. Use a fishhook mechanism for the propagation steps to justify your prediction.

15.64 The following compound is not aromatic even though it has $4n + 2 \pi$ electrons in a continuous cyclic arrangement. Explain why the compound is not aromatic. (*Hint*: Draw out the hydrogens.)



15.65 How would the color of β -carotene (structure in Display 15.11, Sec. 15.2C) be affected by treatment of the compound with a large excess of H_2 over a Pt/C catalyst? Explain.

15.66 Two of the compounds in Fig. P15.66 are used in sunscreens, and one is not. Identify the compound that does not act as a sunscreen; explain.

15.67 Fluorescein (Display 15.17, Sec. 15.2D) was once used to color the Chicago River green on St. Patrick's Day until it was subsequently replaced with a vegetable dye. One problem with fluorescein was that the green color required bright sunshine for maximum effect—definitely a problem for Chicago in March! Explain this observation using the theory of fluorescence.

15.68 (Refer to Figs. 15.11a and b, Sec. 15.2D.) If a solution of fluorescein at pH = 9 is subjected to visible light at 488 nm, it has maximum fluorescence at 510 nm. Calculate the energy difference between the absorbed and fluorescing radiation in kJ mol^{-1} .

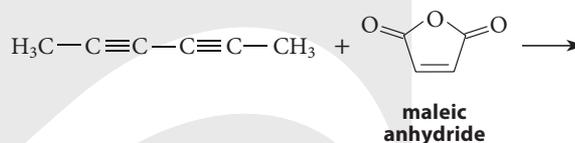
15.69 Draw as many resonance structures as you can for (a) the form of fluorescein present at pH = 9 (Display 15.17) and (b) the fluorescent group of the green fluorescent protein

(Display 15.18). Use the curved-arrow notation to derive your structures. Be sure in both cases that a nonbonding electron pair on the anionic oxygen is involved in the resonance interaction.

15.70 A compound A (C_6H_{10}) is optically active and has an IR absorption at 2083 cm^{-1} . Partial hydrogenation of A with 0.2 equivalent of H_2 over a catalyst gives, in addition to recovered A, a mixture of *cis*-2-hexene and *cis*-3-hexene. Identify compound A, and explain your reasoning.

15.71 Explain the observation that 2,3-dimethyl-1,3-butadiene and maleic anhydride (structure in Problem 15.45a) readily react to give a Diels–Alder adduct, but 2,3-di-*tert*-butyl-1,3-butadiene and maleic anhydride do not.

15.72 Knowing that conjugated dienes react in the Diels–Alder reaction, a student, M. T. Brainpan, has come to you with an original research idea: to use conjugated alkynes as the diene component in the Diels–Alder reaction (such as the following). Would Brainpan's idea work? Explain. (*Hint*: Draw the structure of the Diels–Alder product, and determine whether the structure is reasonable.)



15.73 (Refer to Fig. P15.73.) The *N*-methylquinolinium ion forms a noncovalent complex with molecule A in water that has a standard free energy of dissociation $\Delta G_d^\circ = 28.9 \text{ kJ mol}^{-1}$ ($6.9 \text{ kcal mol}^{-1}$). The neutral molecule 4-methylquinoline forms a noncovalent complex with molecule A in water with $\Delta G_d^\circ = 22.2 \text{ kJ mol}^{-1}$ ($5.3 \text{ kcal mol}^{-1}$).

- (a) Calculate the dissociation constant for each complex.
- (b) Suggest a reason that the binding of the ion to A is stronger than the binding of the neutral molecule to A.
- (c) The *N*-methylquinolinium ion forms a noncovalent complex with molecule B with $\Delta G_d^\circ = 35.2 \text{ kJ mol}^{-1}$ ($8.4 \text{ kcal mol}^{-1}$). Suggest a reason that the complex with molecule B has a smaller dissociation constant than the complex with molecule A.

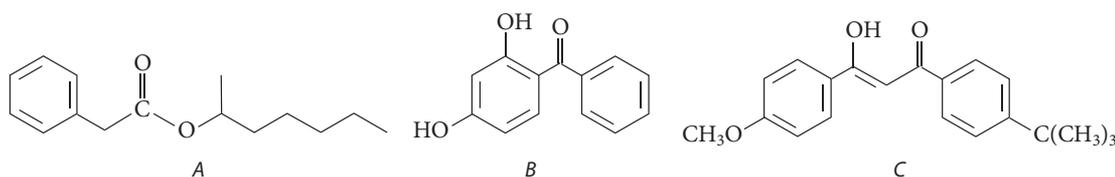


FIGURE P15.66

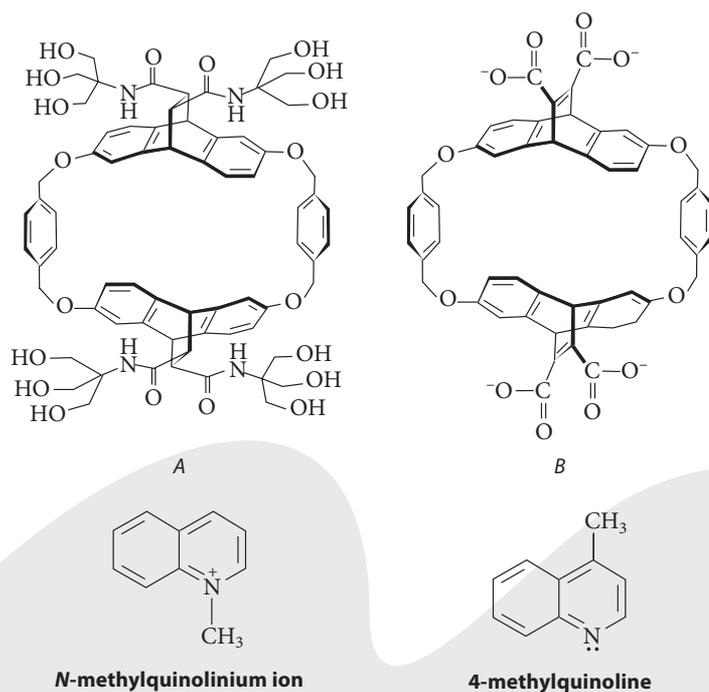


FIGURE P15.73

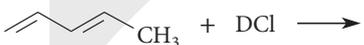
15.74 This problem describes the result that established the intrinsic preference for 1,2-addition as the kinetically controlled product in the reaction of hydrogen halides with conjugated dienes.

- (a) What is the relationship between the products of 1,2- and 1,4-addition in the following reaction?



(E)-1,3-pentadiene

- (b) How does the use of DCl change this relationship, if at all?



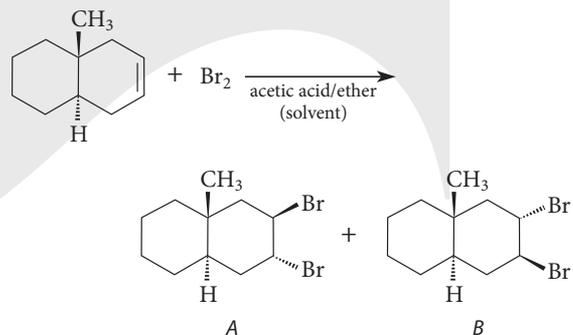
- (c) The reaction with DCl gives mostly the kinetically controlled product. Give the structure of this product.

15.75 When the alcohol **A** undergoes acid-catalyzed dehydration, two isomeric alkenes are formed: **B** and **C** (see Fig. P15.75a). The relative percentage of each alkene formed is shown as a function of time in Fig. P15.75b. The composition of the alkene mixture at very long times is the equilibrium composition. Furthermore, if either alkene is subjected to the conditions of the reaction, the equilibrium mixture of alkenes is obtained.

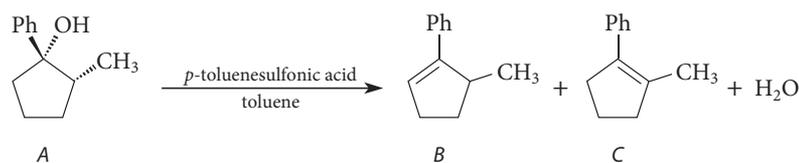
- (a) Is the dehydration a kinetically controlled or thermodynamically controlled reaction? Explain.
- (b) Give a structural reason why compound **C** is favored at equilibrium.

- (c) Suggest one reason why alkene **B** is formed more rapidly. (*Hint*: Think about probabilities.)

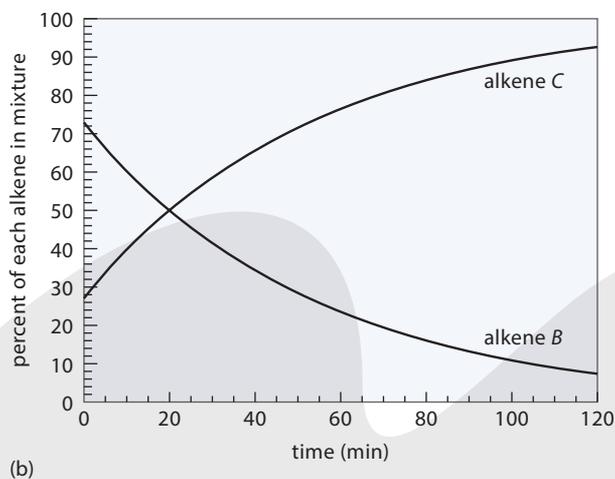
15.76 Consider the bromine addition shown in the following equation. Product **A** is the predominant product formed at low temperature. If the products are allowed to stand under the reaction conditions or are brought to equilibrium at higher temperature, product **B** is the only product formed.



- (a) Which is the kinetic product, and which is the thermodynamic product?
- (b) Give a structural reason that the thermodynamic product is more stable than the kinetic product.
- (c) Propose a mechanism that explains why the kinetic product is formed more rapidly even though it is less stable. (*Hint*: The rate-limiting step of bromine addition is formation of the bromonium ion.)
- (d) Propose a mechanism for the equilibration of the two compounds that does not involve the alkene starting material.



(a)

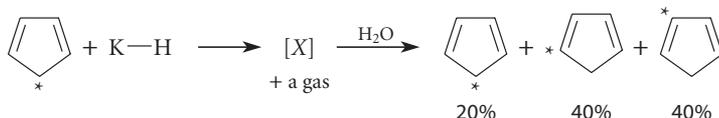


(b)

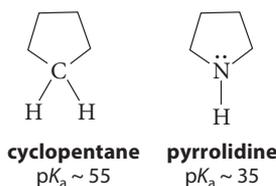
FIGURE P15.75 The relative amounts of alkene products *B* and *C* in Problem 15.75 as a function of time.

15.77 When an excess of 1,3-butadiene reacts with Cl_2 in chloroform solvent, two compounds, *A* and *B*, both with the formula $\text{C}_4\text{H}_6\text{Cl}_2$, are formed. Compound *B* reacts with more Cl_2 to form compound *C*, $\text{C}_4\text{H}_6\text{Cl}_4$, which proves to be a meso compound. Compound *A* reacts with more Cl_2 to form both *C* and a diastereomer *D*. Propose structures for *A*, *B*, *C*, and *D*, and explain your reasoning.

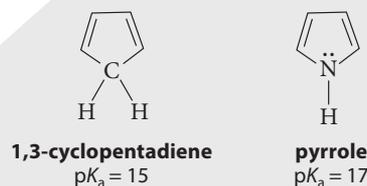
15.78 When 1,3-cyclopentadiene containing carbon-13 (^{13}C) only at carbon-5 (as indicated by the asterisk in the following equation) is treated with potassium hydride (KH), a species *X* is formed and a gas is evolved. When the resulting mixture is added to water, a mixture of ^{13}C -labeled 1,3-cyclopentadienes is formed as shown in the equation. Identify *X*, and explain both the origin and the percentages of the three labeled cyclopentadienes.



15.79 An amine R_2NH is typically more than 20 $\text{p}K_a$ units more acidic than the hydrogens of the carbon analog, R_2CH_2 (the element effect; Sec. 3.7B).

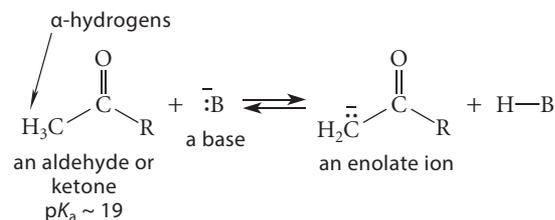


However, the acidities of 1,3-cyclopentadiene and pyrrole are an exception.



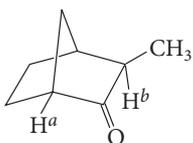
Use the theory of aromaticity to explain this exception. (*Hint*: Remember that the $\text{p}K_a$ of a compound is proportional to the free energy *difference* between an acid and its conjugate base.)

15.80 (a) The α -hydrogens of aldehydes and ketones are more than 30 $\text{p}K_a$ units more acidic than the hydrogens of alkanes.

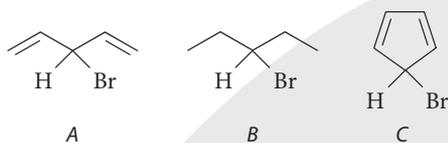


Using polar effects and resonance effects in your argument, explain the enhanced acidity of aldehydes and ketones.

- (b) Which α -hydrogen of the following ketone, H^a or H^b , should be most acidic? Or should they be about equally acidic? Explain.



- 15.81 Invoking Hammond's postulate and the properties of the carbocation intermediates, explain why the doubly allylic alkyl halide **A** undergoes much more rapid S_N1 solvolysis in aqueous acetone than compound **B**. Then explain why compound **C**, which is also a doubly allylic alkyl halide, is solvolytically inert.

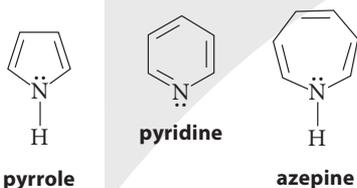


- 15.82 Most alkyl bromides are water-insoluble liquids. When 7-bromo-1,3,5-cycloheptatriene was first isolated, however, its high melting point (203 °C) and its water solubility led its discoverers to comment that it behaves more like a salt. Explain the saltlike behavior of this compound.

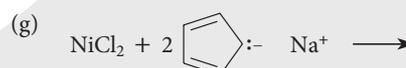
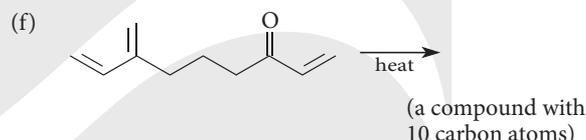
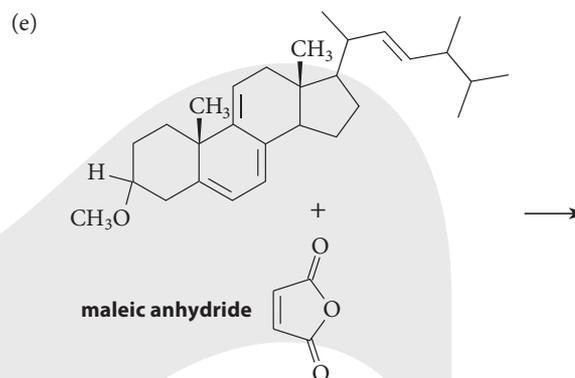
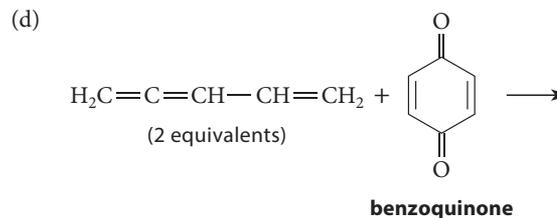
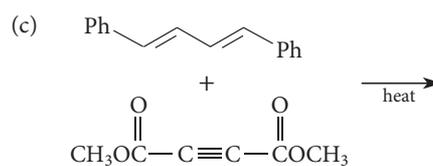
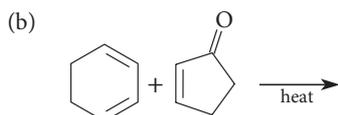
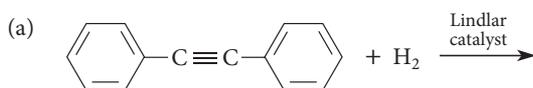


7-bromo-1,3,5-cycloheptatriene (tropylium bromide)

- 15.83 The hybridizations of the nitrogens in two of the following heterocyclic compounds is the same. Which one is different? What is its hybridization, and why?

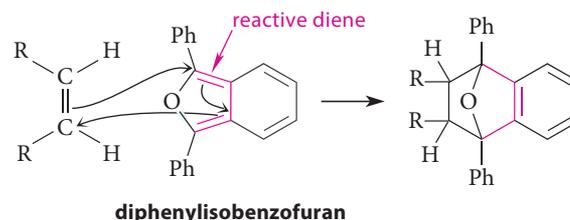


- 15.84 Complete the reactions given in each of the following parts, giving the structures of all reasonable products and the reasoning used to obtain them.



- 15.85 Account for the fact that the antibiotic *mycomycin* (structure in **Figure P15.85**) is optically active.

- 15.86 One interesting use of Diels–Alder reactions is to trap very reactive alkenes that cannot be isolated and studied directly. One compound used as a diene for this purpose is diphenylisobenzofuran, which reacts as follows:



(The formation of an aromatic ring in the product helps ensure that the Diels–Alder reaction is driven to completion.) In the following reaction, use the structure of the Diels–Alder product to deduce the structure of

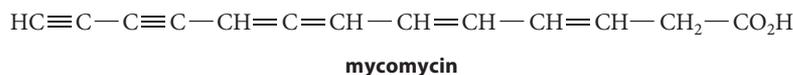
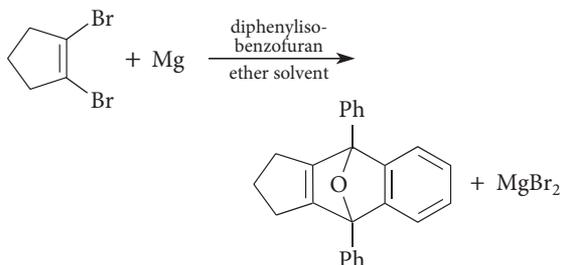
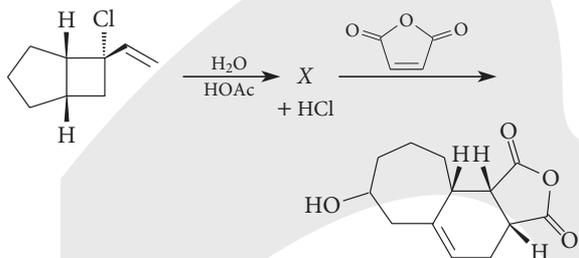


FIGURE P15.85

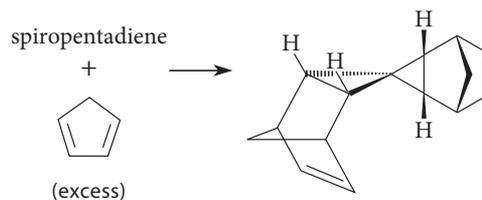
the reactive species formed in the reaction. Show by the curved-arrow notation how the reactive species is formed, and explain what makes it particularly unstable.



- 15.87 Use the structure of the Diels–Alder adduct to deduce the structure of the product X in the following reaction. Then give a curved-arrow mechanism for the formation of X.



- 15.88 In 1991, chemists at Rice University reported that they had trapped an unstable compound called *spiropentadiene* using its Diels–Alder reaction with excess 1,3-cyclopentadiene, giving the product in the following reaction. Use the structure of this product to deduce the structure of *spiropentadiene*.



- 15.89 Account for each of the transformations shown in Fig. P15.89 with a curved-arrow mechanism. (Don't try to explain any percentages.) In part (c), identify X, give the mechanisms for both the formation and the subsequent reaction of X, and explain why the equilibrium for the reaction of X strongly favors the products.

- 15.90 Account for the fact that the central “benzene ring” of [4]phenylene undergoes catalytic hydrogenation readily under conditions usually used for ordinary alkenes, but the other benzene rings do not.

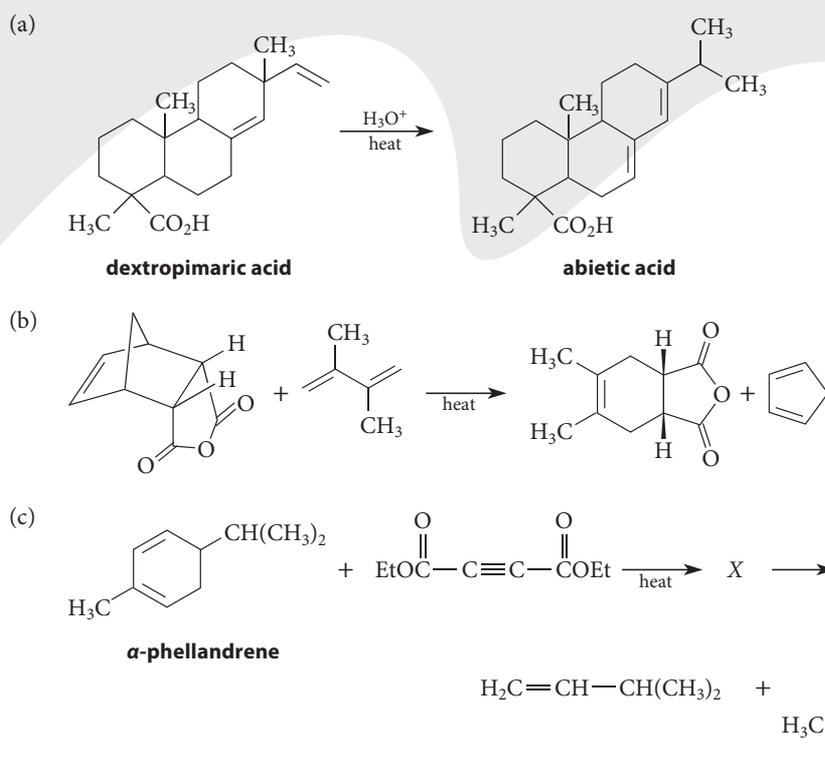
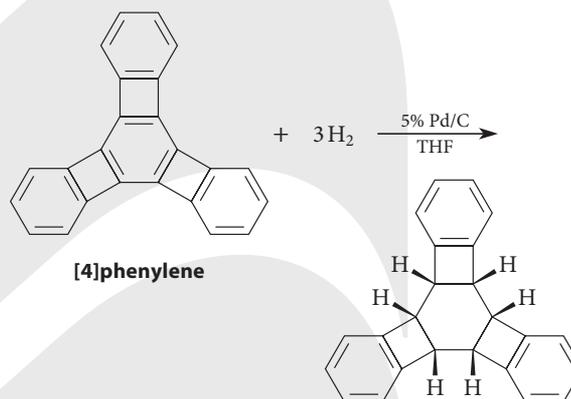


FIGURE P15.89