Aromatic Compounds

I n ordinary conversation, the word "aromatic" conjures pleasant associations—the odor of freshly prepared coffee, a warm cinnamon bun, a freshly cut pine tree. Similar associations occurred in the early history of organic chemistry when pleasantly aromatic compounds were isolated from natural oils produced by plants. Once the structures of these materials were elucidated, many were found to possess a unique, highly unsaturated, six-carbon structural unit also found in benzene. This special ring became known as the benzene ring. Aromatic compounds that contain a benzene ring are now part of a much larger family of compounds classified as aromatic, not because of their smell (since many of the molecules that contain them have no odor—for example, aspirin), but because they have special electronic features.

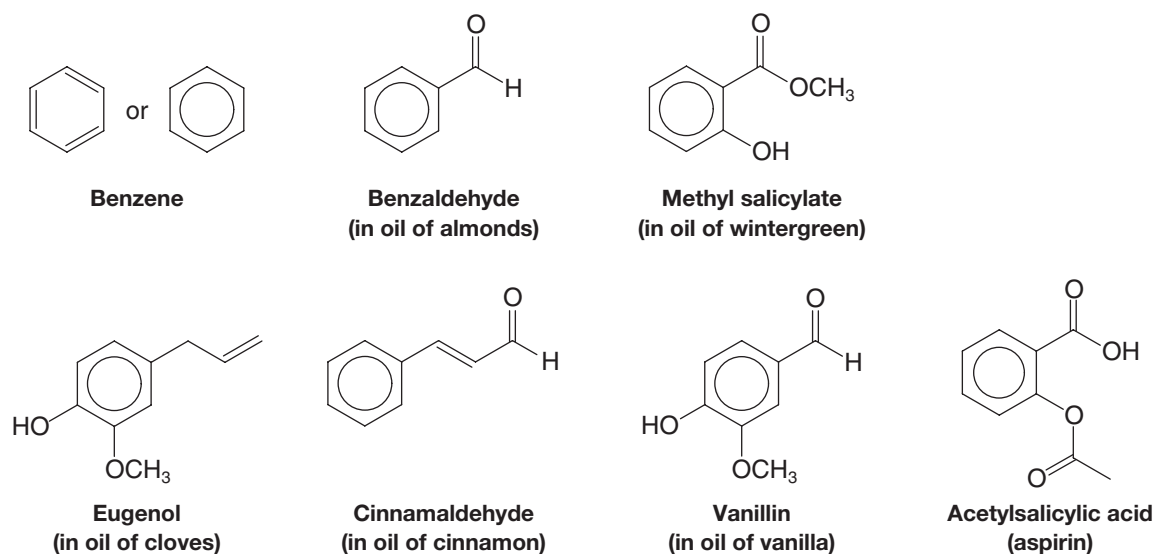**IN THIS CHAPTER WE WILL CONSIDER:**

- the structural principles that underlie the use of the term "aromatic"
- the initial challenge of determining the correct structure of benzene
- a rule that helps to predict what kinds of molecules possess the special property of aromaticity
- special groups of molecules that are also aromatic

[WHY DO THESE TOPICS MATTER?]   At the end of the chapter, we will explore the question of just how large the rings of these molecules can be and still be aromatic, noting that chemists have been able to make aromatic rings far larger in size than those of molecules obtained from nature, but largely using design clues derived from those natural molecules.

14.1 THE DISCOVERY OF BENZENE

The following are a few examples of aromatic compounds, including benzene itself. In these formulas we foreshadow our discussion of the special properties of the benzene ring by using a circle in a hexagon to depict the six π electrons and six-membered ring of these compounds, whereas up to now we have shown benzene rings only as indicated in the left-hand formula for benzene below.

Benzene

Benzaldehyde
(in oil of almonds)

Methyl salicylate
(in oil of wintergreen)

Eugenol
(in oil of cloves)

Cinnamaldehyde
(in oil of cinnamon)

Vanillin
(in oil of vanilla)

Acetylsalicylic acid
(aspirin)

The study of the class of compounds that organic chemists call aromatic compounds (Section 2.1D) began with the discovery in 1825 of a new hydrocarbon by the English chemist Michael Faraday (Royal Institution). Faraday called this new hydrocarbon "bicarburet of hydrogen"; we now call it benzene. Faraday isolated benzene from a compressed illuminating gas that had been made by pyrolyzing whale oil.

In 1834 the German chemist Eilhardt Mitscherlich (University of Berlin) synthesized benzene by heating benzoic acid with calcium oxide. Using vapor density measurements, Mitscherlich further showed that benzene has the molecular formula C_6H_6:

$$C_6H_5CO_2H \ + \ CaO \ \xrightarrow{\text{heat}} \ C_6H_6 \ + \ CaCO_3$$

Benzoic acid   **Benzene**
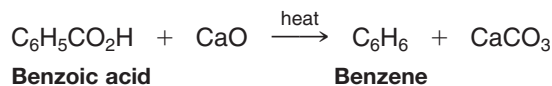
The molecular formula itself was surprising. Benzene has *only as many hydrogen atoms as it has carbon atoms*. Most compounds that were known then had a far greater proportion of hydrogen atoms, usually twice as many. Benzene, having the formula of C_6H_6, should be a highly unsaturated compound because it has an index of hydrogen deficiency equal to 4. Eventually, chemists began to recognize that benzene was a member of a new class of organic compounds with unusual and interesting properties. **As we shall see in Section 14.3, benzene does not show the behavior expected of a highly unsaturated compound**.

During the latter part of the nineteenth century the Kekulé–Couper–Butlerov theory of valence was systematically applied to all known organic compounds. One result of this effort was the placing of organic compounds in either of two broad categories; compounds were classified as being either **aliphatic** or **aromatic**. To be classified as aliphatic meant then that the chemical behavior of a compound was "fatlike." (Now it means that the compound reacts like an alkane, an alkene, an alkyne, or one of their derivatives.) To be classified as aromatic meant then that the compound had a low hydrogen-to-carbon
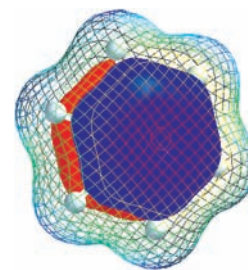
One of the π molecular orbitals of benzene, seen through a mesh representation of its electrostatic potential at its van der Waals surface.

ratio and that it was "fragrant." Most of the early aromatic compounds were obtained from balsams, resins, or essential oils.

Kekulé was the first to recognize that these early aromatic compounds all contain a six-carbon unit and that they retain this six-carbon unit through most chemical transformations and degradations. Benzene was eventually recognized as being the parent compound of this new series. It was not until the development of quantum mechanics in the 1920s, however, that a reasonably clear understanding of its structure emerged.

14.2 NOMENCLATURE OF BENZENE DERIVATIVES

Two systems are used in naming monosubstituted benzenes.

- In many simple compounds, *benzene* is the parent name and the substituent is simply indicated by a prefix.

We have, for example,

Fluorobenzene   **Chlorobenzene**   **Bromobenzene**   **Nitrobenzene**
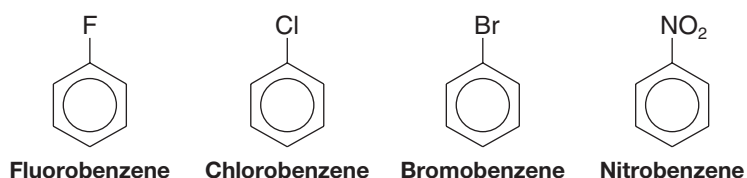
- For other simple and common compounds, the substituent and the benzene ring taken together may form a commonly accepted parent name.

Methylbenzene is usually called *toluene*, hydroxybenzene is almost always called *phenol*, and aminobenzene is almost always called *aniline*. These and other examples are indicated here:
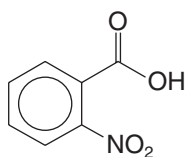
Toluene   **Phenol**   **Aniline**

Benzenesulfonic acid   **Benzoic acid**   **Acetophenone**   **Anisole**
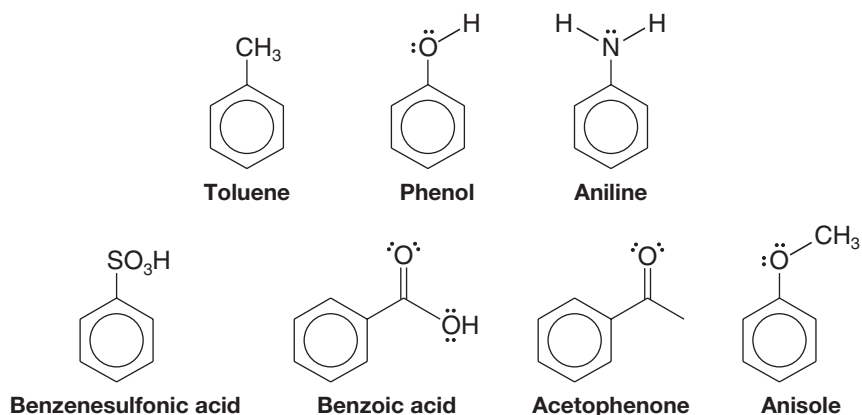
- When two substituents are present, their relative positions are indicated by the prefixes ***ortho-, meta-***, and ***para-*** (abbreviated ***o-, m-***, and ***p-***) or by the use of numbers.

For the dibromobenzenes we have

1,2-Dibromobenzene   **1,3-Dibromobenzene**   **1,4-Dibromobenzene**
(*o*-dibromobenzene)   **(*m*-dibromobenzene)**   **(*p*-dibromobenzene)**
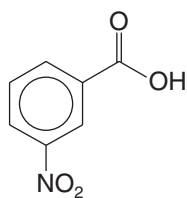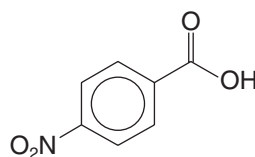ortho   meta   para
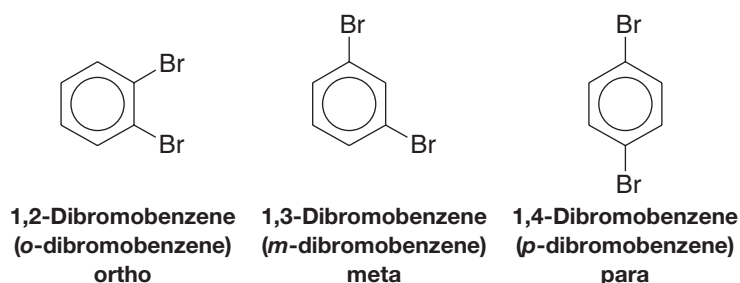
and for the nitrobenzoic acids

2-Nitrobenzoic acid
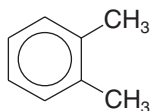(*o*-nitrobenzoic acid)
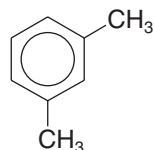
3-Nitrobenzoic acid
(*m*-nitrobenzoic acid)

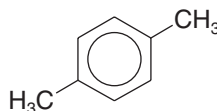**4-Nitrobenzoic acid**
(*p*-nitrobenzoic acid)

The dimethylbenzenes are often called *xylenes*:

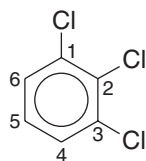**1,2-Dimethylbenzene**
(*o*-xylene)
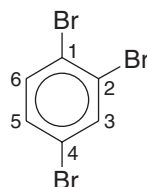
1,3-Dimethylbenzene
(*m*-xylene)

1,4-Dimethylbenzene
(*p*-xylene)

- If more than two groups are present on the benzene ring, their positions must be indicated by the use of *numbers*.

As examples, consider the following two compounds:

1,2,3-Trichlorobenzene

1,2,4-Tribromobenzene
(*not* 1,3,4-tribromobenzene)

- The benzene ring is numbered so as to give ***the lowest possible numbers to the substituents***.
- When more than two substituents are present and the substituents are different, they are listed in alphabetical order.
- When a substituent is one that together with the benzene ring gives a new base name, that substituent is assumed to be in position 1 and the new parent name is used.
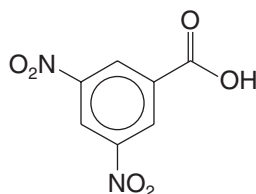
3,5-Dinitrobenzoic acid
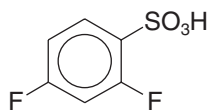
2,4-Difluorobenzenesulfonic acid

- When the C_6H_5— group is named as a substituent, it is called a **phenyl** group. The phenyl group is often abbreviated as C_6H_5—, Ph—, or φ—.

A hydrocarbon composed of one saturated chain and one benzene ring is usually named as a derivative of the larger structural unit. However, if the chain is unsaturated, the compound may be named as a derivative of that chain, regardless of ring size. The following are examples:
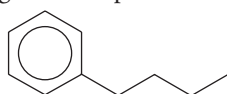
Butylbenzene
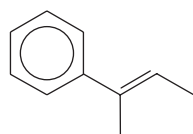
(*E*)-2-Phenyl-2-butene

C_6H_5
2-Phenylheptane

Helpful Hint

Note the abbreviations for common aromatic groups.

• **Benzyl** is an alternative name for the phenylmethyl group. It is sometimes abbreviated Bn.
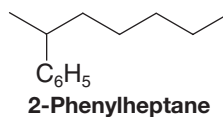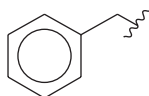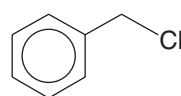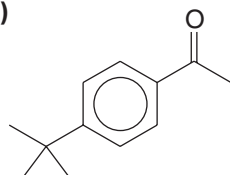
**The benzyl group
(the phenylmethyl
group)**
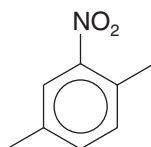
**Benzyl chloride
(phenylmethyl chloride
or BnCl)**

●●● **SOLVED PROBLEM 14.1**

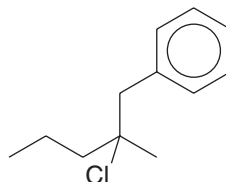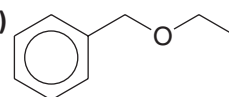Provide a name for each of the following compounds.

(a) **(b)** NO₂ **(c)** **(d)**

STRATEGY AND ANSWER: In each compound we look first to see if a commonly named unit containing a benzene ring is present. If not, we consider whether the compound can be named as a simple derivative of benzene, or if the compound incorporates the benzene ring as a phenyl or benzyl group. In **(a)** we recognize the common structural unit of acetophenone, and find a *tert*-butyl group in the para position. The name is thus *p-tert*-butylacetophenone or 4-*tert*-butylacetophenone. Compound **(b)**, having three substituents on the ring, must have its substituents named in alphabetical order and their positions numbered. The name is 1,4-dimethyl-2-nitrobenzene. In **(c)** there would appear to be a benzyl group, but the benzene ring can be considered a substituent on the alkyl chain, so it is called phenyl in this case. The name is 2-chloro-2-methyl-1-phenylpentane. Because **(d)** contains an ether functional group, we name it according to the groups bonded to the ether oxygen. The name is benzyl ethyl ether, or ethyl phenylmethyl ether.

●●●

PRACTICE PROBLEM 14.1 Provide a name for each of the following compounds.
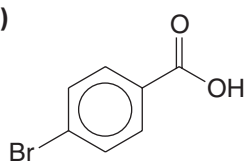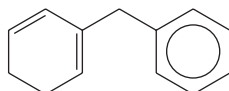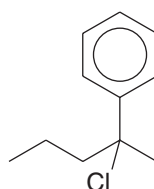
(a) **(b)** **(c)** **(d)**
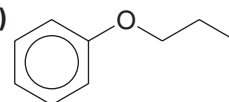
14.3 REACTIONS OF BENZENE

In the mid-nineteenth century, benzene presented chemists with a real puzzle. They knew from its formula (Section 14.1) that benzene was highly unsaturated, and they expected it to react accordingly. They expected it to react like an alkene by decolorizing bromine through *addition*. They expected that it would change the color of aqueous potassium permanganate by being *oxidized*, that it would *add hydrogen* rapidly in the presence of a metal catalyst, and that it would *add water* in the presence of strong acids.

Benzene does none of these. When benzene is treated with bromine in the dark or with aqueous potassium permanganate or with dilute acids, none of the expected reactions occurs. Benzene does add hydrogen in the presence of finely divided nickel, but only at high temperatures and under high pressures:

$$Benzene \begin{cases} \xrightarrow[\text{dark, 25 °C}]{Br_2} & \text{No addition of bromine} \\ \xrightarrow[\text{H}_2\text{O, 25 °C}]{KMnO_4} & \text{No oxidation} \\ \xrightarrow[\text{H}_2\text{O, heat}]{H_3O^+} & \text{No hydration} \\ \xrightarrow{H_2/Ni} & \text{Slow addition at high temperature and pressure} \end{cases}$$
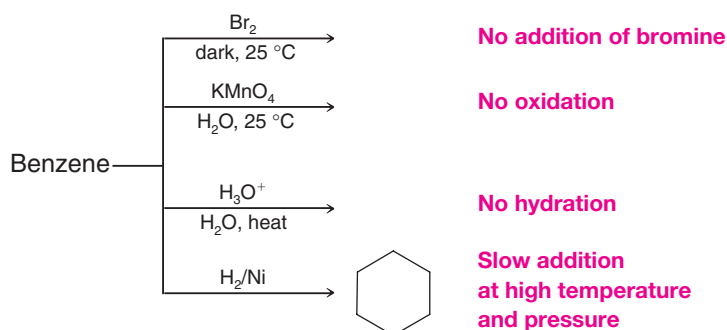
Benzene *does* react with bromine but only in the presence of a Lewis acid catalyst such as ferric bromide. Most surprisingly, however, it reacts not by addition but by *substitution*—**benzene substitution**.

Substitution

$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr \qquad \text{Substitution is observed.}$$

Addition

$$C_6H_6 + Br_2 \not\longrightarrow C_6H_6Br_2 + C_6H_6Br_4 + C_6H_6Br_6 \qquad \text{Addition is not observed.}$$

When benzene reacts with bromine, *only one monobromobenzene* is formed. That is, only one compound with the formula C_6H_5Br is found among the products. Similarly, when benzene is chlorinated, *only one monochlorobenzene* results.

Two possible explanations can be given for these observations. The first is that only one of the six hydrogen atoms in benzene is reactive toward these re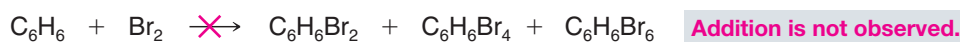agents. The second is that all six hydrogen atoms in benzene are equivalent, and replacing any one of them with a substituent results in the same product. As we shall see, the second explanation is correct.

PRACTICE PROBLEM 14.2

Listed below are four compounds that have the molecular formula C_6H_6. Which of these compounds would yield only one monosubstitution product, if, for example, one hydrogen were replaced by bromine?

(a) ——≡≡—≡—   (b)   (c)   (d)

14.4 THE KEKULÉ STRUCTURE FOR BENZENE

In 1865, August Kekulé, the originator of the structural theory (Section 1.3), proposed the first definite structure for benzene,* a structure that is still used today (although as we shall soon see, we give it a meaning different from the meaning Kekulé gave it). Kekulé suggested that the carbon atoms of benzene are in a ring, that they are bonded to each other by alternating single and double bonds, and that one hydrogen atom is attached to each carbon atom. This structure satisfied the requirements of the structural theory that carbon atoms form four bonds and that all the hydrogen atoms of benzene are equivalent:

or

The Kekulé formula for benzene
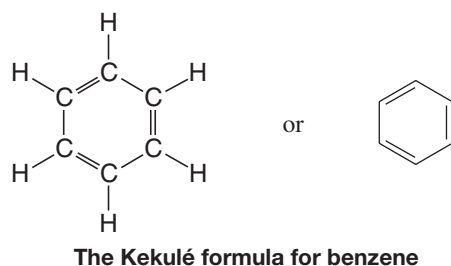
*In 1861 the Austrian chemist Johann Josef Loschmidt represented the benzene ring with a circle, but he made no attempt to indicate how the carbon atoms were actually arranged in the ring.

A problem soon arose with the **Kekulé structure**, however. The Kekulé structure predicts that there should be two different 1,2-dibromobenzenes, but there are not. In one of these hypothetical compounds (below), the carbon atoms that bear the bromines would be separated by a single bond, and in the other they would be separated by a double bond.

These 1,2-dibromobenzenes do not exist as isomers.

- *Only one 1,2-dibromobenzene has ever been found, however.*

To accommodate this objection, Kekulé proposed that the two forms of benzene (and of benzene derivatives) are in a state of equilibrium and that this equilibrium is so rapidly established that it prevents isolation of the separate compounds. Thus, the two 1,2-dibromobenzenes would also be rapidly equilibrated, and this would explain why chemists had not been able to isolate the two forms:

There is no such equilibrium between benzene ring bond isomers.
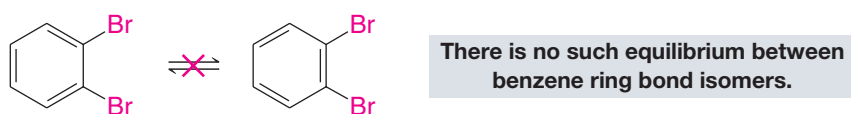
- We now know that this proposal was also incorrect and that *no such equilibrium exists*.

Nonetheless, the Kekulé formulation of benzene's structure was an important step forward and, for very practical reasons, it is still used today. Now we understand its meaning differently, however.

The tendency of benzene to react by substitution rather than addition gave rise to another concept of **aromaticity**. For a compound to be called aromatic meant, experimentally, that it gave substitution reactions rather than addition reactions even though it was highly unsaturated.

Before 1900, chemists assumed that the ring of alternating single and double bonds was the structural feature that gave rise to the aromatic properties. Since benzene and benzene derivatives (i.e., compounds with six-membered rings) were the only aromatic compounds known, chemists naturally sought other examples. The compound cyclooctatetraene seemed to be a likely candidate:

Cyclooctatetraene
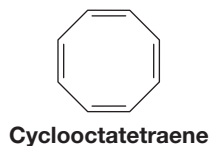
In 1911, Richard Willstätter succeeded in synthesizing cyclooctatetraene. Willstätter found, however, that it is not at all like benzene. Cyclooctatetraene reacts with bromine by addition, it adds hydrogen readily, it is oxidized by solutions of potassium permanganate, and thus it is clearly *not aromatic*. While these findings must have been a keen disappointment to Willstätter, they were very significant for what they did not prove. Chemists, as a result, had to look deeper to discover the origin of benzene's aromaticity.

14.5 THE THERMODYNAMIC STABILITY OF BENZENE

We have seen that benzene shows unusual behavior by undergoing substitution reactions when, on the basis of its Kekulé structure, we should expect it to undergo addition. Benzene is unusual in another sense: it is *more stable thermodynamically* than the Kekulé structure suggests. To see how, consider the following thermochemical results.
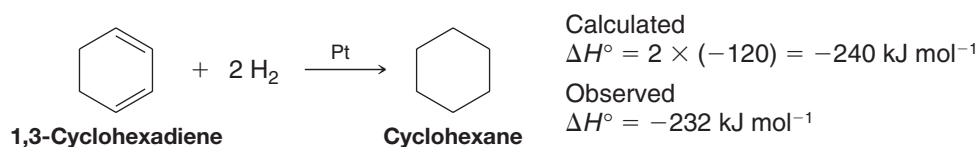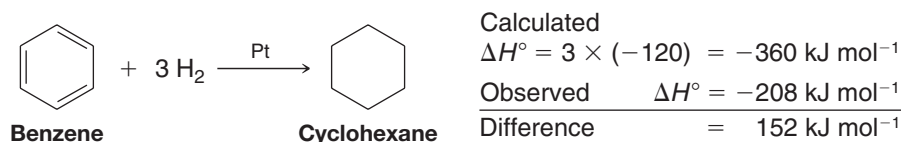
Cyclohexene, a six-membered ring containing one double bond, can be hydrogenated easily to cyclohexane. When the $\Delta H°$ for this reaction is measured, it is found to be -120 kJ mol^{-1}, very much like that of any similarly substituted alkene:

**Cyclohexene** $+$ H$_2$ $\xrightarrow{\text{Pt}}$ **Cyclohexane** $\Delta H° = -120$ kJ mol^{-1}
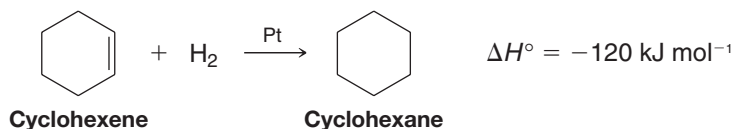
We would expect that hydrogenation of 1,3-cyclohexadiene would liberate roughly twice as much heat and thus have a $\Delta H°$ equal to about -240 kJ mol^{-1}. When this experiment is done, the result is $\Delta H° = -232$ kJ mol^{-1}. This result is quite close to what we calculated, and the difference can be explained by taking into account the fact that compounds containing conjugated double bonds are usually somewhat more stable than those that contain isolated double bonds (Section 13.8):

1,3-Cyclohexadiene $+$ 2 H$_2$ $\xrightarrow{\text{Pt}}$ **Cyclohexane**

Calculated
$\Delta H° = 2 \times (-120) = -240$ kJ mol^{-1}
Observed
$\Delta H° = -232$ kJ mol^{-1}

If we extend this kind of thinking, and if benzene is simply 1,3,5-cyclohexatriene, we would predict benzene to liberate approximately 360 kJ mol^{-1} [$3 \times (-120)$] when it is hydrogenated. When the experiment is actually done, the result is surprisingly different. The reaction is exothermic, but only by 208 kJ mol^{-1}:

Benzene $+$ 3 H$_2$ $\xrightarrow{\text{Pt}}$ **Cyclohexane**

Calculated
$\Delta H° = 3 \times (-120) = -360$ kJ mol^{-1}
Observed $\Delta H° = -208$ kJ mol^{-1}
Difference $= 152$ kJ mol^{-1}

When these results are represented as in Fig. 14.1, it becomes clear that benzene is much more stable than we calculated it to be. Indeed, it is more stable than the hypothetical 1,3,5-cyclohexatriene by 152 kJ mol^{-1}. This difference between the amount of heat actually released and that calculated on the basis of the Kekulé structure is now called the **resonance energy** of the compound.
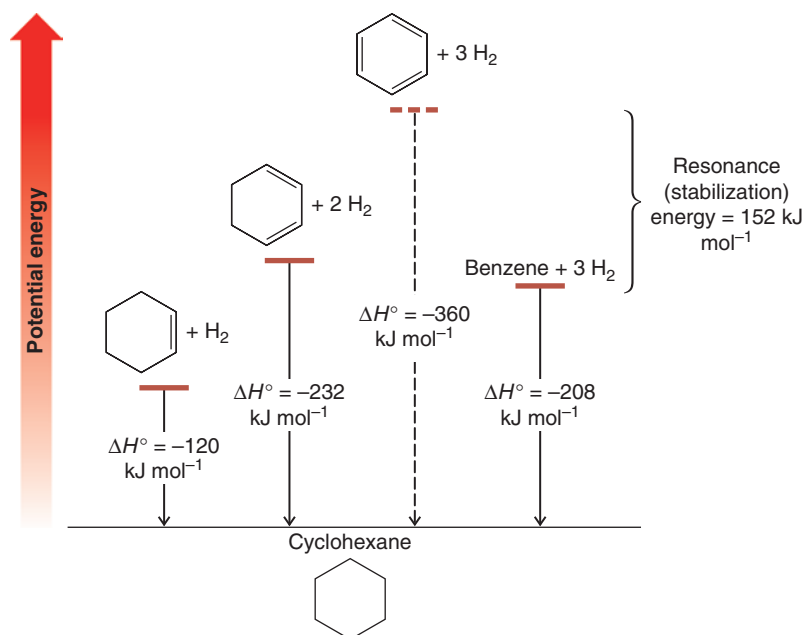
FIGURE 14.1 Relative stabilities of cyclohexene, 1,3-cyclohexadiene, 1,3,5-cyclohexatriene (hypothetical), and benzene.

14.6 MODERN THEORIES OF THE STRUCTURE OF BENZENE

It was not until the development of quantum mechanics in the 1920s that the unusual behavior and stability of benzene began to be understood. Quantum mechanics, as we have seen, produced two ways of viewing bonds in molecules: resonance theory and molecular orbital theory. We now look at both of these as they apply to benzene.

## 14.6A The Resonance Explanation of the Structure of Benzene

A basic postulate of resonance theory (Sections 1.8 and 13.4) is that whenever two or more Lewis structures can be written for a molecule that *differ only in the positions of their electrons*, none of the structures will be in complete accord with the compound's chemical and physical properties. If we recognize this, we can now understand the true nature of the two Kekulé structures (**I** and **II**) for benzene.

- Kekulé structures **I** and **II** below differ only in the positions of their electrons; they do not represent two separate molecules in equilibrium as Kekulé had proposed.

Instead, structures **I** and **II** are the closest we can get to a structure for benzene within the limitations of its molecular formula, the classic rules of valence, and the fact that the six hydrogen atoms are chemically equivalent. The problem with the Kekulé structures is that they are Lewis structures, and Lewis structures portray electrons in localized distributions. (With benzene, as we shall see, the electrons are delocalized.) Resonance theory, fortunately, does not stop with telling us when to expect this kind of trouble; it also gives us a way out.

- According to resonance theory, we consider Kekulé structures **I** and **II** below as *resonance contributors* to the real structure of benzene, and we relate them to each other with one double-headed, double-barbed arrow (not two separate arrows, which we reserve for equilibria).

Resonance contributors, we emphasize again, are not in equilibrium. They are not structures of real molecules. They are the closest we can get if we are bound by simple rules of valence, but they are very useful in helping us visualize the actual molecule as a hybrid:
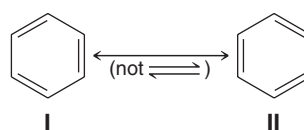
Look at the structures carefully. All of the single bonds in structure **I** are double bonds in structure **II**.

- A hybrid (average) of Kekulé structures **I** and **II** would have neither pure single bonds nor pure double bonds between the carbons. The bond order would be between that of a single and a double bond.

Experimental evidence bears this out. Spectroscopic measurements show that the molecule of benzene is planar and that all of its carbon–carbon bonds are of equal length. Moreover, the carbon–carbon bond lengths in benzene (Fig. 14.2) are 1.39 Å, a value in between that for a carbon–carbon single bond between sp^2-hybridized atoms (1.47 Å) (see Table 13.1) and that for a carbon–carbon double bond (1.34 Å).
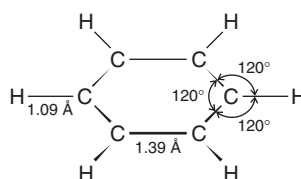
FIGURE 14.2 Bond lengths and angles in benzene. (Only the σ bonds are shown.)

- The hybrid structure of benzene is represented by inscribing a circle inside the hexagon as shown in formula **III** below.

III
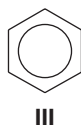
There are times when an accounting of the π electron pairs must be made, however, and for these purposes we use either Kekulé structure **I** or **II**. We do this simply because the electron pairs and total π electron count is obvious in a Kekulé structure, whereas the number of π electron pairs represented by a circle can be ambiguous. As we shall see later in this chapter, there are systems having different ring sizes and different numbers of delocalized π electrons that can also be represented by a circle. In benzene, however, the circle is understood to represent six π electrons that are delocalized around the six carbons of the ring.

- An actual molecule of benzene (depicted by the resonance hybrid **III**) is more stable than either contributing resonance structure because more than one equivalent resonance structure can be drawn for benzene (**I** and **II** above).

The difference in energy between hypothetical 1,3,5-cyclohexatriene (which if it existed would have higher energy) and benzene is called *resonance energy*, and it is an indication of the extra stability of benzene due to electron delocalization.

PRACTICE PROBLEM 14.3

If benzene were 1,3,5-cyclohexatriene, the carbon–carbon bonds would be alternately long and short as indicated in the following structures. However, to consider the structures here as resonance contributors (or to connect them by a double-headed arrow) violates a basic principle of resonance theory. Explain.
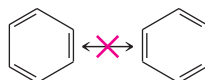
## 14.6B The Molecular Orbital Explanation of the Structure of Benzene

The fact that the bond angles of the carbon atoms in the benzene ring are all 120° strongly suggests that the carbon atoms are sp^2 hybridized. If we accept this suggestion and construct a planar six-membered ring from sp^2 carbon atoms, representations like those shown in Figs. 14.3*a* and *b* emerge. In these models, each carbon is sp^2 hybridized and has a *p* orbital available for overlap with *p* orbitals of its neighboring carbons. If we consider favorable overlap of these *p* orbitals all around the ring, the result is the model shown in Fig. 14.3*c*.

(*a*)   (*b*)   (*c*)
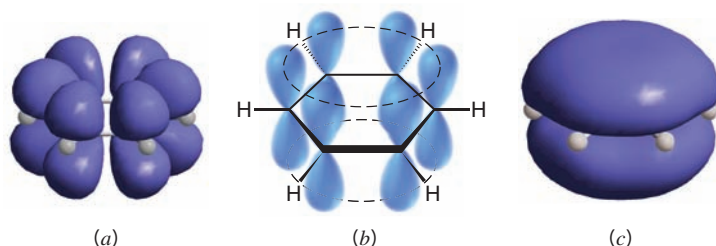
FIGURE 14.3 (*a*) Six sp^2-hybridized carbon atoms joined in a ring (each carbon also bears a hydrogen atom). Each carbon has a *p* orbital with lobes above and below the plane of the ring. (*b*) A stylized depiction of the *p* orbitals in (*a*). (*c*) Overlap of the *p* orbitals around the ring results in a molecular orbital encompassing the top and bottom faces of the ring. (Differences in the mathematical phase of the orbital lobes are not shown in these representations.)
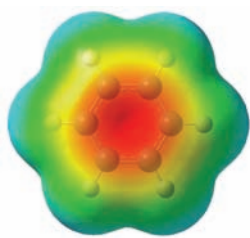
- As we recall from the principles of quantum mechanics (Section 1.11), the number of molecular orbitals in a molecule is the same as the number of atomic orbitals from which they are derived, and each orbital can accommodate a maximum of two electrons if their spins are opposed.

If we consider only the p atomic orbitals contributed by the carbon atoms of benzene, there should be six π molecular orbitals. These orbitals are shown in Fig. 14.4.
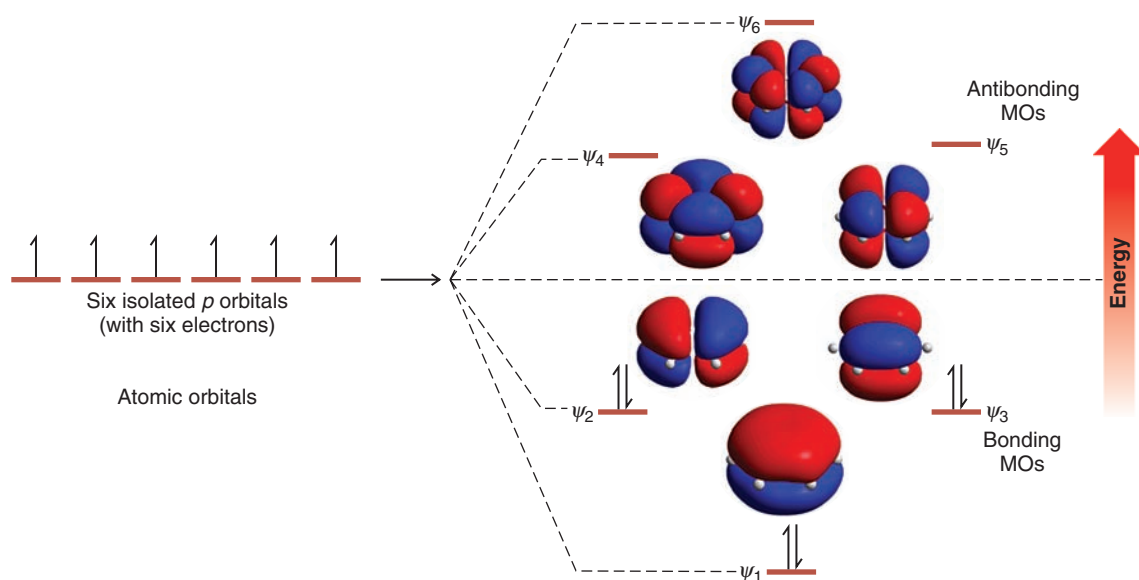
FIGURE 14.4 How six p atomic orbitals (one from each carbon of the benzene ring) combine to form six π molecular orbitals. Three of the molecular orbitals have energies lower than that of an isolated p orbital; these are the bonding molecular orbitals. Three of the molecular orbitals have energies higher than that of an isolated p orbital; these are the antibonding molecular orbitals. Orbitals ψ_2 and ψ_3 have the same energy and are said to be degenerate; the same is true of orbitals ψ_4 and ψ_5.

The electronic configuration of the ground state of benzene is obtained by adding the six π electrons to the π molecular orbitals shown in Fig. 14.4, starting with the orbitals of lowest energy. The lowest energy π molecular orbital in benzene has overlap of p orbitals with the same mathematical phase sign all around the top and bottom faces of the ring. In this orbital there are no nodal planes (changes in orbital phase sign) perpendicular to the atoms of the ring. The orbitals of next higher energy each have one nodal plane. (In general, each set of higher energy π molecular orbitals has an additional nodal plane.) Each of these orbitals is filled with a pair of electrons, as well. These orbitals are of equal energy (degenerate) because they both have one nodal plane. Together, these three orbitals comprise the bonding π molecular orbitals of benzene. The next higher energy set of π molecular orbitals each has two nodal planes, and the highest energy π molecular orbital of benzene has three nodal planes. These three orbitals are the antibonding π molecular orbitals of benzene, and they are unoccupied in the ground state. Benzene is said to have a closed bonding shell of delocalized π electrons because all of its bonding orbitals are filled with electrons that have their spins paired, and no electrons are found in antibonding orbitals. This closed bonding shell accounts, in part, for the stability of benzene.

Having considered the molecular orbitals of benzene, it is now useful to view an electrostatic potential map of the van der Waals surface for benzene, also calculated from quantum mechanical principles (Fig. 14.5). We can see that this representation is consistent with our understanding that the π electrons of benzene are not localized but are evenly distributed around the top face and bottom face (not shown) of the carbon ring in benzene.

It is interesting to note the recent discovery that crystalline benzene involves perpendicular interactions between benzene rings, so that the relatively positive periphery of one molecule associates with the relatively negative faces of the benzene molecules aligned above and below it.

FIGURE 14.5 Electrostatic potential map of benzene.

14.7 HÜCKEL'S RULE: THE $4n + 2$ π ELECTRON RULE

In 1931 the German physicist Erich Hückel carried out a series of mathematical calculations based on the kind of theory that we have just described. **Hückel's rule** is concerned with compounds containing **one planar ring in which each atom has a p orbital** as in benzene. His calculations showed that planar monocyclic rings containing $4n + 2$ π electrons, where $n = 0, 1, 2, 3$, and so on (i.e., rings containing 2, 6, 10, 14,..., etc., π electrons), have closed shells of delocalized electrons like benzene and should have substantial resonance energies.

- In other words, Hückel's rule states that **planar monocyclic rings with 2, 6, 10, 14,..., delocalized electrons should be aromatic**.

14.7A HOW TO Diagram the Relative Energies of π Molecular Orbitals in Monocyclic Systems Based on Hückel's Rule

There is a simple way to make a diagram of the relative energies of orbitals in monocyclic conjugated systems based on Hückel's calculations. To do so, we use the following procedure.

1. We start by drawing a polygon corresponding to the number of carbons in the ring, *placing a corner of the polygon at the bottom*.

2. Next we surround the polygon with a circle that touches each corner of the polygon.

3. At the points where the polygon touches the circle, we draw short horizontal lines outside the circle. The height of each line represents the relative energy of each π molecular orbital.

4. Next we draw a dashed horizontal line across and halfway up the circle. The energies of bonding π molecular orbitals are below this line. The energies of antibonding π molecular orbitals are above, and those for nonbonding orbitals are at the level of the dashed line.

5. Based on the number of π electrons in the ring, we then place electron arrows on the lines corresponding to the respective orbitals, beginning at the lowest energy level and working upward. In doing so, we fill degenerate orbitals each with one electron first, then add to each unpaired electron another with opposite spin if it is available.

Applying this method to benzene, for example (Fig. 14.6), furnishes the same energy levels that we saw earlier in Fig. 14.4, energy levels that were based on quantum mechanical calculations.

Polygon in circle   Energy levels of MOs   Type of π orbital

Antibonding π orbitals
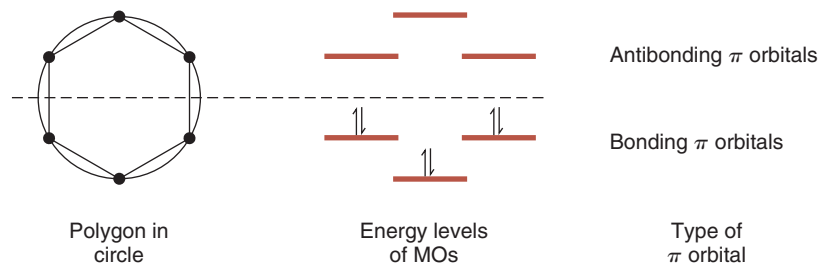
Bonding π orbitals

FIGURE 14.6 The polygon-and-circle method for deriving the relative energies of the π molecular orbitals of benzene. A horizontal line halfway up the circle divides the bonding orbitals from the antibonding orbitals. If an orbital falls on this line, it is a nonbonding orbital. This method was developed by C. A. Coulson (of Oxford University).

We can now understand why cyclooctatetraene is not aromatic. Cyclooctatetraene has a total of eight π electrons. Eight is not a Hückel number; it is a *4n number*, not a *4n + 2 number*. Using the polygon-and-circle method (Fig. 14.7), we find that cyclooctatetraene, if it were planar, *would not* have a closed shell of π electrons like benzene; it would have an unpaired electron in each of two nonbonding orbitals. Molecules with unpaired electrons (radicals) are *not* unusually stable; they are typically highly reactive and unstable. A planar form of cyclooctatetraene, therefore, should not be at all like benzene and should not be aromatic.

FIGURE 14.7 The π molecular orbitals that cyclooctatetraene would have if it were planar. Notice that, unlike benzene, this molecule is predicted to have two nonbonding orbitals, and because it has eight π electrons, it would have an unpaired electron in each of the two nonbonding orbitals (Hund's rule, Section 1.11). Such a system would not be expected to be aromatic.

Antibonding π orbitals

(Nonbonding π orbitals)

Bonding π orbitals
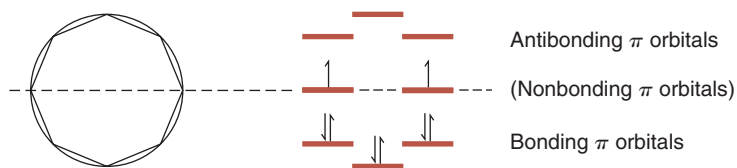
Because cyclooctatetraene does not gain stability by becoming planar, it assumes the tub shape shown below. (In Section 14.7E we shall see that cyclooctatetraene would actually lose stability by becoming planar.) The bonds of cyclooctatetraene are known to be alternately long and short; X-ray studies indicate that they are 1.48 and 1.34 Å, respectively.
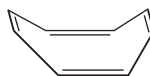
14.7B The Annulenes

The word **annulene** is incorporated into the class name for monocyclic compounds that can be represented by structures having alternating single and double bonds. The ring size of an annulene is indicated by a number in brackets. Thus, benzene is [6]annulene and cyclooctatetraene is [8]annulene.

- Hückel's rule predicts that annulenes will be aromatic if their molecules have $4n + 2$ π electrons and have a planar carbon skeleton:

Benzene
([6]annulene)

Cyclooctatetraene
([8]annulene)

Helpful Hint

These names are often used for conjugated rings of 10 or more carbon atoms, but they are seldom used for benzene and cyclooctatetraene.
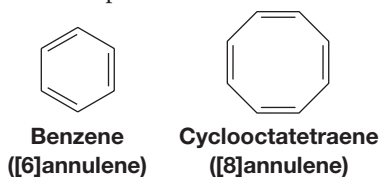
Before 1960 the only annulenes that were available to test Hückel's predictions were benzene and cyclooctatetraene. During the 1960s, and largely as a result of research by F. Sondheimer, a number of large-ring annulenes were synthesized, and the predictions of Hückel's rule were verified.

Consider the [14], [16], [18], [20], [22], and [24]annulenes as examples. Of these, *as Hückel's rule predicts*, the [14], [18], and [22]annulenes ($4n + 2$ when $n = 3, 4, 5$, respectively) have been found to be aromatic. The [16]annulene and the [24]annulene are not aromatic; they are *antiaromatic* (see Section 14.7E). They are $4n$ compounds, not $4n + 2$ compounds:

[14]Annulene
(aromatic)

[16]Annulene
(antiaromatic)

[18]Annulene
(aromatic)
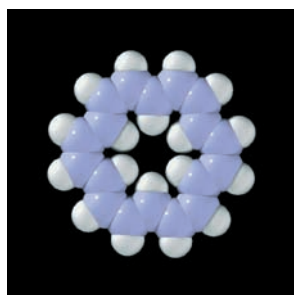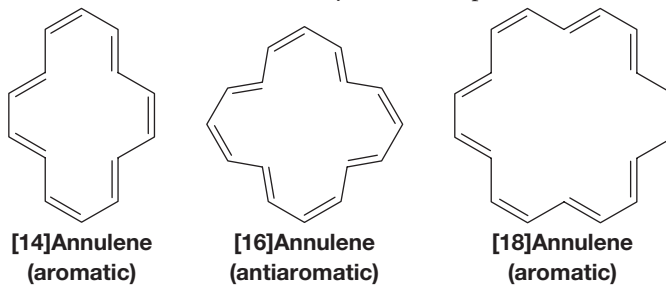
[18]Annulene.

Examples of [10] and [12]annulenes have also been synthesized and none is aromatic. We would not expect [12]annulenes to be aromatic since they have 12 π electrons and do not obey Hückel's rule. The following [10]annulenes would be expected to be aromatic on the basis of electron count, but their rings are not planar.

H
H

I

II

III

[10]Annulenes
None is aromatic because none is planar.
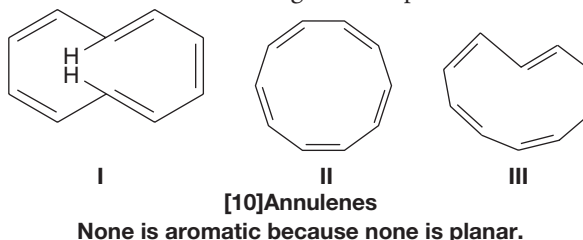
The [10]annulene **I** has two trans double bonds. Its bond angles are approximately 120°; therefore, it has no appreciable angle strain. The carbon atoms of its ring, however, are prevented from becoming coplanar because the two hydrogen atoms in the center of the ring interfere with each other. Because the ring is not planar, the p orbitals of the carbon atoms are not parallel and, therefore, cannot overlap effectively around the ring to form the π molecular orbitals of an aromatic system.

The [10]annulene with all cis double bonds (**II**) would, if it was planar, have considerable angle strain because the internal bond angles would be 144°. Consequently, any stability this isomer gained by becoming planar in order to become aromatic would be more than offset by the destabilizing effect of the increased angle strain. A similar problem of a large angle strain associated with a planar form prevents molecules of the [10]annulene isomer with one trans double bond (**III**) from being aromatic.

After many unsuccessful attempts over many years, in 1965 [4]annulene (or cyclobutadiene) was synthesized by R. Pettit and co-workers at the University of Texas, Austin. Cyclobutadiene is a $4n$ molecule, not a $4n + 2$ molecule, and, as we would expect, it is a highly unstable compound and *it is antiaromatic* (see Section 14.7E):
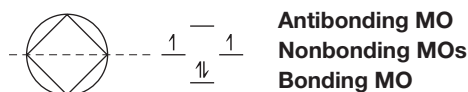

**Cyclobutadiene
or [4]annulene
(antiaromatic)**

●●● **SOLVED PROBLEM 14.2**

Using the polygon-and-circle method to outline the molecular orbitals of cyclobutadiene, explain why cyclobutadiene is not aromatic.

STRATEGY AND ANSWER: We inscribe a square inside a circle with one corner at the bottom.

We see that cyclobutadiene, according to this model, would have an unpaired electron in each of its two nonbonding molecular orbitals. We would, therefore, not expect cyclobutadiene to be aromatic.

14.7C NMR Spectroscopy: Evidence for Electron Delocalization in Aromatic Compounds

The ^{1}H NMR spectrum of benzene consists of a single unsplit signal at δ 7.27. That only a single unsplit signal is observed is further proof that all of the hydrogens of benzene are equivalent. That the signal occurs at relatively high frequency is, as we shall see, compelling evidence for the assertion that the π electrons of benzene are delocalized.

We learned in Section 9.6 that circulations of σ electrons of C—H bonds cause the protons of alkanes to be *shielded* from the applied magnetic field of an NMR spectrometer and, consequently, these protons absorb at lower frequency. We shall now explain the high-frequency absorption of benzene protons on the basis of *deshielding caused by circulation of the π electrons of benzene*, and this explanation, as you will see, requires that the π electrons be delocalized.

When benzene molecules are placed in the powerful magnetic field of the NMR spectrometer, electrons circulate in the direction shown in Fig. 14.8; by doing so, they generate a **ring current**. (If you have studied physics, you will understand why the electrons circulate in this way.)

- The circulation of π electrons in benzene creates an induced magnetic field that, *at the position of the protons, reinforces the applied magnetic field*. This reinforcement causes the protons to be strongly *deshielded* and to have a relatively high frequency ($\delta \sim 7$) absorption.

By "deshielded" we mean that the protons sense the sum of the two fields, and, therefore, the net magnetic field strength is greater than it would have been in the absence of the induced field. This strong deshielding, which we attribute to a ring current created by the *delocalized* π electrons, explains why aromatic protons absorb at relatively high frequency.
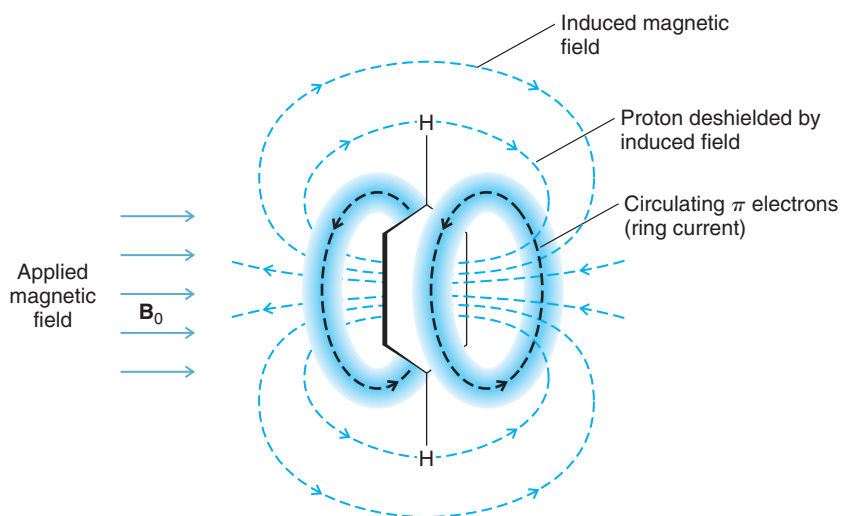
FIGURE 14.8 The induced magnetic field of the π electrons of benzene deshields the benzene protons. Deshielding occurs because at the location of the protons the induced field is in the same direction as the applied field.

The deshielding of external aromatic protons that results from the ring current is one of the best pieces of physical evidence that we have for π-electron delocalization in aromatic rings. In fact, relatively high frequency proton absorption is often used as a criterion for assessing aromaticity in newly synthesized conjugated cyclic compounds.

Not all aromatic protons have high frequency absorptions, however. The internal protons of large-ring aromatic compounds that have hydrogens in the center of the ring (in the π-electron cavity) absorb at unusually low frequency because they are highly shielded by the opposing induced magnetic field in the center of the ring (see Fig. 14.8). An example is [18]annulene (Fig. 14.9). The internal protons of [18]annulene absorb far upfield at δ −3.0, above the signal for tetramethylsilane (TMS); the external protons, on the other hand, absorb far downfield at δ 9.3. Considering that [18]annulene has $4n + 2$ π electrons, this evidence provides strong support for π-electron delocalization as a criterion for aromaticity and for the predictive power of Hückel's rule.
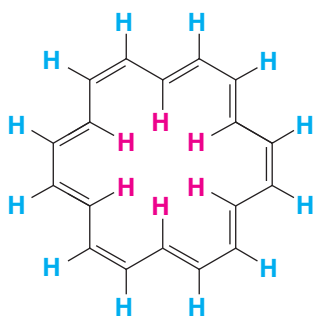
FIGURE 14.9 [18]Annulene. The internal protons (red) are highly shielded and absorb at δ −3.0. The external protons (blue) are highly deshielded and absorb at δ 9.3.
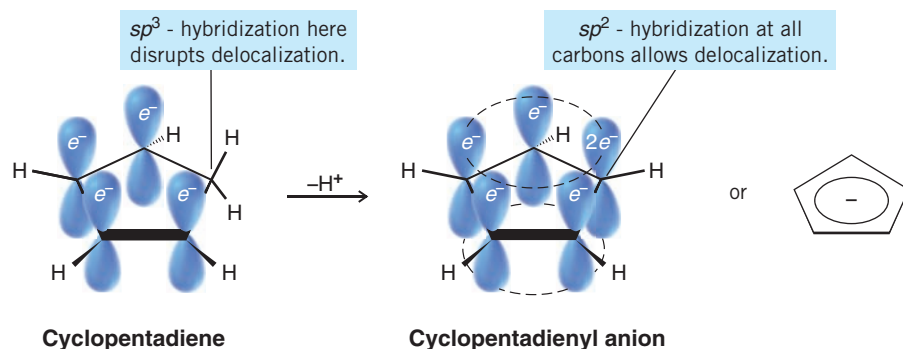
14.7D Aromatic Ions

In addition to the neutral molecules that we have discussed so far, there are a number of monocyclic species that bear either a positive or a negative charge. Some of these ions show unexpected stabilities that suggest that they are **aromatic ions**. Hückel's rule is helpful in accounting for the properties of these ions as well. We shall consider two examples: the cyclopentadienyl anion and the cycloheptatrienyl cation.

Cyclopentadiene is not aromatic; however, it is unusually acidic for a hydrocarbon. (The pK_a for cyclopentadiene is 16 and, by contrast, the pK_a for cycloheptatriene is 36.) Because of its acidity, cyclopentadiene can be converted to its anion by treatment with moderately strong bases. The cyclopentadienyl anion, moreover, is unusually stable, and NMR spectroscopy shows that all five hydrogen atoms in the cyclopentadienyl anion are equivalent and absorb downfield.

Cyclopentadiene   **Cyclopentadienyl anion**
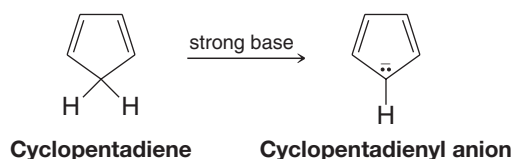
The orbital structure of cyclopentadiene (Fig. 14.10) shows why cyclopentadiene, itself, is not aromatic. Not only does it not have the proper number of π electrons, but the π electrons cannot be delocalized about the entire ring because of the intervening sp^3-hybridized —CH_2— group with no available p orbital.

sp³ - hybridization here disrupts delocalization.

sp² - hybridization at all carbons allows delocalization.
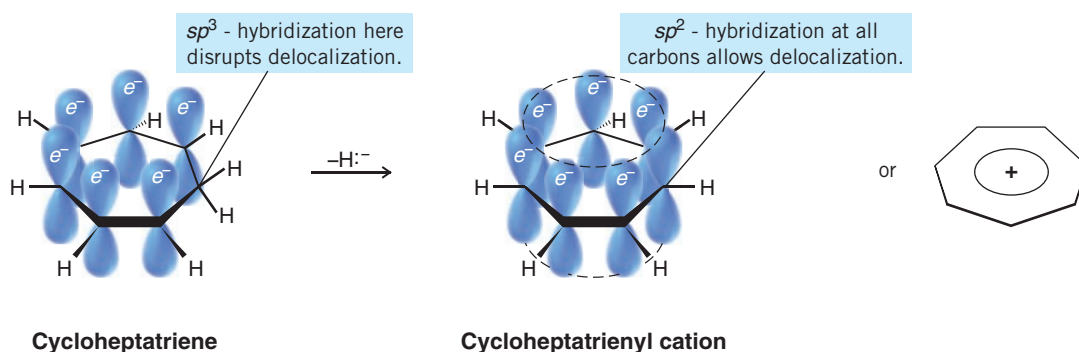
Cyclopentadiene   **Cyclopentadienyl anion**

FIGURE 14.10 Cyclopentadiene is not aromatic because it has only four π electrons and the sp^3-hybridized carbon prevents complete delocalization around the ring. Removal of a proton produces the cyclopentadienyl anion, which is aromatic because it has 6 π electrons and all of its carbon atoms have a p orbital.

On the other hand, if the —CH_2— carbon atom becomes sp^2 hybridized after it loses a proton (Fig. 14.10), the two electrons left behind can occupy the new p orbital that is produced. Moreover, this new p orbital can overlap with the p orbitals on either side of it and give rise to a ring with *six* delocalized π electrons. Because the electrons are delocalized, all of the hydrogen atoms are equivalent, and this agrees with what NMR spectroscopy tells us. A calculated electrostatic potential map for cyclopentadienyl anion (Fig. 14.11) also shows the symmetrical distribution of negative charge within the ring, and the overall symmetry of the ring structure.

Six, the number of π electrons in the cyclopentadienyl anion is, of course, a Hückel number ($4n + 2$, where $n = 1$).
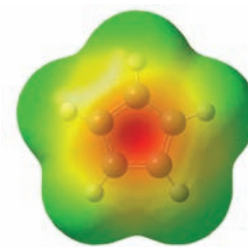
- The cyclopentadienyl anion is, therefore, an **aromatic anion**, and the unusual acidity of cyclopentadiene is a result of the unusual stability of its anion.

Cycloheptatriene (Fig. 14.12) (a compound with the common name tropylidene) has six π electrons. However, the six π electrons of cycloheptatriene cannot be fully delocalized because of the presence of the —CH_2— group, a group that does not have an available p orbital (Fig. 14.12).

FIGURE 14.11 An electrostatic potential map of the cyclopentadienyl anion. The ion is negatively charged overall, of course, but regions with greatest negative potential are shown in red, and regions with least negative potential are in blue. The concentration of negative potential in the center of the top face and bottom face (not shown) indicates that the extra electron of the ion is involved in the aromatic π-electron system.

sp³ - hybridization here disrupts delocalization.

sp² - hybridization at all carbons allows delocalization.

Cycloheptatriene   **Cycloheptatrienyl cation**

FIGURE 14.12 Cycloheptatriene is not aromatic, even though it has six π electrons, because it has an sp^3-hybridized carbon that prevents delocalization around the ring. Removal of a hydride (H:⁻) produces the cycloheptatrienyl cation, which is aromatic because all of its carbon atoms now have a p orbital, and it still has 6 π electrons.

When cycloheptatriene is treated with a reagent that can abstract a hydride ion, it is converted to the cycloheptatrienyl (or tropylium) cation. The loss of a hydride ion from cycloheptatriene occurs with unexpected ease, and the cycloheptatrienyl cation is found to be unusually stable. The NMR spectrum of the cycloheptatrienyl cation indicates that all seven hydrogen atoms are equivalent. If we look closely at Fig. 14.12, we see how we can account for these observations.

FIGURE 14.13 An electrostatic potential map of the tropylium cation. The ion is positive overall, of course, but a region of relatively greater negative electrostatic potential can clearly be seen around the top face (and bottom face, though not shown) of the ring where electrons are involved in the π system of the aromatic ring.

Cycloheptatriene   **Cycloheptatrienyl cation (tropylium cation)**

As a hydride ion is removed from the —CH_2— group of cycloheptatriene, a vacant p orbital is created, and the carbon atom becomes sp^2 hybridized. The cation that results has seven overlapping p orbitals containing *six* delocalized π electrons. The cycloheptatrienyl cation is, therefore, an aromatic cation, and all of its hydrogen atoms should be equivalent; again, this is exactly what we find experimentally.

The calculated electrostatic potential map for cycloheptatrienyl (tropylium) cation (Fig. 14.13) also shows the symmetry of this ion. Electrostatic potential from the π electrons involved in the aromatic system is indicated by the yellow-orange color that is evenly distributed around the top face (and bottom face, though not shown) of the carbon framework. The entire ion is positive, of course, and the region of greatest positive potential is indicated by blue around the periphery of the ion.

●●● SOLVED PROBLEM 14.3

Apply the polygon-and-circle method to explain why the cyclopentadienyl anion is aromatic.

STRATEGY AND ANSWER: We inscribe a pentagon inside a circle with one corner at the bottom and find that the energy levels of the molecular orbitals are such that three molecular orbitals are bonding and two are antibonding:

Antibonding MOs

Bonding MOs

Cyclopentadienyl anion has six π electrons, which is a Hückel number, and they fill all the bonding orbitals. There are no unpaired electrons and no electrons in antibonding orbitals. This is what we would expect of an aromatic ion.

●●●

PRACTICE PROBLEM 14.4 Apply the polygon-and-circle method to cyclopentadienyl cation and explain whether it would be aromatic or not.

Cyclopentadienyl cation

●●●

PRACTICE PROBLEM 14.5 Apply the polygon-and-circle method to the cycloheptatrienyl anion and cation and explain whether each would be aromatic or not.

(a)

Cycloheptatrienyl anion

(b)

Cycloheptatrienyl cation

●●●

PRACTICE PROBLEM 14.6 1,3,5-Cycloheptatriene is even less acidic than 1,3,5-heptatriene. Explain how this experimental observation might help to confirm your answer to part (b) of the previous problem.

When 1,3,5-cycloheptatriene reacts with one molar equivalent of bromine at 0 °C, it undergoes 1,6 addition. **(a)** Write the structure of this product. **(b)** On heating, this 1,6-addition product loses HBr readily to form a compound with the molecular formula C_7H_7Br, called *tropylium bromide*. Tropylium bromide is insoluble in nonpolar solvents but is soluble in water; it has an unexpectedly high melting point (mp 203 °C), and when treated with silver nitrate, an aqueous solution of tropylium bromide gives a precipitate of AgBr. What do these experimental results suggest about the bonding in tropylium bromide?

14.7E Aromatic, Antiaromatic, and Nonaromatic Compounds

- An aromatic compound has its π electrons *delocalized* over the entire ring and it is *stabilized* by the π-electron delocalization.

As we have seen, a good way to determine whether the π electrons of a cyclic system are delocalized is through the use of NMR spectroscopy. It provides direct physical evidence of whether or not the π electrons are delocalized.

But what do we mean by saying that a compound is stabilized by π-electron delocalization? We have an idea of what this means from our comparison of the heat of hydrogenation of benzene and that calculated for the hypothetical 1,3,5-cyclohexatriene. We saw that benzene—in which the π electrons are delocalized—is much more stable than 1,3,5-cyclohexatriene (a model in which the π electrons are not delocalized). We call the energy difference between them the resonance energy (delocalization energy) or stabilization energy.

In order to make similar comparisons for other aromatic compounds, we need to choose proper models. But what should these models be?

One way to evaluate whether a cyclic compound is stabilized by delocalization of π electrons through its ring is to compare it with an open-chain compound having the same number of π electrons. This approach is particularly useful because it furnishes us with models not only for annulenes but for aromatic cations and anions, as well. (Corrections need to be made, of course, when the cyclic system is strained.)

To use this approach we do the following:

1. We take as our model a linear chain of sp^2-hybridized atoms having the same number of π electrons as our cyclic compound.

2. Then we imagine removing a hydrogen atom from each end of the chain and joining the ends to form a ring.

   - If, based on sound calculations or experiments, the ring has *lower* π-electron energy, then the ring is aromatic.
   - If the ring and the chain have the *same* π-electron energy, then the ring is nonaromatic.
   - If the ring has *greater* π-electron energy than the open chain, then the ring is **antiaromatic**.

The actual calculations and experiments used in determining π-electron energies are beyond our scope, but we can study four examples that illustrate how this approach has been used.

Cyclobutadiene For cyclobutadiene we consider the change in π-electron energy for the following *hypothetical* transformation:

1,3-Butadiene	**Cyclobutadiene**	
4 π electrons	**4 π electrons (antiaromatic)**	

π-electron energy increases → + H_2
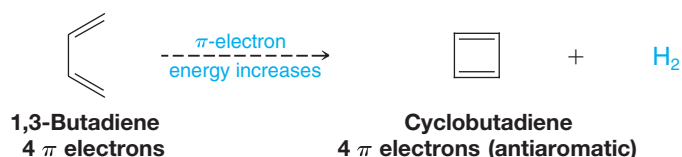
Calculations indicate and experiments appear to confirm that the π-electron energy of cyclobutadiene is higher than that of its open-chain counterpart. Thus cyclobutadiene is classified as antiaromatic.

**Benzene** Here our comparison is based on the following hypothetical transformation:

1,3,5-Hexatriene
6 π electrons

Benzene
6 π electrons (aromatic)
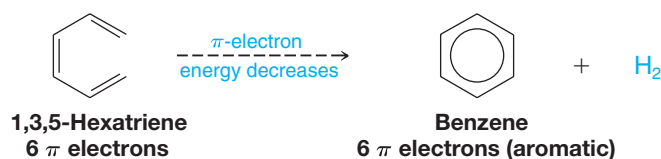
Calculations indicate and experiments confirm that benzene has a much lower π-electron energy than 1,3,5-hexatriene. Benzene is classified as being aromatic on the basis of this comparison as well.

Cyclopentadienyl Anion Here we use a linear anion for our hypothetical transformation:

6 π electrons

Cyclopentadienyl anion
6 π electrons (aromatic)
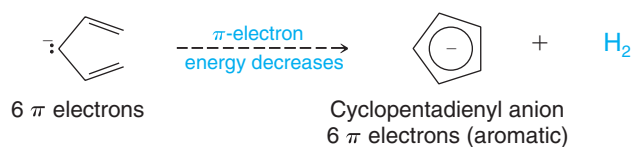
Both calculations and experiments confirm that the cyclic anion has a lower π-electron energy than its open-chain counterpart. Therefore the cyclopentadienyl anion is classified as aromatic.

Cyclooctatetraene For cyclooctatetraene we consider the following hypothetical transformation:

8 π electrons

**Hypothetical planar
cyclooctatetraene
8 π electrons (antiaromatic)**
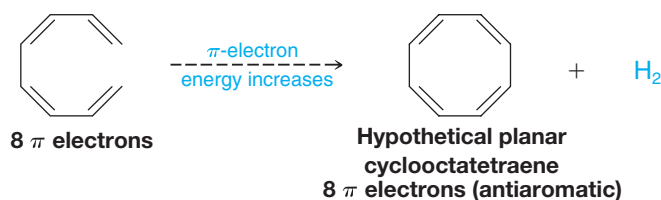
Here calculations and experiments indicate that a planar cyclooctatetraene would have higher π-electron energy than the open-chain octatetraene. Therefore, a planar form of cyclooctatetraene would, if it existed, be *antiaromatic*. As we saw earlier, cyclooctatetraene is not planar and behaves like a simple cyclic polyene.

●●● **SOLVED PROBLEM 14.4**

Calculations indicate that the π-electron energy decreases for the hypothetical transformation from the allyl cation to the cyclopropenyl cation below. What does this indicate about the possible aromaticity of the cyclopropenyl cation
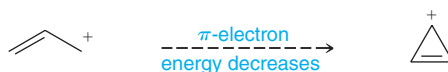
STRATEGY AND ANSWER: Because the π-electron energy of the cyclic cation is less than that of the allyl cation, we can conclude that the cyclopropenyl cation would be aromatic. (See Practice Problem 14.9 for more information on this cation.)

●●●

PRACTICE PROBLEM 14.8 The cyclopentadienyl cation is apparently *antiaromatic*. Explain what this means in terms of the π-electron energies of a cyclic and an open-chain compound.

In 1967 R. Breslow (of Columbia University) and co-workers showed that adding $SbCl_5$ to a solution of 3-chlorocyclopropene in CH_2Cl_2 caused the precipitation of a white solid with the composition $C_3H_3^+SbCl_6^-$. NMR spectroscopy of a solution of this salt showed that all of its hydrogen atoms were equivalent. **(a)** What new aromatic ion had these researchers prepared? **(b)** How many ^{13}C NMR signals would you predict for this ion?

14.8 OTHER AROMATIC COMPOUNDS

14.8A Benzenoid Aromatic Compounds

In addition to those that we have seen so far, there are many other examples of aromatic compounds. Representatives of one broad class of **benzenoid aromatic compounds**, called **polycyclic aromatic hydrocarbons (PAH)**, are illustrated in Fig. 14.14.
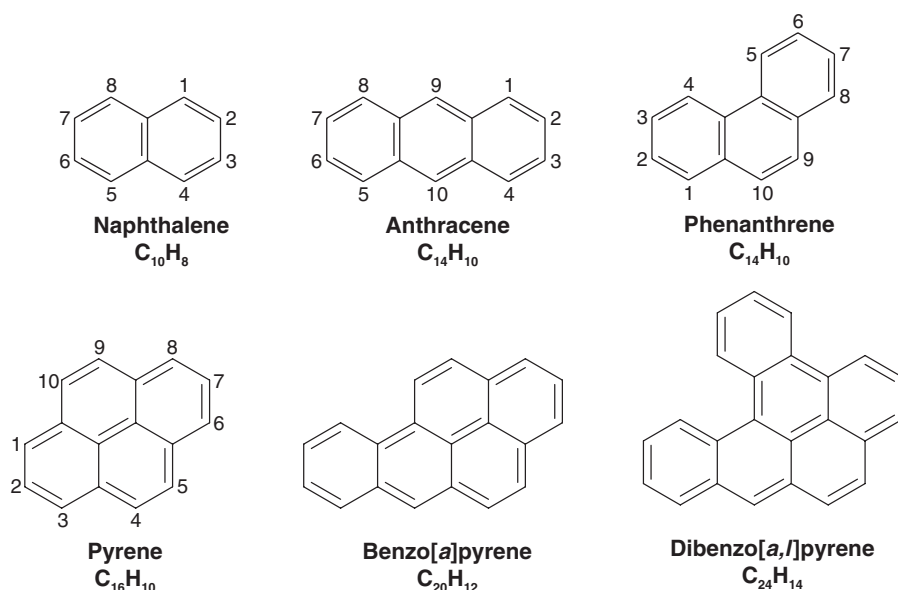
FIGURE 14.14 Benzenoid aromatic hydrocarbons. Some polycyclic aromatic hydrocarbons (PAHs), such as dibenzo[a,l]pyrene, are carcinogenic. (See "Important, but hidden, epoxides" at the end of Chapter 11.)

- Benzenoid polycyclic **aromatic** hydrocarbons consist of molecules having two or more benzene rings *fused* together.

A close look at one example, naphthalene, will illustrate what we mean by this.

According to resonance theory, a molecule of naphthalene can be considered to be a hybrid of three Kekulé structures. One of these Kekulé structures, the most important one, is shown in Fig. 14.15. There are two carbon atoms in naphthalene (**C4a** and **C8a**) that are common to both rings. These two atoms are said to be at the points of *ring fusion*. They direct all of their bonds toward other carbon atoms and do not bear hydrogen atoms.
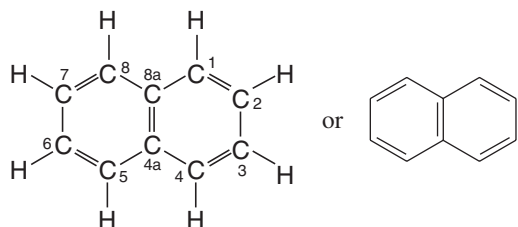
FIGURE 14.15 One Kekulé structure for naphthalene.

●●● **SOLVED PROBLEM 14.5**

How many ^{13}C NMR signals would you expect for acenaphthylene?

Acenaphthylene

STRATEGY AND ANSWER: Acenaphthylene has a plane of symmetry which makes the five carbon atoms on the left (a–e, at right) equivalent to those on the right. Carbon atoms f and g are unique. Consequently, acenaphthylene should give seven ^{13}C NMR signals.
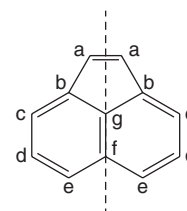
Acenaphthylene

·●●●

PRACTICE PROBLEM 14.10   How many ^{13}C NMR signals would you predict for **(a)** naphthalene, **(b)** anthracene, **(c)** phenanthrene, and **(d)** pyrene?
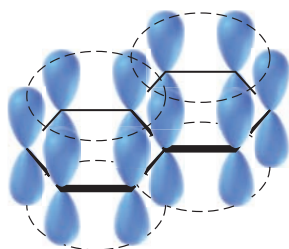
FIGURE 14.16 The stylized *p* orbitals of naphthalene.

Molecular orbital calculations for naphthalene begin with the model shown in Fig. 14.16. The *p* orbitals overlap around the periphery of both rings and across the points of ring fusion.

When molecular orbital calculations are carried out for naphthalene using the model shown in Fig. 14.16, the results of the calculations correlate well with our experimental knowledge of naphthalene. The calculations indicate that delocalization of the 10 π electrons over the two rings produces a structure with considerably lower energy than that calculated for any individual Kekulé structure. Naphthalene, consequently, has a substantial resonance energy. Based on what we know about benzene, moreover, naphthalene's tendency to react by substitution rather than addition and to show other properties associated with aromatic compounds is understandable.

Anthracene and phenanthrene (Fig. 14.14) are isomers. In anthracene the three rings are fused in a linear way, and in phenanthrene they are fused so as to produce an angular molecule. Both of these molecules also show large resonance energies and chemical properties typical of aromatic compounds.

Pyrene (Fig. 14.17) is also aromatic. Pyrene itself has been known for a long time; a pyrene derivative, however, has been the object of research that shows another interesting application of Hückel's rule.

FIGURE 14.17 One Kekulé structure for pyrene. The internal double bond is enclosed in a dotted circle for emphasis.

To understand this particular research, we need to pay special attention to the Kekulé structure for pyrene (Fig. 14.17). The total number of π electrons in pyrene is 16 (8 double bonds = 16 π electrons). Sixteen is a non-Hückel number, but **Hückel's rule is intended to be applied only to monocyclic compounds** and pyrene is clearly tetracyclic. If we disregard the internal double bond of pyrene, however, and look only at the periphery, we see that the periphery is a planar ring with 14 π electrons. The periphery is, in fact, very much like that of [14]annulene. Fourteen *is* a Hückel number ($4n + 2$, where $n = 3$), and one might then predict that the periphery of pyrene would be aromatic by itself, in the absence of the internal double bond.

[14]Annulene   ***trans*-15,16-Dimethyldihydropyrene**

This prediction was confirmed when V. Boekelheide (University of Oregon) synthesized *trans*-15,16-dimethyldihydropyrene and showed that it is aromatic.

In addition to a signal downfield, the ^{1}H NMR spectrum of *trans*-15,16-dimethyldihydropyrene has a signal far upfield at δ −4.2. Account for the presence of this upfield signal.

14.8B Nonbenzenoid Aromatic Compounds

Naphthalene, phenanthrene, and anthracene are examples of *benzenoid* aromatic compounds. On the other hand, the cyclopentadienyl anion, the cycloheptatrienyl cation, *trans*-15,16-dimethyldihydropyrene, and the aromatic annulenes (except for [6]annulene) are classified as **nonbenzenoid aromatic compounds**.

Another example of a *nonbenzenoid* aromatic hydrocarbon is the compound azulene. Azulene has a resonance energy of 205 kJ mol^{-1}. There is substantial separation of charge between the rings in azulene, as is indicated by the electrostatic potential map for azulene shown in Fig. 14.18. Factors related to aromaticity account for this property of azulene (see Practice Problem 14.12).
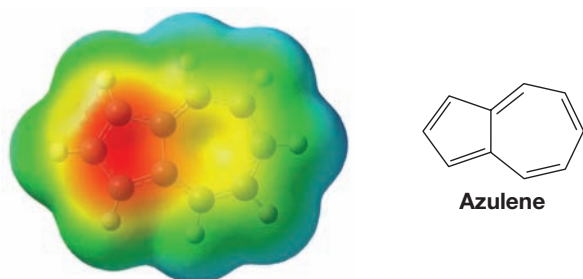
Azulene

FIGURE 14.18 A calculated electrostatic potential map for azulene. (Red areas are more negative and blue areas are less negative.)

Azulene has an appreciable dipole moment. Write resonance structures for azulene that explain this dipole moment and that help explain its aromaticity.

14.8C Fullerenes

In 1990 W. Krätschmer (Max Planck Institute, Heidelberg), D. Huffman (University of Arizona), and their co-workers described the first practical synthesis of C_{60}, a molecule shaped like a soccer ball and called buckminsterfullerene. Formed by the resistive heating of graphite in an inert atmosphere, C_{60} is a member of an exciting new group of aromatic compounds called **fullerenes**. Fullerenes are cagelike molecules with the geometry of a truncated icosahedron or geodesic dome, named after the architect Buckminster Fuller, renowned for his development of structures with geodesic domes. The structure of C_{60} and its existence had been established five years earlier, by H. W. Kroto (University of Sussex), R. E. Smalley and R. F. Curl (Rice University), and their co-workers. Kroto, Curl, and Smalley had found both C_{60} and C_{70} (Fig. 14.19) as highly stable components

The Nobel Prize in Chemistry was awarded in 1996 to Professors Curl, Kroto, and Smalley for their discovery of fullerenes.

C_{60} C_{70}
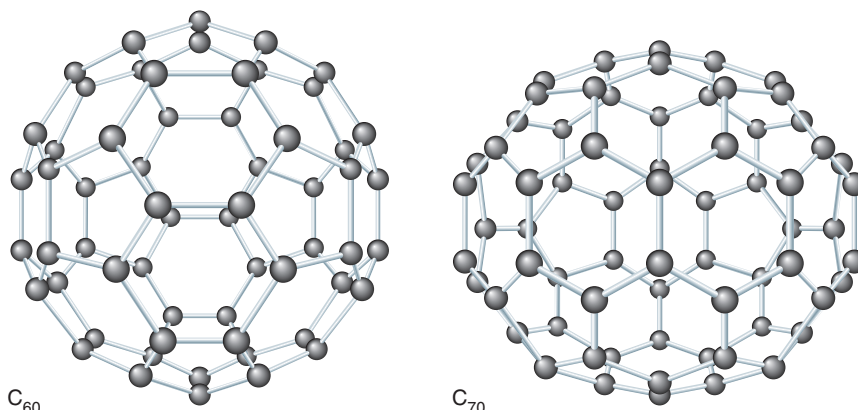
FIGURE 14.19 The structures of C_{60} and C_{70}. (Reprinted with permission from Diederich, F., and Whetten, R. L. *Accounts of Chemical Research, Vol. 25,* pp. 119–126. Copyright 1992 American Chemical Society.)

of a mixture of carbon clusters formed by laser-vaporizing graphite. Since 1990 chemists have synthesized many other higher and lower fullerenes and have begun exploring their interesting chemistry.

Like a geodesic dome, a fullerene is composed of a network of pentagons and hexagons. To close into a spheroid, a fullerene must have exactly 12 five-membered faces, but the number of six-membered faces can vary widely. The structure of C_{60} has 20 hexagonal faces; C_{70} has 25. Each carbon of a fullerene is sp^2 hybridized and forms σ bonds to three other carbon atoms. The remaining electron at each carbon is delocalized into a system of molecular orbitals that gives the whole molecule aromatic character.

The chemistry of fullerenes is proving to be even more fascinating than their synthesis. Fullerenes have a high electron affinity and readily accept electrons from alkali metals to produce a new metallic phase—a "buckide" salt. One such salt, K_3C_{60}, is a stable metallic crystal consisting of a face-centered-cubic structure of "buckyballs" with a potassium ion in between; it becomes a superconductor when cooled below 18 K. Fullerenes have even been synthesized that have metal atoms in the interior of the carbon atom cage.

THE CHEMISTRY OF... Nanotubes

Nanotubes are a relatively new class of carbon-based materials related to buckminsterfullerenes. A **nanotube** is a structure that looks as though it were formed by rolling a sheet of graphite-like carbon (a flat network of fused benzene rings resembling chicken wire) into the shape of a tube and capping each end with half of a buckyball. Nanotubes are very tough—about 100 times as strong as steel. Besides their potential as strengtheners for new composite materials, some nanotubes have been shown to act as electrical conductors or semiconductors depending on their precise form. They are also being used as probe tips for analysis of DNA and proteins by atomic force microscopy (AFM). Many other applications have been envisioned for them as well, including use as molecular-size test tubes or capsules for drug delivery.
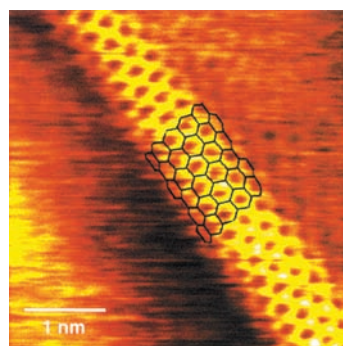
Image courtesy of C. M. Lieber, Harvard University

A network of benzene rings, highlighted in black on this scanning tunneling microscopy (STM) image, comprise the wall of a nanotube.

14.9 HETEROCYCLIC AROMATIC COMPOUNDS

Almost all of the cyclic molecules that we have discussed so far have had rings composed solely of carbon atoms. However, in many cyclic compounds an element other than carbon is present in the ring.

- Cyclic compounds that include an element other than carbon are called **heterocyclic compounds**.

Heterocyclic molecules are quite commonly encountered in nature. For this reason, and because some of these molecules are aromatic, we shall now describe a few examples of **heterocyclic aromatic compounds**.

Heterocyclic compounds containing nitrogen, oxygen, or sulfur are by far the most common. Four important examples are given here in their Kekulé forms. *These four compounds are all aromatic:*

- Pyridine is electronically related to benzene.
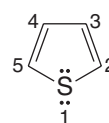- Pyrrole, furan, and thiophene are related to the cyclopentadienyl anion.
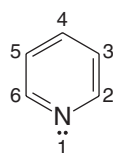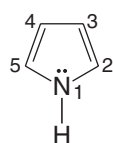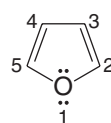
**Pyridine**   **Pyrrole**   **Furan**   **Thiophene**

The nitrogen atoms in molecules of both pyridine and pyrrole are sp^2 hybridized. In pyridine (Fig. 14.20) the sp^2-hybridized nitrogen donates one bonding electron to the π system. This electron, together with one from each of the five carbon atoms, gives pyridine a sextet of electrons like benzene. The two unshared electrons of the nitrogen of pyridine are in an sp^2 orbital that lies in the same plane as the atoms of the ring. This sp^2 orbital does not overlap with the p orbitals of the ring (it is, therefore, said to be *orthogonal* to the p orbitals). The unshared pair on nitrogen is not a part of the π system, and these electrons confer on pyridine the properties of a weak base.

In pyrrole (Fig. 14.21) the electrons are arranged differently. Because only four π electrons are contributed by the carbon atoms of the pyrrole ring, the sp^2-hybridized nitrogen must contribute two electrons to give an aromatic sextet. Because these electrons are a part of the aromatic sextet, they are not available for donation to a proton. Thus, in aqueous solution, pyrrole is not appreciably basic.
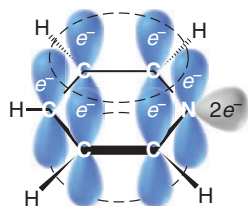
FIGURE 14.20 Pyridine is aromatic and weakly basic. Its nitrogen atom has an unshared electron pair in an sp^2 orbital (shown in gray) that is not part of the aromatic system.
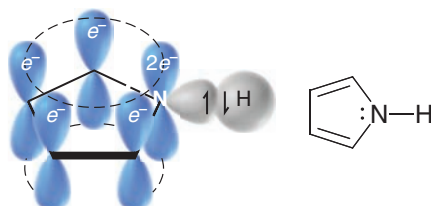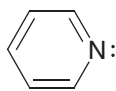
FIGURE 14.21 Pyrrole is aromatic but not basic. It does not have any unshared electron pairs. The electron pair on nitrogen is part of the aromatic system.

●●● **SOLVED PROBLEM 14.6**

Imidazole (at right) has two nitrogens. N3 is relatively basic (like the nitrogen of pyridine). N1 is relatively nonbasic (like the nitrogen of pyrrole). Explain the different basicities of these two nitrogens.
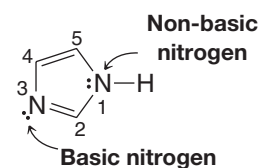
STRATEGY AND ANSWER: When imidazole accepts a proton at N3 the electron pair that accepts the proton is not a part of the π system of six electrons that makes imidazole aromatic. Consequently, the conjugate base that is formed is still aromatic (it is an aromatic cation) and retains its resonance energy of stabilization.
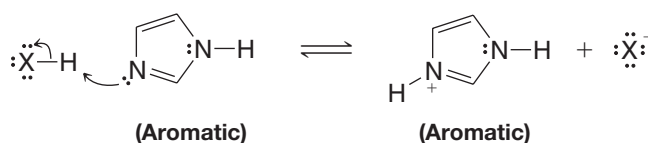
On the other hand, if imidazole were to accept a proton at N1 the resulting ion (which is not formed) would **not** be aromatic and would have much greater potential energy (its resonance stabilization would be lost). Hence, N1 is not appreciably basic.
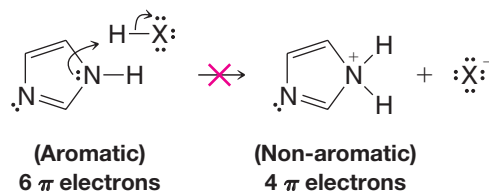
Furan and thiophene are structurally quite similar to pyrrole. The oxygen atom in furan and the sulfur atom in thiophene are sp^2 hybridized. In both compounds the p orbital of the heteroatom donates two electrons to the π system. The oxygen and sulfur atoms of furan and thiophene carry an unshared pair of electrons in an sp^2 orbital (Fig. 14.22) that is orthogonal to the π system.

Furan　　　　　　**Thiophene**

14.10 AROMATIC COMPOUNDS IN BIOCHEMISTRY

Compounds with aromatic rings occupy numerous and important positions in reactions that occur in living systems. It would be impossible to describe them all in this chapter. We shall, however, point out a few examples now and we shall see others later.

Two amino acids necessary for protein synthesis contain the benzene ring:


Phenylalanine　　　　　　**Tyrosine**
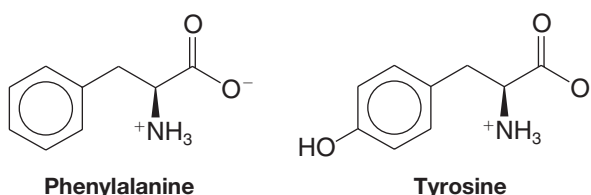
A third aromatic amino acid, tryptophan, contains a benzene ring fused to a pyrrole ring. (This aromatic ring system is called an indole system; see Section 20.1B.)
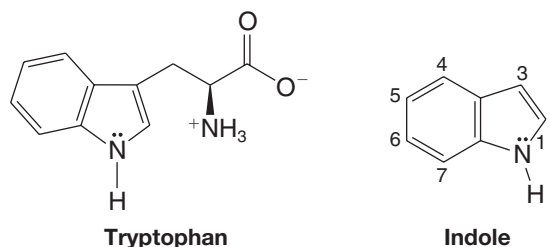
Tryptophan　　　　　　**Indole**

It appears that humans, because of the course of evolution, do not have the biochemical ability to synthesize the benzene ring. As a result, phenylalanine and tryptophan derivatives are essential in the human diet. Because tyrosine can be synthesized from phenylalanine in a reaction catalyzed by an enzyme known as *phenylalanine hydroxylase*, it is not essential in the diet as long as phenylalanine is present.

Heterocyclic aromatic compounds are also present in many biochemical systems. Derivatives of purine and pyrimidine are essential parts of DNA and RNA:

Purine　　　　**Pyrimidine**
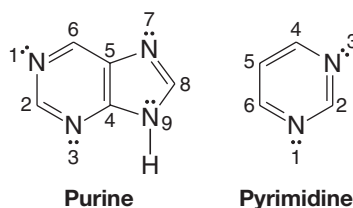
DNA is the molecule responsible for the storage of genetic information, and RNA is prominently involved in the synthesis of enzymes and other proteins (Chapter 25).

Dairy products, beans, fish, meat, and poultry are dietary sources of the essential amino acids.

• • •

PRACTICE PROBLEM 14.13 **(a)** The —SH group is sometimes called the *mercapto group*. 6-Mercaptopurine is used in the treatment of acute leukemia. Write its structure. **(b)** Allopurinol, a compound used to treat gout, is 6-hydroxypurine. Write its structure.

Nicotinamide adenine dinucleotide, one of the most important coenzymes (Section 24.9) in biological oxidations and reductions, includes both a pyridine derivative (nicotinamide) and a purine derivative (adenine) in its structure. Its formula is shown in Fig. 14.23 as NAD^+, the oxidized form that contains the pyridinium aromatic ring. The reduced form of the coenzyme is NADH, in which the pyridine ring is no longer aromatic due to presence of an additional hydrogen and two electrons in the ring.
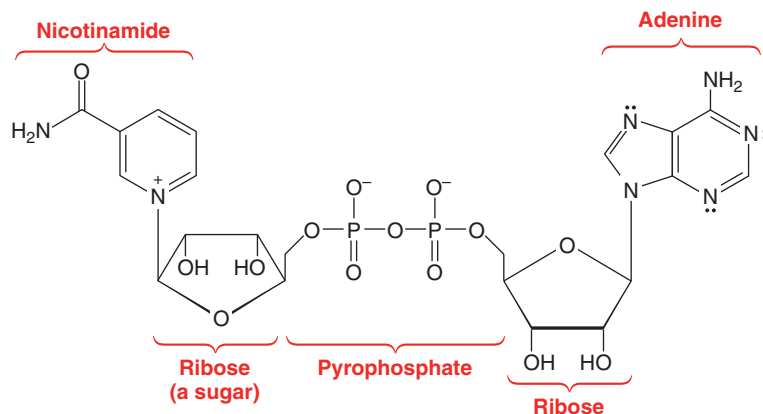
FIGURE 14.23 Nicotinamide adenine dinucleotide (NAD^+).

A key role of NAD^+ in metabolism is to serve as a coenzyme for glyceraldehyde-3-phosphate dehydrogenase (GAPDH) in glycolysis, the pathway by which glucose is broken down for energy production. In the reaction catalyzed by GAPDH (Fig. 14.24), the aldehyde group of glyceraldehyde-3-phosphate (GAP) is oxidized to a carboxyl group (incorporated as a phosphoric anhydride) in 1,3-bisphosphoglycerate (1,3-BPG). Concurrently, the aromatic pyridinium ring of NAD^+ is reduced to its higher energy form, NADH. One of the ways the chemical energy stored in the nonaromatic ring of NADH is used is in the mitochondria for the production of ATP, where cytochrome electron transport and oxidative phosphorylation take place. There, release of chemical energy from NADH by oxidation to the more stable aromatic form NAD^+ (and a proton) is coupled with the pumping of protons across the inner mitochondrial membrane. An electrochemical gradient is created across the mitochondrial membrane, which drives the synthesis of ATP by the enzyme ATP synthase.
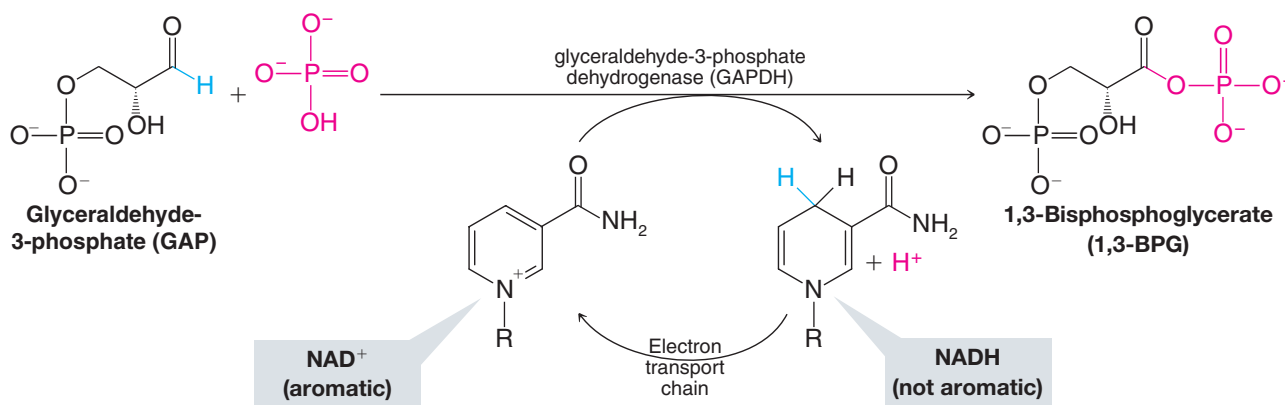
FIGURE 14.24 NAD^+, as the coenzyme in glyceraldehyde-3-phosphate dehydrogenase (GAPDH), is used to oxidize glyceraldehyde-3-phosphate (GAP) to 1,3-bisphosphoglycerate during the degradation of glucose in glycolysis. One of the ways that NADH can be reoxidized to NAD^+ is by the electron transport chain in mitochondria, where, under aerobic conditions, rearomatization of NADH helps to drive ATP synthesis.

The chemical energy stored in NADH is used to bring about many other essential biochemical reactions as well. NADH is part of an enzyme called lactate dehydrogenase that reduces the ketone group of pyruvic acid to the alcohol group of lactic acid. Here, the nonaromatic ring of NADH is converted to the aromatic ring of NAD^+. This process

is important in muscles operating under oxygen-depleted conditions (anaerobic metabolism), where reduction of pyruvic acid to lactic acid by NADH serves to regenerate NAD$^+$ that is needed to continue glycolytic synthesis of ATP:

Pyruvic acid

lactate dehydrogenase
(regenerates NAD$^+$ in muscle
under anaerobic conditions)

Lactic acid
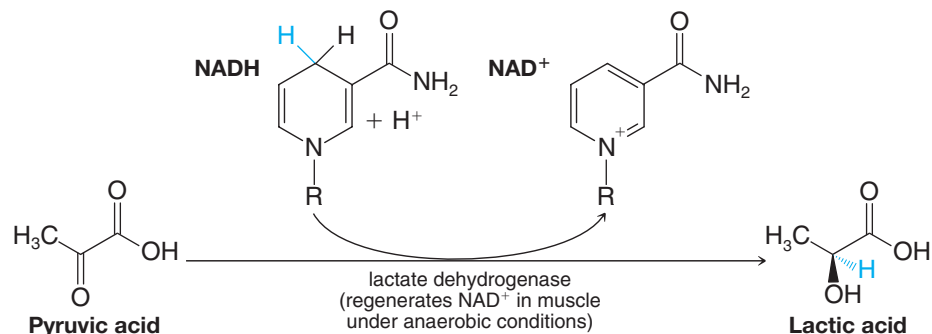
Yeasts growing under anaerobic conditions (fermentation) also have a pathway for regenerating NAD$^+$ from NADH. Under oxygen-deprived conditions, yeasts convert pyruvic acid to acetaldehyde by decarboxylation (CO_2 is released, (see "The Chemistry of… Thiamine" in *WileyPLUS*); then NADH in alcohol dehydrogenase reduces acetaldehyde to ethanol. As in oxygen-starved muscles, this pathway occurs for the purpose of regenerating NAD$^+$ needed to continue glycolytic ATP synthesis:

Pyruvic acid

CO_2

pyruvate
decarboxylase
(with thiamine as a
coenzyme)

Acetaldehyde

NADH   NAD$^+$

alcohol dehydrogenase
(regenerates NAD$^+$ in
yeast under anaerobic
conditions)

Ethanol
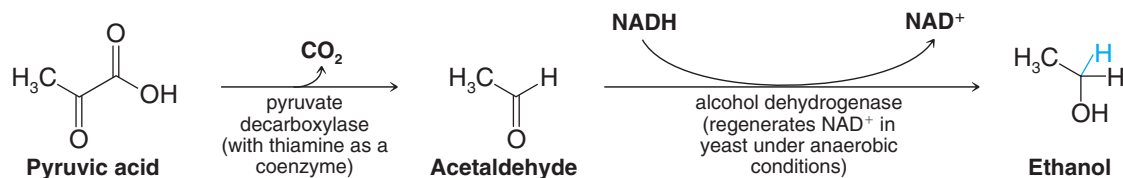
Although many aromatic compounds are essential to life, others are hazardous. Many are quite toxic, and several benzenoid compounds, including benzene itself, are **carcinogenic.** Two other examples are benzo[*a*]pyrene and 7-methylbenz[*a*]anthracene:
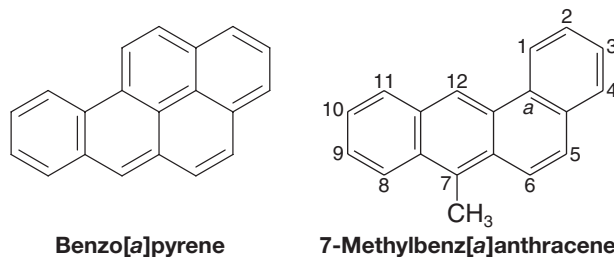
Benzo[*a*]pyrene   **7-Methylbenz[*a*]anthracene**

The hydrocarbon benzo[*a*]pyrene has been found in cigarette smoke and in the exhaust from automobiles. It is also formed in the incomplete combustion of any fossil fuel. It is found on charcoal-broiled steaks and exudes from asphalt streets on a hot summer day. Benzo[*a*]pyrene is so carcinogenic that one can induce skin cancers in mice with almost total certainty simply by shaving an area of the body of the mouse and applying a coating of benzo[*a*]pyrene.

14.11 SPECTROSCOPY OF AROMATIC COMPOUNDS

14.11A ^{1}H NMR Spectra

- The ring hydrogens of benzene derivatives absorb downfield in the region between δ 6.0 and δ 9.5.

In Section 14.7C we found that absorption takes place far downfield because a ring current generated in the benzene ring creates a magnetic field, called "the induced field," which reinforces the applied magnetic field at the position of the protons of the ring. This reinforcement causes the protons of benzene to be highly deshielded.

We also learned in Section 14.7C that internal hydrogens of large-ring **aromatic** compounds such as [18]annulene, because of their position, are highly shielded by this induced field. They therefore absorb at unusually low frequency, often at negative delta values.

14.11B ^{13}C NMR Spectra

- The carbon atoms of benzene rings generally absorb in the δ 100–170 region of ^{13}C NMR spectra.

Figure 14.25 gives the broadband proton-decoupled ^{13}C NMR spectrum of 4-*N,N*-diethylaminobenzaldehyde and permits an exercise in making ^{13}C assignments of a compound with both aromatic and aliphatic carbon atoms.
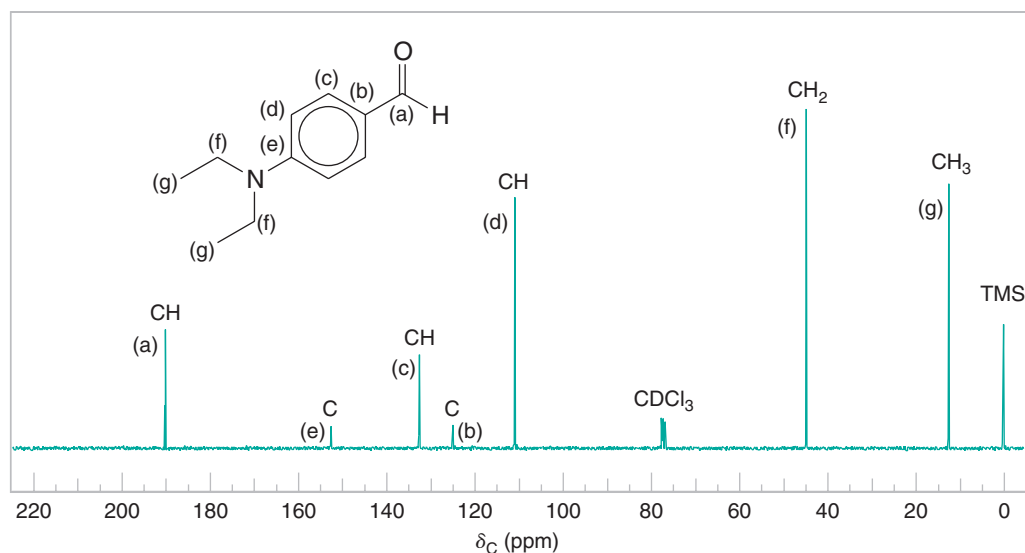
FIGURE 14.25 The broadband proton-decoupled ^{13}C NMR spectrum of 4-*N,N*-diethylaminobenz-aldehyde. DEPT information and carbon assignments are shown by each peak.

The DEPT spectra (not given to save space) show that the signal at δ 45 arises from a CH$_2$ group and the one at δ 13 arises from a CH$_3$ group. This allows us to assign these two signals immediately to the two carbons of the equivalent ethyl groups.

The signals at δ 126 and δ 153 appear in the DEPT spectra as carbon atoms that do not bear hydrogen atoms and are assigned to carbons b and e (see Fig. 14.25). The greater electronegativity of nitrogen (when compared to carbon) causes the signal from e to be further downfield (at δ 153). The signal at δ 190 appears as a CH group in the DEPT spectra and arises from the carbon of the aldehyde group. Its chemical shift is the most downfield of all the peaks because of the great electronegativity of its oxygen and because the second resonance structure below contributes to the hybrid. Both factors cause the electron density at this carbon to be very low, and, therefore, this carbon is strongly deshielded.
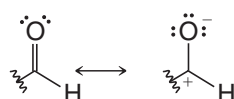
Resonance contributors for an aldehyde group

This leaves the signals at δ 112 and δ 133 and the two sets of carbon atoms of the benzene ring labeled c and d to be accounted for. Both signals are indicated as CH groups in the DEPT spectra. But which signal belongs to which set of carbon atoms? Here we find another interesting application of resonance theory.

If we write resonance structures **A–D** involving the unshared electron pair of the amino group, we see that contributions made by **B** and **D** increase the electron density at the set of carbon atoms labeled d:
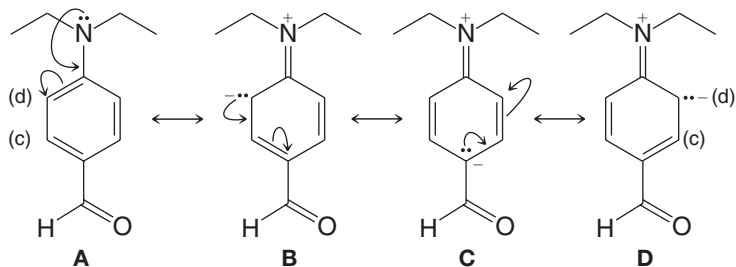
On the other hand, writing structures **E–H** involving the aldehyde group shows us that contributions made by **F** and **H** decrease the electron density at the set of carbon atoms labeled c:
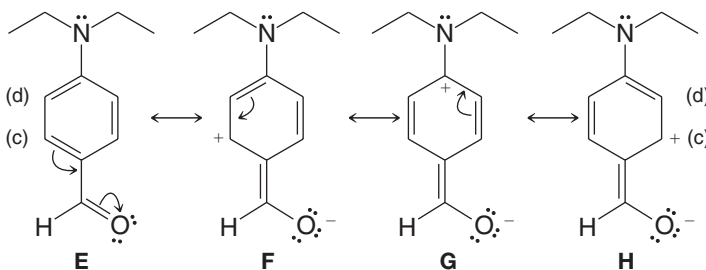
(Other resonance structures are possible but are not pertinent to the argument here.)

Increasing the electron density at a carbon should increase its shielding and should shift its signal upfield. Therefore, we assign the signal at δ 112 to the set of carbon atoms labeled d. Conversely, decreasing the electron density at a carbon should shift its signal downfield, so we assign the signal at δ 133 to the set labeled c.

Carbon-13 spectroscopy can be especially useful in recognizing a compound with a high degree of symmetry. The following Solved Problem illustrates one such application.

••• SOLVED PROBLEM 14.7

The broadband proton-decoupled ^{13}C spectrum given in Fig. 14.26 is of a tribromobenzene ($C_6H_3Br_3$). Which tribromobenzene is it?
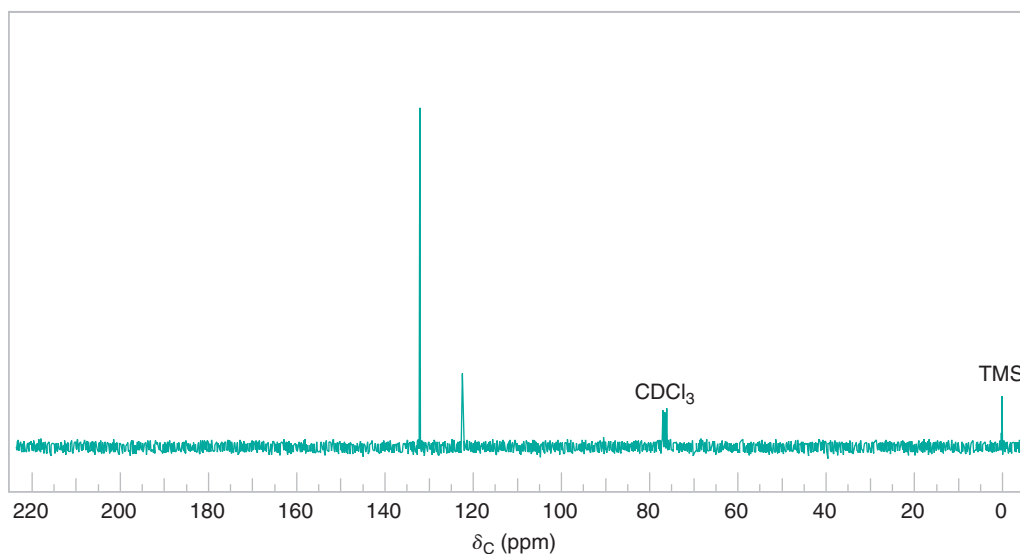
FIGURE 14.26 The broadband proton-decoupled ^{13}C NMR spectrum of a tribromobenzene.

ANSWER: There are three possible tribromobenzenes:

1,2,3-Tribromobenzene   1,2,4-Tribromobenzene   1,3,5-Tribromobenzene
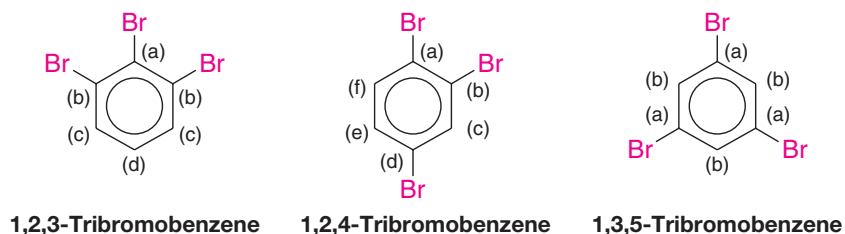
Our spectrum (Fig. 14.26) consists of only two signals, indicating that only two different types of carbon atoms are present in the compound. Only 1,3,5-tribromobenzene has a degree of symmetry such that it would give only two signals, and, therefore, it is the correct answer. 1,2,3-Tribromobenzene would give four ^{13}C signals and 1,2,4-tribromobenzene would give six.

Explain how ^{13}C NMR spectroscopy could be used to distinguish the *ortho-*, *meta-*, and *para-*dibromobenzene isomers one from another.

PRACTICE PROBLEM 14.14

14.11C Infrared Spectra of Substituted Benzenes

Benzene derivatives give characteristic C—H stretching peaks near 3030 cm^{-1} (Table 2.7). Stretching motions of the benzene ring can give as many as four bands in the 1450–1600-cm^{-1} region, with two peaks near 1500 and 1600 cm^{-1} being stronger.

Absorption peaks in the 680–860-cm^{-1} region from out-of-plane C—H bending can often (but not always) be used to characterize the substitution patterns of benzene compounds (Table 14.1). **Monosubstituted benzenes** give two very strong peaks, between 690 and 710 cm^{-1} and between 730 and 770 cm^{-1}.

TABLE 14.1 INFRARED ABSORPTIONS IN THE 680–860-CM^{-1} REGION[a]

[a]s, strong; vs, very strong.

Ortho-disubstituted benzenes show a strong absorption peak between 735 and 770 cm^{-1} that arises from bending motions of the C—H bonds. **Meta-disubstituted benzenes** show two peaks: one strong peak between 680 and 725 cm^{-1} and one very strong peak between 750 and 810 cm^{-1}. **Para-disubstituted benzenes** give a single very strong absorption between 800 and 860 cm^{-1}.

●●●

PRACTICE PROBLEM 14.15 Four benzenoid compounds, all with the formula C_7H_7Br, gave the following IR peaks in the 680–860-cm^{-1} region:

A, 740 cm^{-1} (strong)   **C**, 680 cm^{-1} (strong) and 760 cm^{-1} (very strong)

B, 800 cm^{-1} (very strong)   **D**, 693 cm^{-1} (very strong) and 765 cm^{-1} (very strong)

Propose structures for **A**, **B**, **C**, and **D**.

14.11D Ultraviolet–Visible Spectra of Aromatic Compounds

The conjugated π electrons of a benzene ring give characteristic ultraviolet absorptions that indicate the presence of a benzene ring in an unknown compound. One absorption band of moderate intensity occurs near 205 nm and another, less intense band appears in the 250–275-nm range. Conjugation outside the benzene ring leads to absorptions at other wavelengths.

THE CHEMISTRY OF... Sunscreens (Catching the Sun's Rays and What Happens to Them)

The use of sunscreens in recent years has increased due to heightened concern over the risk of skin cancer and other conditions caused by exposure to UV radiation. In DNA, for example, UV radiation can cause adjacent thymine bases to form mutagenic dimers. Sunscreens afford protection from UV radiation because they contain aromatic molecules that absorb energy in the UV region of the electromagnetic spectrum. Absorption of UV radiation by these molecules promotes π and nonbonding electrons to higher energy levels (Section 13.9C), after which the energy is dissipated by relaxation through molecular vibration. In essence, the UV radiation is converted to heat (IR radiation).
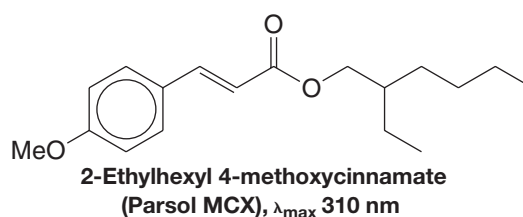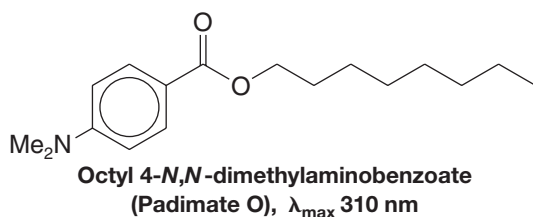
Sunscreens are classified according to the portion of the UV spectrum where their maximum absorption occurs. Three regions of the UV spec-
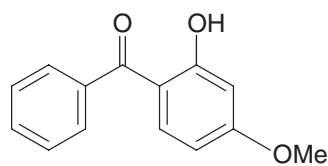

Photo by Lisa Gee

A UV-A and UV-B sunscreen product whose active ingredients are octyl 4-methoxycinnamate and 2-hydroxy-4-methoxy-benzophenone (oxybenzone).
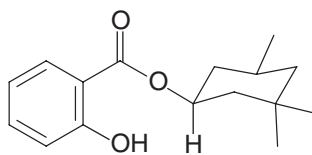
trum are typically discussed. The region from 320 to 400 nm is called UV-A, the region from 280 to 320 nm is called UV-B, and the region from 100 to 280 nm is called UV-C. The UV-C region is potentially the most dangerous because it encompasses the shortest UV wavelengths and is therefore of the highest energy. However, ozone and other components in Earth's atmosphere absorb UV-C wavelengths, and thus we are protected from radiation in this part of the spectrum so long as Earth's atmosphere is not compromised further by ozone-depleting pollutants. Most of the UV-A and some of the UV-B radiation passes through the atmosphere to reach us, and it is against these regions of the spectrum that sunscreens are formulated. Tanning and sunburn are caused by UV-B radiation. Risk of skin cancer is primarily associated with UV-B radiation, although some UV-A wavelengths may be important as well.

The specific range of protection provided by a sunscreen depends on the structure of its UV-absorbing groups. Most sunscreens have structures derived from the following parent compounds: p-aminobenzoic acid (PABA), cinnamic acid (3-phenylpropenoic acid), benzophenone (diphenyl ketone), and salicylic acid (o-hydroxybenzoic acid). The structures and λ_{max} for a few of the most common sunscreen agents are given below. The common theme among them is an aromatic core in conjugation with other functional groups.
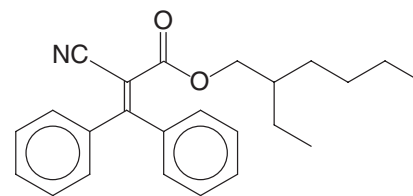

Octyl 4-N,N-dimethylaminobenzoate (Padimate O), λ_{max} 310 nm

2-Ethylhexyl 4-methoxycinnamate (Parsol MCX), λ_{max} 310 nm

**2-Hydroxy-4-methoxybenzophenone
(Oxybenzone),** λ_{max} **288 and 325 nm**

**Homomenthyl salicylate
(Homosalate),** λ_{max} **309 nm**

**2-Ethylhexyl 2-cyano-3,3-diphenylacrylate
(Octocrylene),** λ_{max} **310 nm**

14.11E Mass Spectra of Aromatic Compounds

The major ion in the mass spectrum of an alkyl-substituted benzene is often m/z 91 ($C_6H_5CH_2^+$), resulting from cleavage between the first and second carbons of the alkyl chain attached to the ring. The ion presumably originates as a benzylic cation that rearranges to a tropylium cation ($C_7H_7^+$, Section 14.7D). Another ion frequently seen in mass spectra of monoalkylbenzene compounds is m/z 77, corresponding to $C_6H_5^+$.

[WHY Do These Topics Matter?

MAKING EVEN LARGER AROMATIC MOLECULES

Although Hückel's rule can readily be used to suggest whether or not a molecule might be aromatic, we know that it is not always accurate because it cannot predict molecular shape. For example, as we discussed previously, [10]annulene is not aromatic, because two hydrogen atoms would have to occupy the same space for the system to be flat; instead, the molecule twists out of conjugation to allow space for the hydrogens. While larger molecules, such as [18]annulene, can overcome that problem and are aromatic as a result ($4n + 2$, $n = 4$), for a long time it was expected that there might be an upper limit to how large a molecule could be and still have aromaticity as predicted by Hückel's rule. In fact, until the late 1980s, a system with 22 π electrons appeared to be the maximum that could still retain aromaticity ($4n + 2$, $n = 5$) based on both experimental and theoretical calculations. Larger rings were thought to be too flexible, rendering them unable to maintain a structure that consistently placed all of their π systems in a flat, planar, conjugated
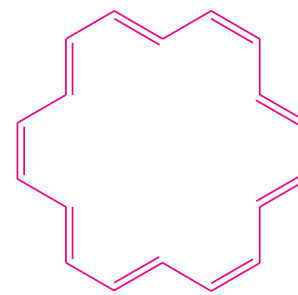
**[10]Annulene
$n = 2$
not aromatic**
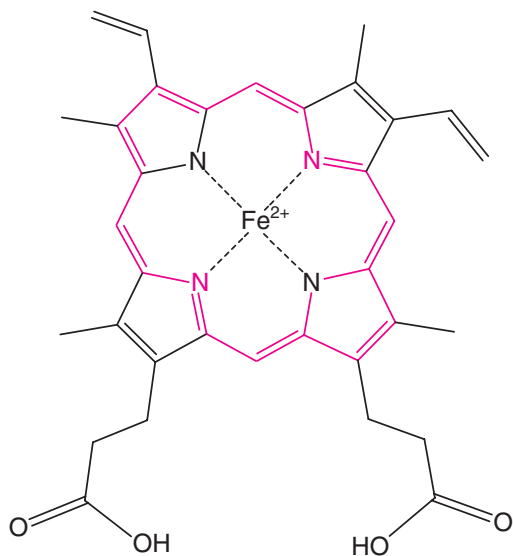
**[18]Annulene
$n = 4$**

**Heme
[18 electron system; $n = 4$]**
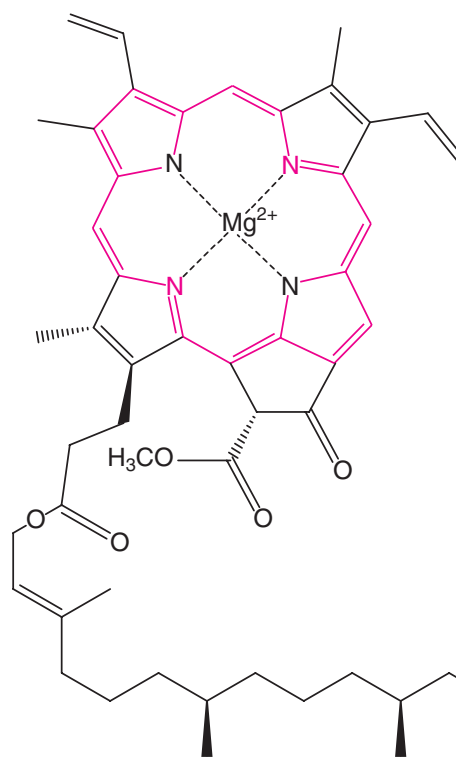
**Chlorophyll a
[18 electron system; $n = 4$]**

array. As with many problems, however, nature provided chemists with the inspiration for how to push the boundaries of aromaticity much further than anticipated.

Many important biomolecules possess [18]annulene systems known as porphyrins, such as those highlighted in chlorophyll a and heme. What is important to note is that rather than just possess olefins with conjugation, these molecules have many of those double bonds within pyrrole-like rings that make their structures rigid, enhancing their aromaticity by ensuring flatness. They also provide nitrogen atoms that can bind to metal ions, such as magnesium and iron, in their central pores; these metals are required to perform the redox chemistry of photosynthesis or to carry oxygen to all the cells of the body. While porphyrins with more than 18 electrons have not yet been found in nature, the idea of using rings to help enhance ridigity is what inspired chemists to design artificial porphyrins that are not only larger, but also break the hypothesized 22-electron aromaticity barrier.
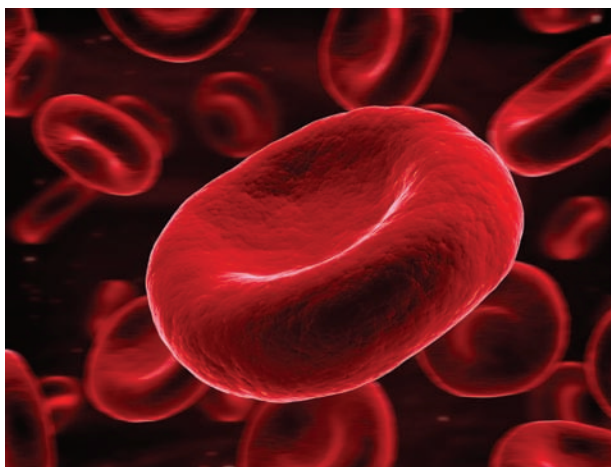
One example, shown below, is from molecules synthesized in 2001 that contain 8 pyrrole rings. This system has 30 electrons based on the highlighted atoms, showing that n can equal 7 in the Hückel paradigm of $4n + 2$. Another example comes from chemists in Germany who made a molecule containing 34 π electrons; ^{1}H NMR spectroscopy revealed that it was aromatic based on ring current, meaning that Hückel's rule can apply to systems as large as $n = 8$. Its central cavity is so big, in fact, that a number of molecules can fit within it. Where the upper limit to Hückel's rule is, no one knows, but clearly even large molecules have the potential to show the unique properties of aromaticity.
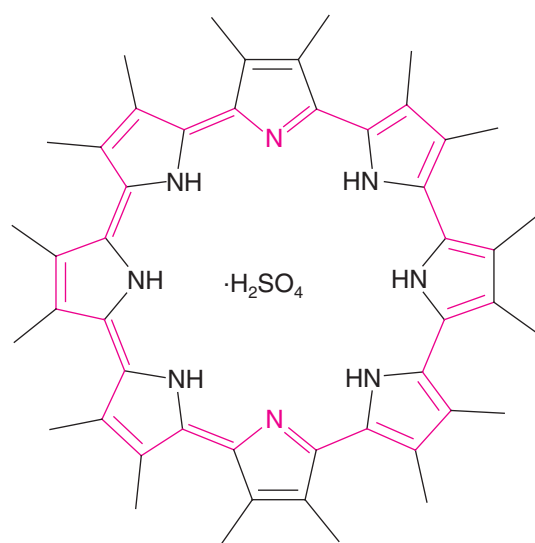
Octaporphyrin
[30 electron system; $n = 7$]
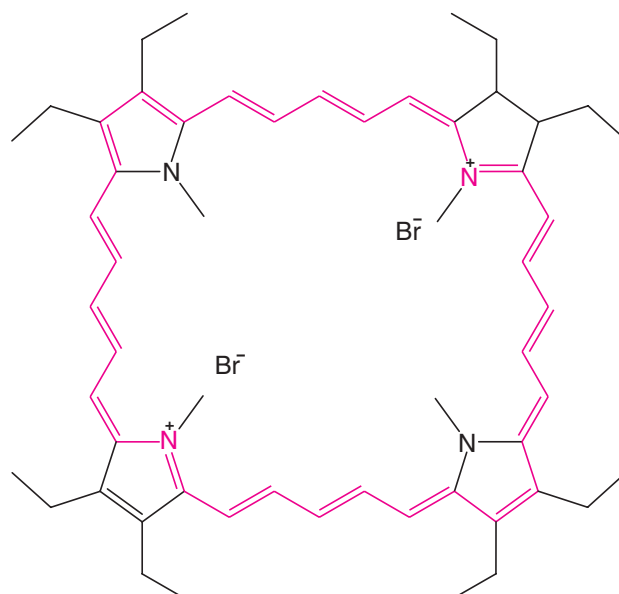
[34 electron system; $n = 8$]

To learn more about these topics, see:

1. Milgrom, L. "How big can aromatic compounds grow?" in *New Scientist*, 18 February 1989, 32.

2. Seidel, D.; Lynch, V.; Sessler, J. L. "Cyclo[8]pyrrole: A Simple-to-Make Expanded Porphyrin with No Meso Bridges" in *Angew. Chem. Int. Ed*. **2002**, *41*, 1422–1425.

3. Knubel, G.; Franck, B. Biomimetic Synthesis of an Octavinylogous Porphyrin with an Aromatic [34]Annulene System in *Angew. Chem. Int. Ed. Engl*. **1988**, *27*, 1170–1172.

SUMMARY AND REVIEW TOOLS

The study aids for this chapter include key terms and concepts (which are hyperlinked to the Glossary from the bold, blue terms in the *WileyPLUS* version of the book at wileyplus.com) and a Concept Map relating to properties and reactivity of aromatic compounds.

PROBLEMS WILEY PLUS

Note to Instructors: Many of the homework problems are available for assignment via *WileyPLUS*, an online teaching and learning solution.

NOMENCLATURE

14.16 Write structural formulas for each of the following:

(a) 3-Nitrobenzoic acid
(b) *p*-Bromotoluene
(c) *o*-Dibromobenzene
(d) *m*-Dinitrobenzene
(e) 3,5-Dinitrophenol
(f) *p*-Nitrobenzoic acid

(g) 3-Chloro-1-ethoxybenzene
(h) *p*-Chlorobenzenesulfonic acid
(i) Methyl *p*-toluenesulfonate
(j) Benzyl bromide
(k) *p*-Nitroaniline
(l) *o*-Xylene

(m) *tert*-Butylbenzene
(n) *p*-Methylphenol
(o) *p*-Bromoacetophenone
(p) 3-Phenylcyclohexanol
(q) 2-Methyl-3-phenyl-1-butanol
(r) *o*-Chloroanisole

14.17 Write structural formulas and give acceptable names for all representatives of the following:

(a) Tribromobenzenes
(b) Dichlorophenols

(c) Nitroanilines
(d) Methylbenzenesulfonic acids

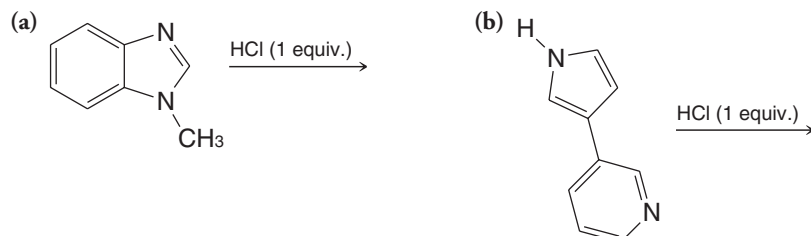(e) Isomers of $C_6H_5 - C_4H_9$

AROMATICITY

14.18 Which of the following molecules would you expect to be aromatic?
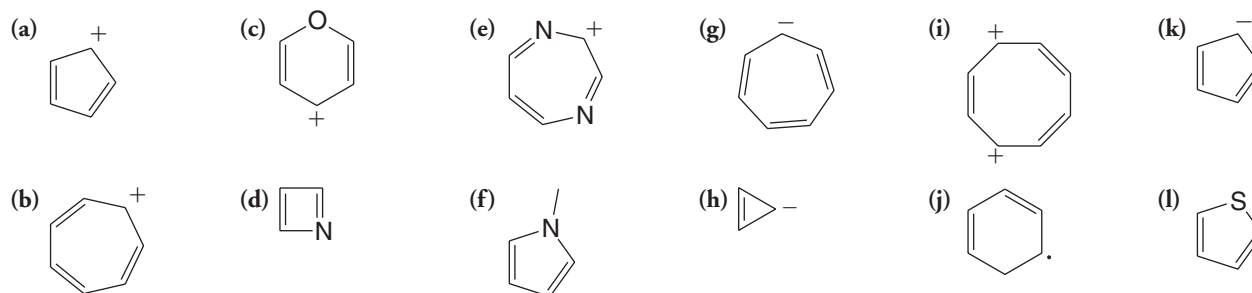
14.19 Use the polygon-and-circle method to draw an orbital diagram for each of the following compounds.


14.20 Write the structure of the product formed when each of the following compounds reacts with one molar equivalent of HCl.


14.21 Which of the hydrogen atoms shown below is more acidic? Explain your answer.

14.22 The rings below are joined by a double bond that undergoes cis–trans isomerization much more readily than the bond of a typical alkene. Provide an explanation.
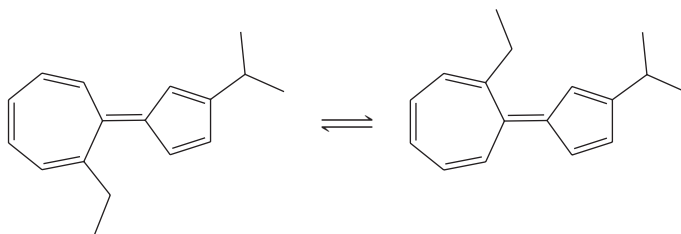

14.23 Although Hückel's rule (Section 14.7) strictly applies only to monocyclic compounds, it does appear to have application to certain bicyclic compounds, if one assumes use of resonance structures involving only the perimeter double bonds, as shown with one resonance contributor for naphthalene below.
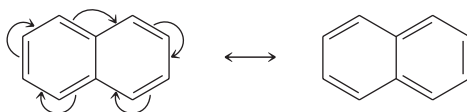
Both naphthalene (Section 14.8A) and azulene (Section 14.8B) have 10 π electrons and are aromatic. Pentalene (below) is apparently antiaromatic and is unstable even at −100 °C. Heptalene has been made but it adds bromine, it reacts with acids, and it is not planar. Is Hückel's rule applicable to these compounds? If so, explain their lack of aromaticity.
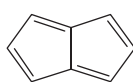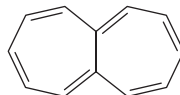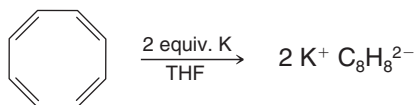

Pentalene   **Heptalene**

14.24

(a) In 1960 T. Katz (Columbia University) showed that cyclooctatetraene adds two electrons when treated with potassium metal and forms a stable, planar dianion, $C_8H_8^{2-}$ (as the dipotassium salt):

Use the molecular orbital diagram given in Fig. 14.7 and explain this result.

(b) In 1964 Katz also showed that removing two protons from the compound below (using butyllithium as the base) leads to the formation of a stable dianion with the formula $C_8H_6^{2-}$ (as the dilithium salt).

Propose a reasonable structure for the product and explain why it is stable.

14.25 Although none of the [10]annulenes given in Section 14.7B is aromatic, the following 10 π-electron system is aromatic:
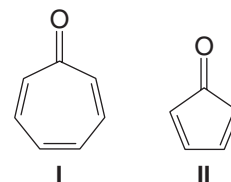

What factor makes this possible?

14.26 Cycloheptatrienone (**I**) is very stable. Cyclopentadienone (**II**) by contrast is quite unstable and rapidly undergoes a Diels–Alder reaction with itself.

(a) Propose an explanation for the different stabilities of these two compounds.

(b) Write the structure of the Diels–Alder adduct of cyclopentadienone.

I   **II**

14.27 5-Chloro-1,3-cyclopentadiene (below) undergoes S_N1 solvolysis in the presence of silver ion extremely slowly even though the chlorine is doubly allylic and allylic halides normally ionize readily (Section 15.15). Provide an explanation for this behavior.
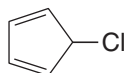
14.28 Explain the following: (**a**) Cyclononatetraenyl anion is planar (in spite of the angle strain involved) and appears to be aromatic. (**b**) Although [16]annulene is not aromatic, it adds two electrons readily to form an aromatic dianion.

14.29 Furan possesses less aromatic character than benzene as measured by their resonance energies (96 kJ mol^{-1} for furan; 151 kJ mol^{-1} for benzene). What reaction have we studied earlier that shows that furan is less aromatic than benzene and can react in a way characteristic of some dienes?

SPECTROSCOPY AND STRUCTURE ELUCIDATION

14.30 For each of the pairs below, predict specific aspects in their ^{1}H NMR spectra that would allow you to distinguish one compound from the other.

(**a**)

(**c**)

(**b**)
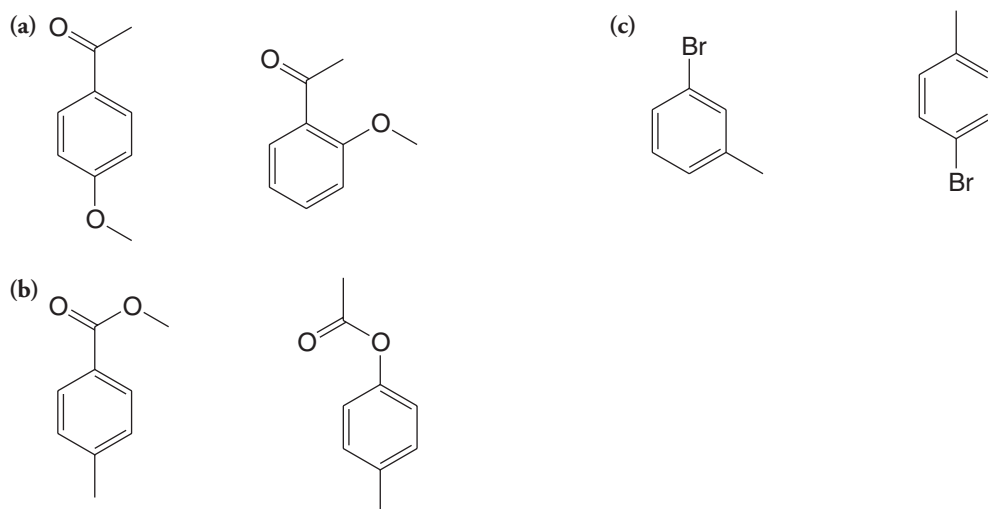
14.31 Assign structures to each of the compounds **A, B,** and **C** whose ^{1}H NMR spectra are shown in Fig. 14.27.

14.32 The ^{1}H NMR spectrum of cyclooctatetraene consists of a single line located at δ 5.78. What does the location of this signal suggest about electron delocalization in cyclooctatetraene?

14.33 Give a structure for compound **F** that is consistent with the ^{1}H NMR spectrum in Fig. 14.28 and IR absorptions at 3020, 2965, 2940, 2870, 1517, 1463, and 818 cm^{-1}.

14.34 A compound (**L**) with the molecular formula C_9H_{10} reacts with bromine and gives an IR absorption spectrum that includes the following absorption peaks: 3035 cm^{-1}(m), 3020 cm^{-1}(m), 2925 cm^{-1}(m), 2853 cm^{-1}(w), 1640 cm^{-1}(m), 990 cm^{-1}(s), 915 cm^{-1}(s), 740 cm^{-1}(s), 695 cm^{-1}(s). The ^{1}H NMR spectrum of **L** consists of:

> Doublet δ 3.1 (2H)   Multiplet δ 5.1   Multiplet δ 7.1 (5H)
> Multiplet δ 4.8   Multiplet δ 5.8

The UV spectrum shows a maximum at 255 nm. Propose a structure for compound **L** and make assignments for each of the IR peaks.

14.35 Compound **M** has the molecular formula C_9H_{12}. The ^{1}H NMR spectrum of **M** is given in Fig. 14.29 and the IR spectrum in Fig. 14.30. Propose a structure for **M**.

14.36 A compound (**N**) with the molecular formula $C_9H_{10}O$ reacts with osmium tetroxide. The ^{1}H NMR spectrum of **N** is shown in Fig. 14.31 and the IR spectrum of **N** is shown in Fig. 14.32. Propose a structure for **N**.

14.37 The IR and ^{1}H NMR spectra for compound **X** (C_8H_{10}) are given in Fig. 14.33. Propose a structure for compound **X**.

14.38 The IR and ^{1}H NMR spectra of compound **Y** ($C_9H_{12}O$) are given in Fig. 14.34. Propose a structure for **Y**.
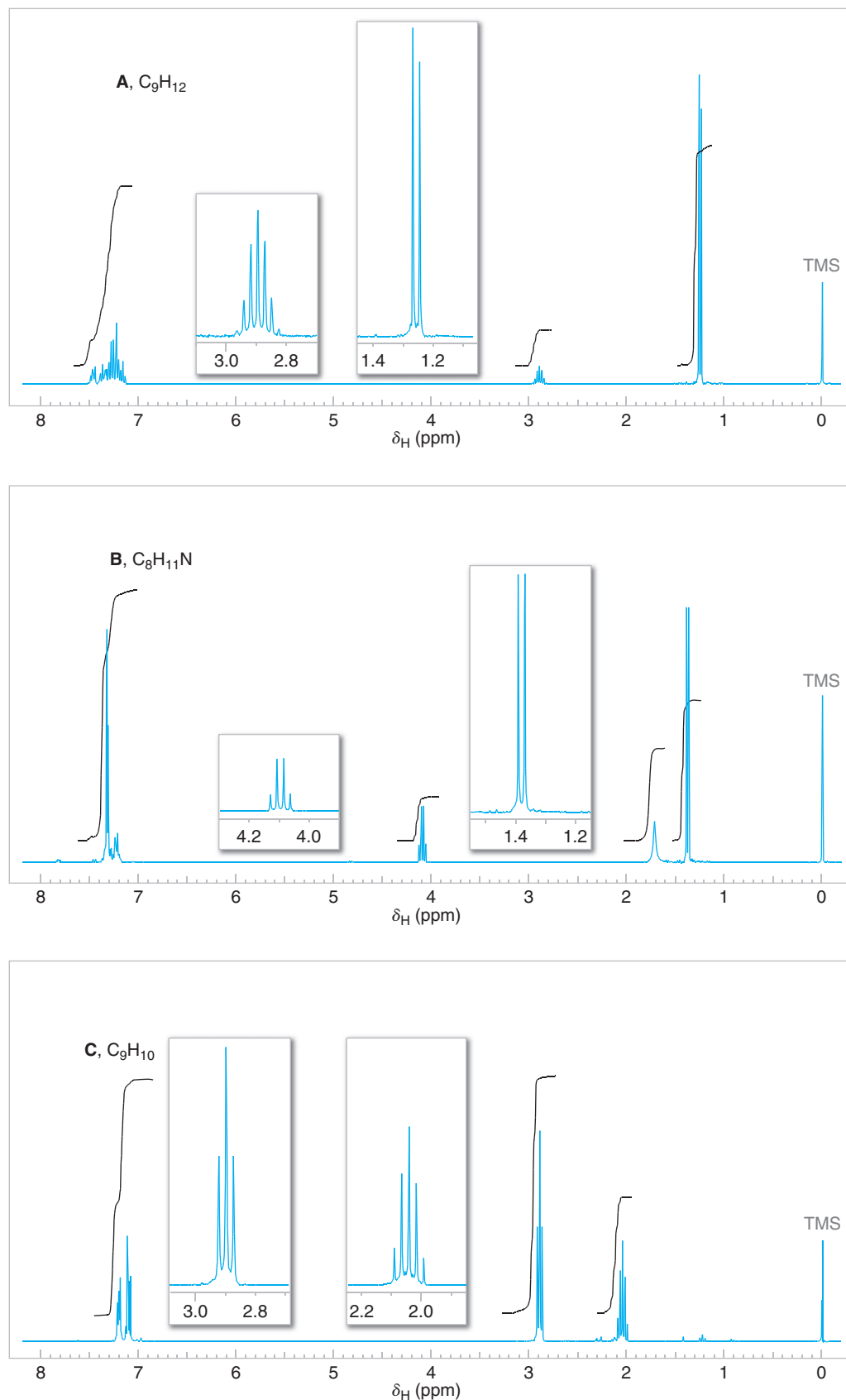
14.39

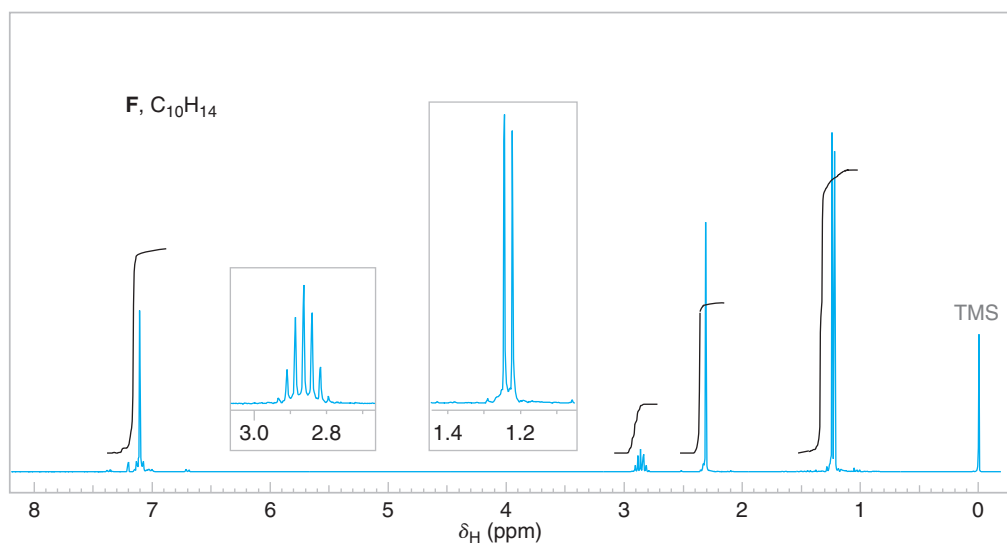(**a**) How many signals would you expect to find in the ^{1}H NMR spectrum of caffeine?
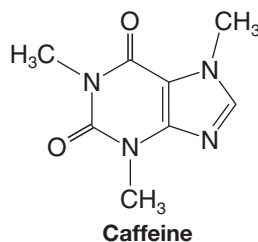
Caffeine

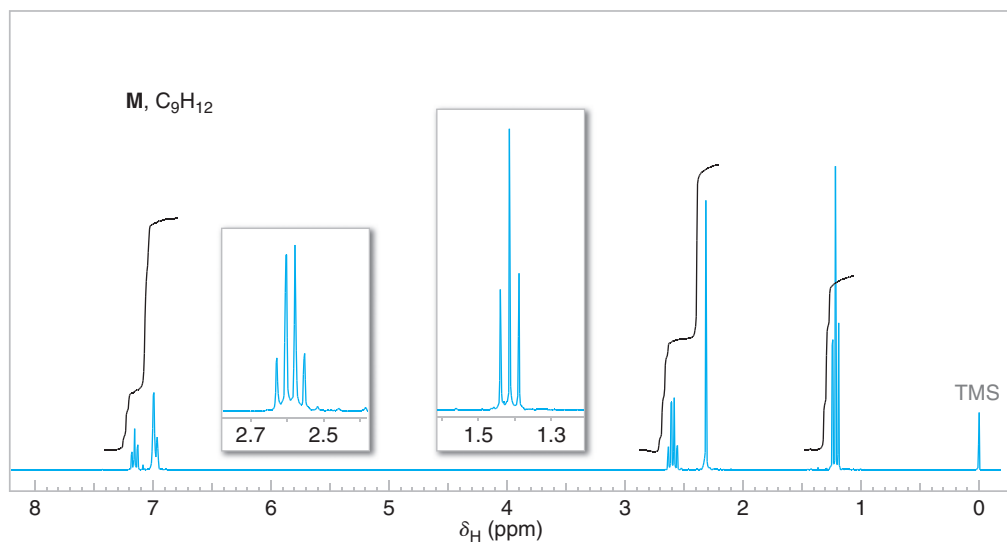(**b**) What characteristic peaks would you expect to find in the IR spectrum of caffeine?

FIGURE 14.27 The 300-MHz ^{1}H NMR spectra for Problem 14.31. Expansions of the signals are shown in the offset plots.

FIGURE 14.28 The 300-MHz ^{1}H NMR spectrum of compound **F**, Problem 14.33. Expansions of the signals are shown in the offset plots.

FIGURE 14.29 The 300-MHz ^{1}H NMR spectrum of compound **M**, Problem 14.35. Expansions of the signals are shown in the offset plots.

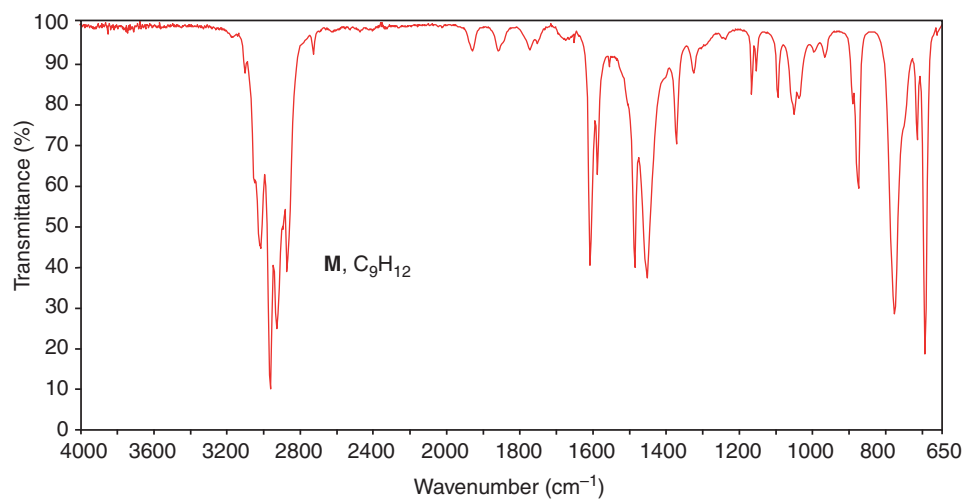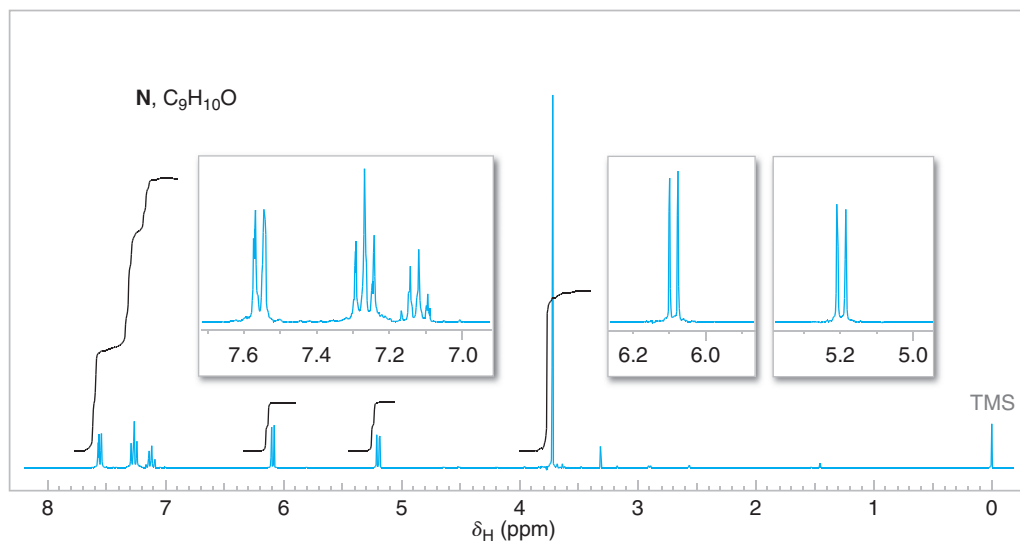**FIGURE 14.30** The IR spectrum of compound **M**, Problem 14.35.

FIGURE 14.31 The 300-MHz ^{1}H NMR spectrum of compound **N**, Problem 14.36. Expansions of the signals are shown in the offset plots.

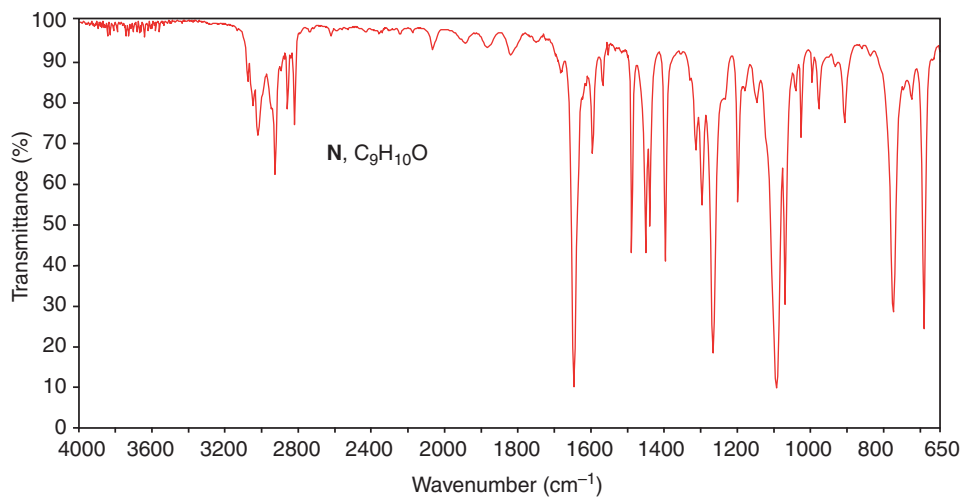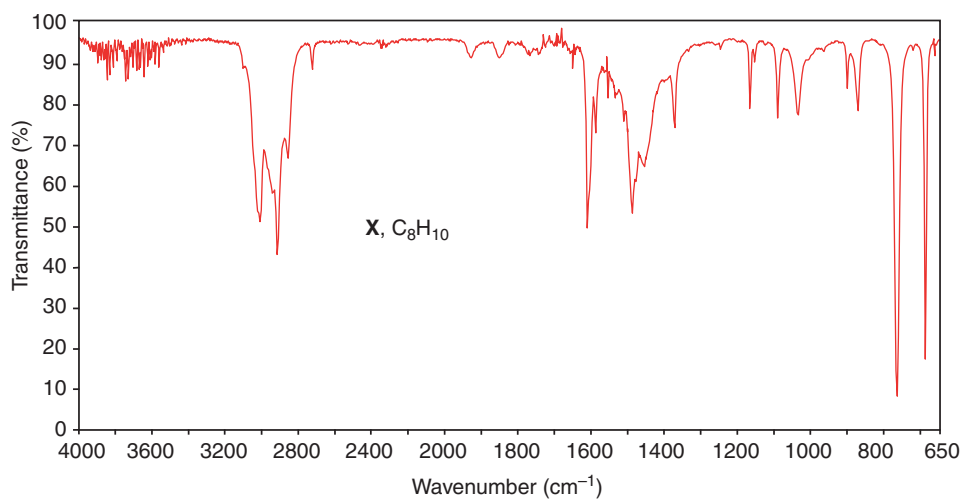**FIGURE 14.32** The IR spectrum of compound **N**, Problem 14.36.

FIGURE 14.33 The IR and 300-MHz ^{1}H NMR spectra of compound **X**, Problem 14.37. Expansions of the signals are shown in the offset plots.

X, C$_8$H$_{10}$

7.2   7.0

TMS

8   7   6   5   4   3   2   1   0

δ_H (ppm)

FIGURE 14.33 *(Continued)*

Y, C$_9$H$_{12}$O

100
90
80
70
60
50
40
30
20
10
0

Transmittance (%)

4000 3600 3200 2800 2400 2000 1800 1600 1400 1200 1000 800 650

Wavenumber (cm^{-1})

Y, C$_9$H$_{12}$O

4.6   4.4

1.8   1.6

0.9 0.8

TMS

8   7   6   5   4   3   2   1   0

δ_H (ppm)
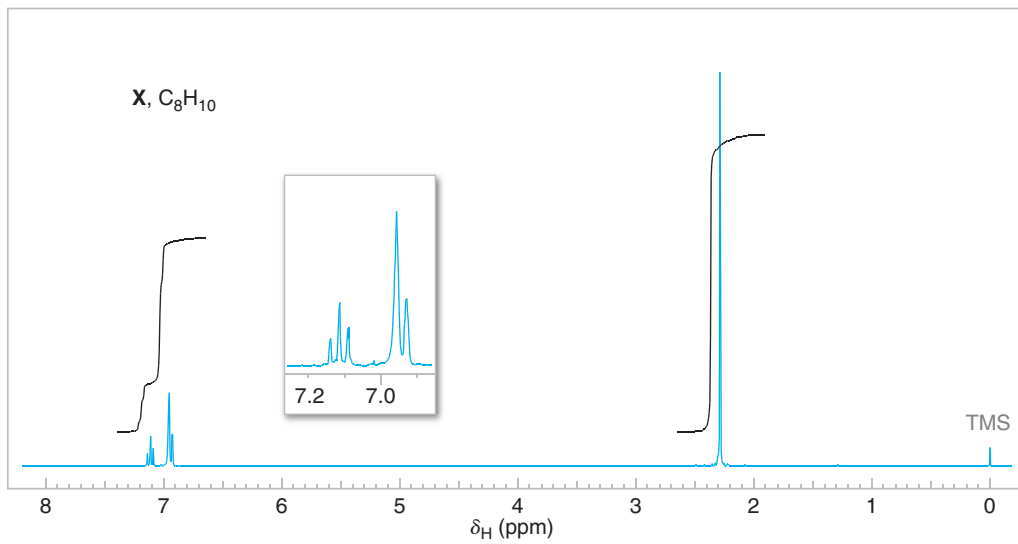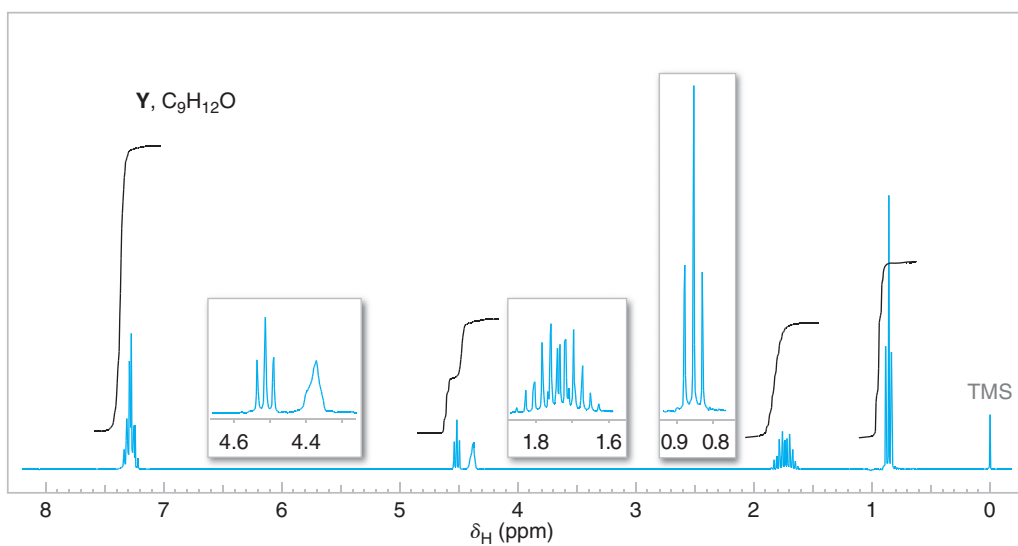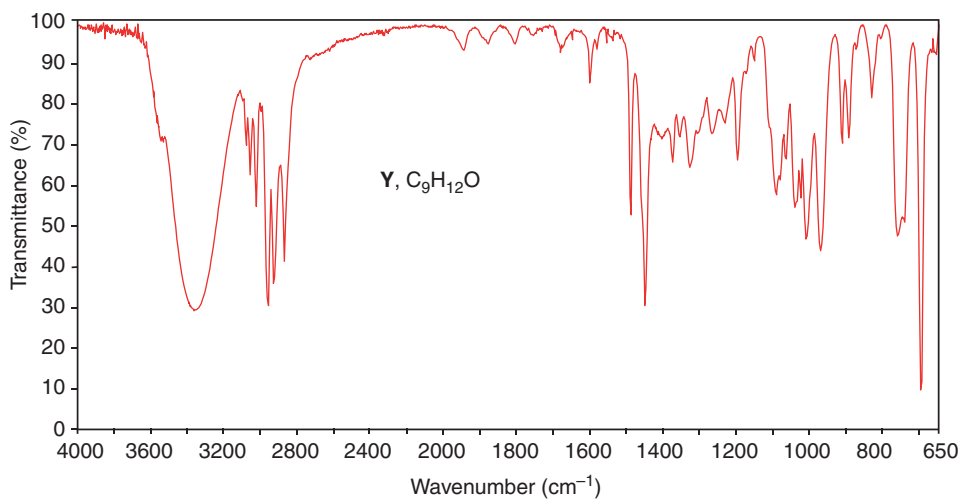
FIGURE 14.34 The IR and 300-MHz ^{1}H NMR spectra (next page) of compound **Y**, Problem 14.38. Expansions of the signals are shown in the offset plots.

CHALLENGE PROBLEMS

14.40 Given the following information, predict the appearance of the ^{1}H NMR spectrum arising from the vinyl hydrogen atoms of *p*-chlorostyrene. Deshielding by the induced magnetic field of the ring is greatest at proton c (δ 6.7) and is least at proton b (δ 5.3). The chemical shift of a is about δ 5.7. The coupling constants have the following approximate magnitudes: $J_{ac} \cong 18$ Hz, $J_{bc} \cong 11$ Hz, and $J_{ab} \cong 2$ Hz. (These coupling constants are typical of those given by vinylic systems: coupling constants for trans hydrogen atoms are larger than those for cis hydrogen atoms, and coupling constants for geminal vinylic hydrogen atoms are very small.)
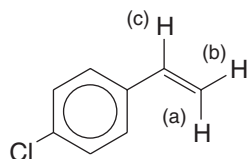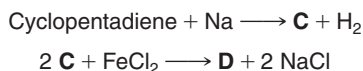

14.41 Consider these reactions:
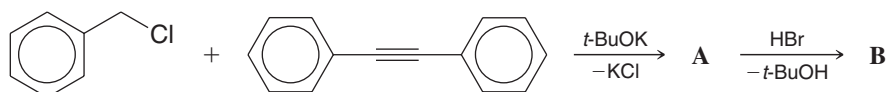
The intermediate **A** is a covalently bonded compound that has typical ^{1}H NMR signals for aromatic ring hydrogens and only one additional signal at δ 1.21, with an area ratio of 5:3, respectively. Final product **B** is ionic and has only aromatic hydrogen signals.

What are the structures of **A** and **B**?

14.42 The final product of this sequence, **D**, is an orange, crystalline solid melting at 174 °C and having molecular weight 186:

$$\text{Cyclopentadiene} + \text{Na} \longrightarrow \textbf{C} + \text{H}_2$$

$$2\,\textbf{C} + \text{FeCl}_2 \longrightarrow \textbf{D} + 2\,\text{NaCl}$$

In its ^{1}H and ^{13}C NMR spectra, product **D** shows only one kind of hydrogen and only one kind of carbon, respectively.

Draw the structure of **C** and make a structural suggestion as to how the high degree of symmetry of **D** can be explained. (**D** belongs to a group of compounds named after something you might get at a deli for lunch.)

14.43 Compound **E** has the spectral features given below. What is its structure?

MS (*m/z*):   M$^{+\cdot}$ 202

IR (cm^{-1}): 3030–3080, 2150 (very weak), 1600, 1490, 760, and 690

^{1}**H NMR** (δ): narrow multiplet centered at 7.34

UV (nm): 287 ($\epsilon = 25{,}000$), 305 ($\epsilon = 36{,}000$), and 326 ($\epsilon = 33{,}000$)

14.44 Draw all of the π molecular orbitals for (3*E*)-1,3,5-hexatriene, order them from lowest to highest in energy, and indicate the number of electrons that would be found in each in the ground state for the molecule. After doing so, open the computer molecular model for (3*E*)-1,3,5-hexatriene and display the calculated molecular orbitals. How well does the appearance and sequence of the orbitals you drew (e.g., number of nodes, overall symmetry of each, etc.) compare with the orbitals in the calculated model? Are the same orbitals populated with electrons in your analysis as in the calculated model?

LEARNING GROUP PROBLEMS

1. Write mechanism arrows for the following step in the chemical synthesis by A. Robertson and R. Robinson (*J. Chem. Soc.* **1928**, 1455–1472) of callistephin chloride, a red flower pigment from the purple-red aster. Explain why this transformation is a reasonable process.


Callistephin chloride
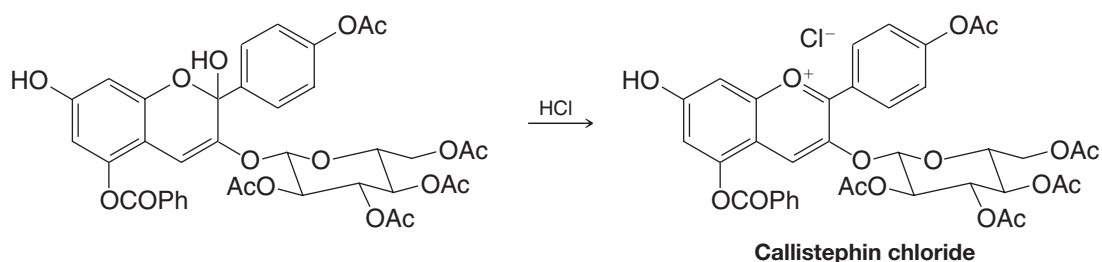
2. The following reaction sequence was used by E. J. Corey (*J. Am. Chem. Soc.* **1969**, *91*, 5675–5677) at the beginning of a synthesis of prostaglandin F$_{2\alpha}$ and prostaglandin E$_2$. Explain what is involved in this reaction and why it is a reasonable process.
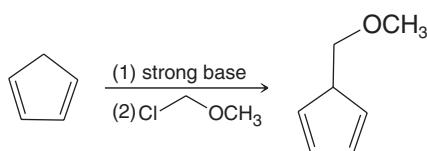
3. The ^{1}H NMR signals for the aromatic hydrogens of methyl *p*-hydroxybenzoate appear as two doublets at approximately 7.05 and 8.04 ppm (δ). Assign these two doublets to the respective hydrogens that produce each signal. Justify your assignments using arguments of relative electron density based on contributing resonance structures.
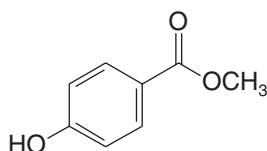
4. Draw the structure of adenine, a heterocyclic aromatic compound incorporated in the structure of DNA. Identify the nonbonding electron pairs that are *not* part of the aromatic system in the rings of adenine. Which nitrogen atoms in the rings would you expect to be more basic and which should be less basic?

5. Draw structures of the nicotinamide ring in NADH and NAD$^+$. In the transformation of NADH to NAD$^+$, in what form must a hydrogen be transferred in order to produce the aromatic pyridinium ion in NAD$^+$?

$$\left[\text{C O N C E P T \quad M A P}\right]$$

Aromatic Compounds

must be

→ Cyclic

→ Planar

have

→ A p orbital at each atom of the ring

→ $4n + 2$ π electrons (Hückel's rule for monocyclic aromatic compounds)

→ Delocalized π electrons

→ Resonance stabilization

include

→ Benzenoid aromatic compounds

Mono- and polycyclic benzenoid aromatic compounds (e.g., naphthalene, anthracene, pyrene)

Fullerenes and nanotubes

→ Nonbenzenoid aromatic compounds

Heterocyclic aromatic compounds (e.g., pyridine, furan, pyrrole, thiophene)

Aromatic anions and cations (e.g., cyclopentadienyl anion, cycloheptatrienyl cation)

Aromatic annulenes (e.g., [14]annulene)

have

→ Characteristic spectroscopic properties

^{1}H NMR: δ ~6.0–9.5 (benzene ring protons)

^{13}C NMR: δ ~100–170 (aromatic carbons)

IR: sp^2 C—H stretch ~3030 cm^{-1}; ring stretch 1450–1600 cm^{-1}; ring bending 700–900 cm^{-1} (with specific characteristics according to substitution pattern)

UV–Vis: $\lambda_{max} > 200$ nm (~300 nm with additional conjugation)