

15

Benzene and Aromaticity

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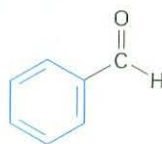


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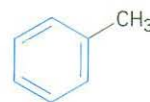
In the early days of organic chemistry, the word *aromatic* was used to describe such fragrant substances as benzaldehyde (from cherries, peaches, and almonds), toluene (from Tolu balsam), and benzene (from coal distillate). It was soon realized, however, that substances grouped as aromatic differed from most other organic compounds in their chemical behavior.



Benzene



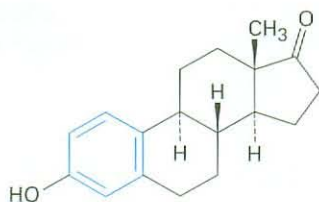
Benzaldehyde



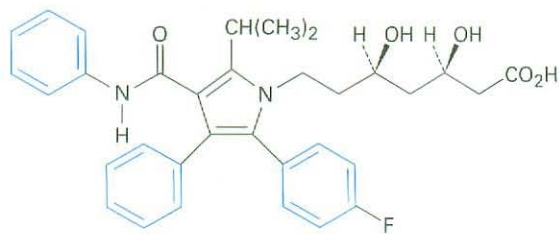
Toluene

Today, we use the word **aromatic** to refer to the class of compounds that contain six-membered benzene-like rings with three double bonds. As we'll see in this and the next chapter, aromatic compounds show chemical behavior quite different from the aliphatic compounds we've studied to this point. Thus, chemists of the early 19th century were correct about there being a chemical difference between aromatic compounds and others, but the association of aromaticity with fragrance has long been lost.

Many valuable compounds are aromatic in part, including steroids such as estrone and well-known pharmaceuticals such as the cholesterol-lowering drug atorvastatin, marketed as Lipitor. Benzene itself has been found to cause bone marrow depression and a consequent lowered white blood cell count on prolonged exposure. Benzene should therefore be handled cautiously if used as a laboratory solvent.



Estrone



Atorvastatin
(Lipitor)

WHY THIS CHAPTER?

The reactivity of substituted aromatic compounds, more than that of any other class of substances, is intimately tied to their exact structure. As a result, aromatic compounds provide an extraordinarily sensitive probe for studying the relationship between structure and reactivity. We'll examine that relationship in this and the next chapter, and we'll find that the lessons learned are applicable to all other organic compounds, including such particularly important substances as the nucleic acids that control our genetic makeup.

15.1 Sources and Names of Aromatic Compounds

Simple aromatic hydrocarbons come from two main sources: coal and petroleum. Coal is an enormously complex mixture made up primarily of large arrays of benzene-like rings joined together. Thermal breakdown of coal occurs when it is heated to 1000 °C in the absence of air, and a mixture of volatile products called *coal tar* boils off. Fractional distillation of coal tar yields benzene, toluene, xylene (dimethylbenzene), naphthalene, and a host of other aromatic compounds (Figure 15.1).

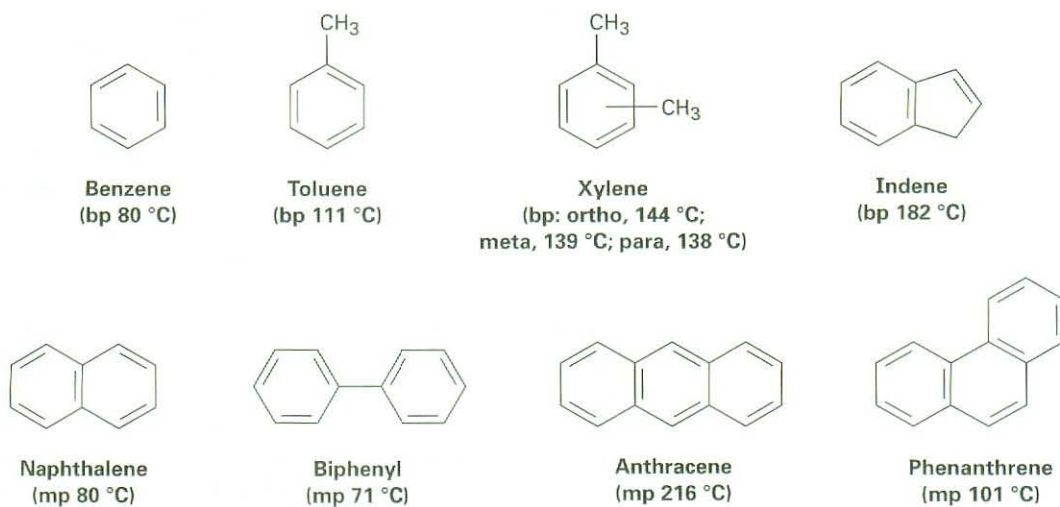
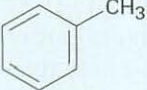
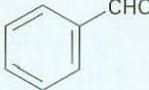
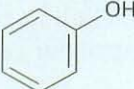
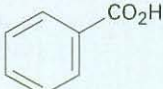
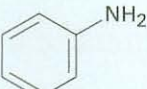
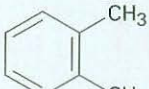
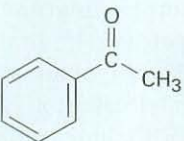
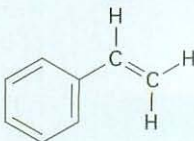


Figure 15.1 Some aromatic hydrocarbons found in coal tar.

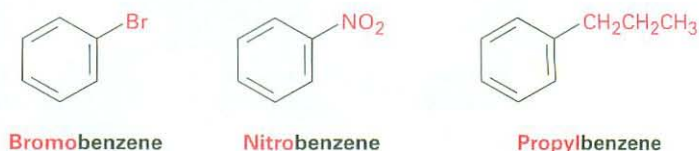
Unlike coal, petroleum contains few aromatic compounds and consists largely of alkanes (Chapter 3 *Focus On*). During petroleum refining, however, aromatic molecules are formed when alkanes are passed over a catalyst at about 500 °C under high pressure.

Aromatic substances, more than any other class of organic compounds, have acquired a large number of nonsystematic names. The use of such names is discouraged, but IUPAC rules allow for some of the more widely used ones to be retained (Table 15.1). Thus, methylbenzene is known commonly as *toluene*; hydroxybenzene, as *phenol*; aminobenzene, as *aniline*; and so on.

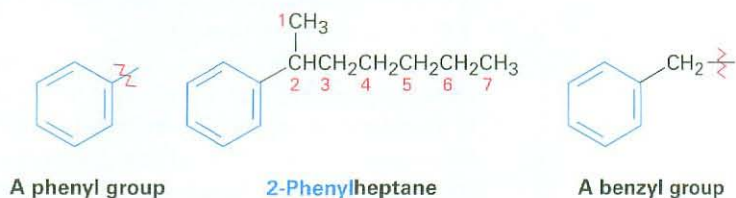
Table 15.1 Common Names of Some Aromatic Compounds

Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		<i>ortho</i> -Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

Monosubstituted benzenes are systematically named in the same manner as other hydrocarbons, with *-benzene* as the parent name. Thus, C_6H_5Br is bromobenzene, $C_6H_5NO_2$ is nitrobenzene, and $C_6H_5CH_2CH_2CH_3$ is propylbenzene.



Alkyl-substituted benzenes are sometimes referred to as **arenes** and are named in different ways depending on the size of the alkyl group. If the alkyl substituent is smaller than the ring (six or fewer carbons), the arene is named as an alkyl-substituted benzene. If the alkyl substituent is larger than the ring (seven or more carbons), the compound is named as a phenyl-substituted alkane. The name **phenyl**, pronounced **fen**-nil and sometimes abbreviated as Ph or Φ (Greek phi), is used for the $-C_6H_5$ unit when the benzene ring is considered as a substituent. The word is derived from the Greek *pheno* ("I bear light"), commemorating the discovery of benzene by Michael Faraday in 1825 from the oily residue left by the illuminating gas used in London street lamps. In addition, the name **benzyl** is used for the $C_6H_5CH_2-$ group.



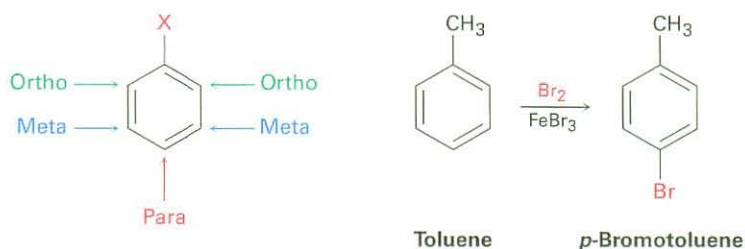
Michael Faraday

Michael Faraday (1791–1867) was born in Newington Butts, Surrey, England, the son of a blacksmith. Although he received little formal schooling, he was one of the greatest scientists of the 19th century. As a young man in 1812, he became a laboratory assistant to Sir Humphry Davy at the Royal Institution and learned chemistry through this apprenticeship. By 1820, he was said to know as much chemistry as any living person; by 1825, he was director of a laboratory at the Royal Institution; and by 1833, he was Fullerton Professor of Chemistry. He is best remembered for his work on electricity and magnetism.

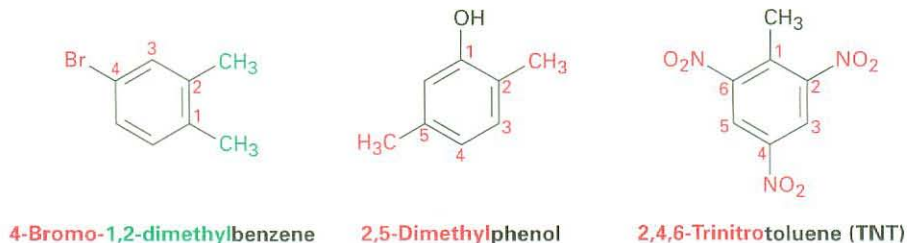
Disubstituted benzenes are named using one of the prefixes *ortho-* (*o*), *meta-* (*m*), or *para-* (*p*). An ortho-disubstituted benzene has its two substituents in a 1,2 relationship on the ring, a meta-disubstituted benzene has its two substituents in a 1,3 relationship, and a para-disubstituted benzene has its substituents in a 1,4 relationship.



The ortho, meta, para system of nomenclature is also useful when discussing reactions. For example, we might describe the reaction of bromine with toluene by saying, “Reaction occurs at the para position”—in other words, at the position para to the methyl group already present on the ring.

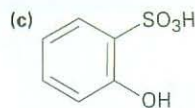
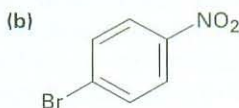


As with cycloalkanes (Section 4.1), benzenes with more than two substituents are named by choosing a point of attachment as carbon 1 and numbering the substituents on the ring so that the *second* substituent has as low a number as possible. If ambiguity still exists, number so that the third or fourth substituent has as low a number as possible, until a point of difference is found. The substituents are listed alphabetically when writing the name.

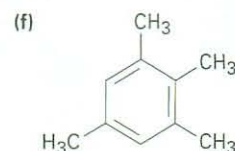
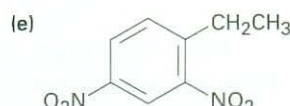
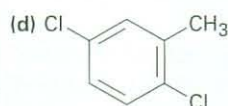
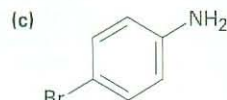
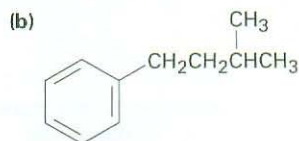
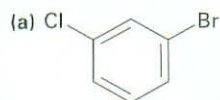


Note in the second and third examples shown that *-phenol* and *-toluene* are used as the parent names rather than *-benzene*. Any of the monosubstituted aromatic compounds shown in Table 15.1 can serve as a parent name, with the principal substituent (–OH in phenol or –CH₃ in toluene) attached to C1 on the ring.

Problem 15.1 Tell whether the following compounds are ortho-, meta-, or para-disubstituted:



Problem 15.2 Give IUPAC names for the following compounds:



Problem 15.3 Draw structures corresponding to the following IUPAC names:

(a) *p*-Bromochlorobenzene

(b) *p*-Bromotoluene

(c) *m*-Chloroaniline

(d) 1-Chloro-3,5-dimethylbenzene

15.2 Structure and Stability of Benzene: Molecular Orbital Theory

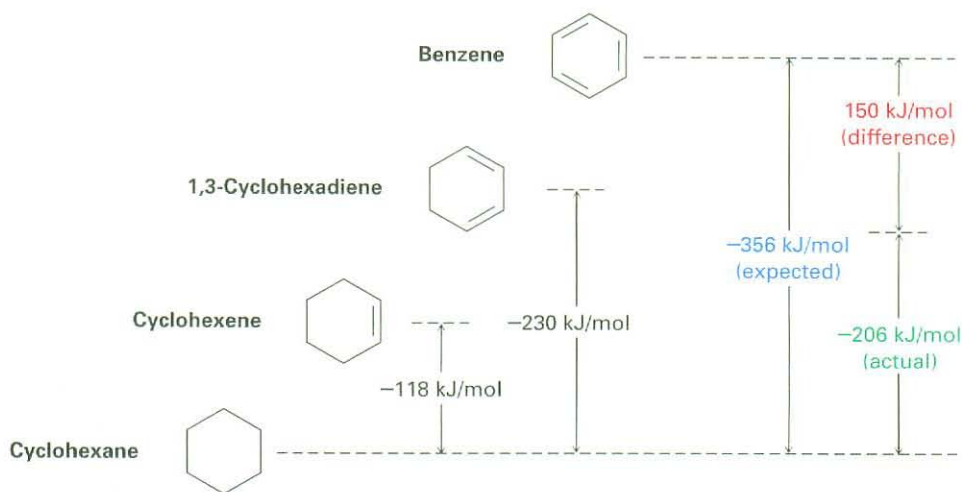
Although benzene is clearly unsaturated, it is much more stable than typical alkenes and fails to undergo the usual alkene reactions. Cyclohexene, for instance, reacts rapidly with Br_2 and gives the addition product 1,2-dibromocyclohexane, but benzene reacts only slowly with Br_2 and gives the *substitution* product $\text{C}_6\text{H}_5\text{Br}$. As a result of this substitution, the cyclic conjugation of the benzene ring is retained.



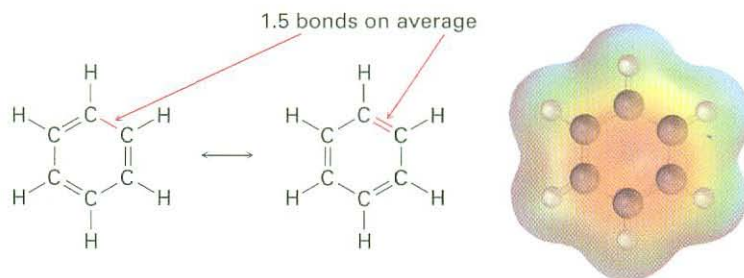
We can get a quantitative idea of benzene's stability by measuring heats of hydrogenation (Section 6.6). Cyclohexene, an isolated alkene, has $\Delta H^\circ_{\text{hydrog}} = -118 \text{ kJ/mol}$ (-28.2 kcal/mol), and 1,3-cyclohexadiene, a conjugated diene, has $\Delta H^\circ_{\text{hydrog}} = -230 \text{ kJ/mol}$ (-55.0 kcal/mol). As noted in Section 14.1, this value for 1,3-cyclohexadiene is a bit less than twice that for cyclohexene because conjugated dienes are more stable than isolated dienes.

Carrying the process one step further, we might expect $\Delta H^\circ_{\text{hydrog}}$ for “cyclohexatriene” (benzene) to be a bit less than -356 kJ/mol , or three times the cyclohexene value. The actual value, however, is -206 kJ/mol , some 150 kJ/mol (36 kcal/mol) less than expected. Since 150 kJ/mol less heat than expected is released during hydrogenation of benzene, benzene must have 150 kJ/mol less energy to begin with. In other words, benzene is more stable than expected by 150 kJ/mol (Figure 15.2).

Figure 15.2 A comparison of the heats of hydrogenation for cyclohexene, 1,3-cyclohexadiene, and benzene. Benzene is 150 kJ/mol (36 kcal/mol) more stable than might be expected for “cyclohexatriene.”



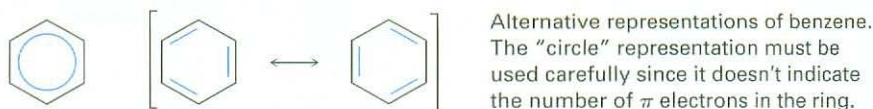
Further evidence for the unusual nature of benzene is that all its carbon–carbon bonds have the same length— 139 pm —intermediate between typical single (154 pm) and double (134 pm) bonds. In addition, an electrostatic potential map shows that the electron density in all six carbon–carbon bonds is identical. Thus, benzene is a planar molecule with the shape of a regular hexagon. All C–C–C bond angles are 120° , all six carbon atoms are sp^2 -hybridized, and each carbon has a p orbital perpendicular to the plane of the six-membered ring.



Because all six carbon atoms and all six p orbitals in benzene are equivalent, it's impossible to define three localized π bonds in which a given p orbital overlaps only one neighboring p orbital. Rather, each p orbital overlaps equally well with both neighboring p orbitals, leading to a picture of benzene in which the six π electrons are completely delocalized around the ring. In resonance terms (Sections 2.4 and 2.5), benzene is a hybrid of two equivalent forms. Neither form

is correct by itself; the true structure of benzene is somewhere in between the two resonance forms but is impossible to draw with our usual conventions.

Chemists sometimes represent the two benzene resonance forms by using a circle to indicate the equivalence of the carbon–carbon bonds. This kind of representation has to be used carefully, however, because it doesn't indicate the number of π electrons in the ring. (How many electrons does a circle represent?) In this book, benzene and other aromatic compounds will be represented by a single line-bond structure. We'll be able to keep count of π electrons this way but must be aware of the limitations of the drawings.



Having just seen a resonance description of benzene, let's now look at the alternative molecular orbital description. We can construct π molecular orbitals for benzene just as we did for 1,3-butadiene in Section 14.1. If six p atomic orbitals combine in a cyclic manner, six benzene molecular orbitals result, as shown in Figure 15.3. The three low-energy molecular orbitals, denoted ψ_1 , ψ_2 , and ψ_3 , are bonding combinations, and the three high-energy orbitals are antibonding.

Note that the two bonding orbitals ψ_2 and ψ_3 have the same energy, as do the two antibonding orbitals ψ_4^* and ψ_5^* . Such orbitals with the same energy are said to be *degenerate*. Note also that the two orbitals ψ_3 and ψ_4^* have nodes passing through ring carbon atoms, thereby leaving no π electron density on these carbons. The six p electrons of benzene occupy the three bonding molecular orbitals and are delocalized over the entire conjugated system, leading to the observed 150 kJ/mol stabilization of benzene.

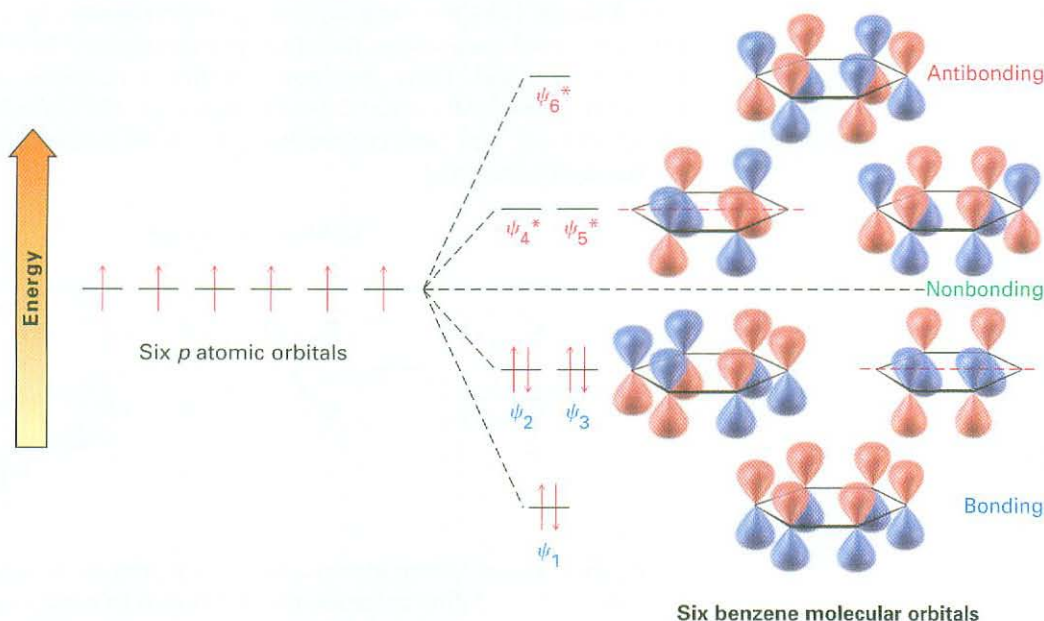
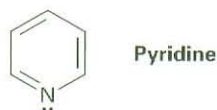


Figure 15.3 The six benzene π molecular orbitals. The bonding orbitals ψ_2 and ψ_3 have the same energy and are said to be degenerate, as are the antibonding orbitals ψ_4^* and ψ_5^* . The orbitals ψ_3 and ψ_4^* have no π electron density on two carbons because of a node passing through these atoms.

Problem 15.4 Pyridine is a flat, hexagonal molecule with bond angles of 120° . It undergoes substitution rather than addition and generally behaves like benzene. Draw a picture of the π orbitals of pyridine to explain its properties. Check your answer by looking ahead to Section 15.7.



15.3 Aromaticity and the Hückel $4n + 2$ Rule

Let's list what we've said thus far about benzene and, by extension, about other benzene-like aromatic molecules.

- Benzene is cyclic and conjugated.
- Benzene is unusually stable, having a heat of hydrogenation 150 kJ/mol less negative than we might expect for a conjugated cyclic triene.
- Benzene is planar and has the shape of a regular hexagon. All bond angles are 120° , all carbon atoms are sp^2 -hybridized, and all carbon-carbon bond lengths are 139 pm.
- Benzene undergoes substitution reactions that retain the cyclic conjugation rather than electrophilic addition reactions that would destroy the conjugation.
- Benzene is a resonance hybrid whose structure is intermediate between two line-bond structures.

Erich Hückel

Erich Hückel (1896–1980) was born in Stuttgart, Germany, and received his Ph.D. at the University of Göttingen with Peter Debye. He was professor of physics, first at Stuttgart and later at Marburg (1937–1961).

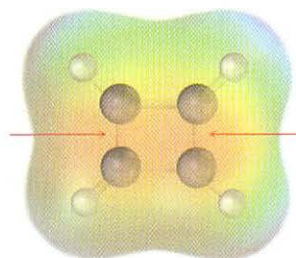
This list would seem to provide a good description of benzene and other aromatic molecules, but it isn't enough. Something else, called the **Hückel $4n + 2$ rule**, is needed to complete a description of aromaticity. According to a theory devised by the German physicist Erich Hückel in 1931, a molecule is aromatic only if it has a planar, monocyclic system of conjugation and contains a total of $4n + 2$ π electrons, where n is an integer ($n = 0, 1, 2, 3, \dots$). In other words, only molecules with 2, 6, 10, 14, 18, \dots π electrons can be aromatic. Molecules with $4n$ π electrons (4, 8, 12, 16, \dots) *can't* be aromatic, even though they may be cyclic, planar, and apparently conjugated. In fact, planar, conjugated molecules with $4n$ π electrons are said to be **antiaromatic**, because delocalization of their π electrons would lead to their *destabilization*. Let's look at several examples to see how the Hückel $4n + 2$ rule works.

- **Cyclobutadiene** has four π electrons and is antiaromatic. The π electrons are localized into two double bonds rather than delocalized around the ring, as indicated by an electrostatic potential map.



Cyclobutadiene

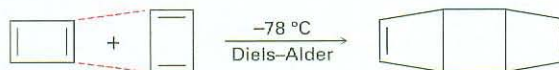
Two double bonds;
four π electrons



Rowland Pettit

Rowland Pettit (1927–1981) was born in Port Lincoln, Australia. He received two doctoral degrees, one from the University of Adelaide in 1952 and the second from the University of London in 1956, working with Michael Dewar. He then became professor of chemistry at the University of Texas, Austin (1957–1981).

Cyclobutadiene is highly reactive and shows none of the properties associated with aromaticity. In fact, it was not even prepared until 1965, when Rowland Pettit of the University of Texas was able to make it at low temperature. Even at $-78\text{ }^{\circ}\text{C}$, however, cyclobutadiene is so reactive that it dimerizes by a Diels–Alder reaction. One molecule behaves as a diene and the other as a dienophile.



- Benzene has six π electrons ($4n + 2 = 6$ when $n = 1$) and is aromatic.



Benzene

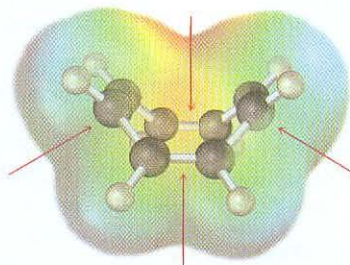
Three double bonds;
six π electrons

- Cyclooctatetraene has eight π electrons and is not aromatic. The π electrons are localized into four double bonds rather than delocalized around the ring, and the molecule is tub-shaped rather than planar.



Cyclooctatetraene

Four double bonds;
eight π electrons



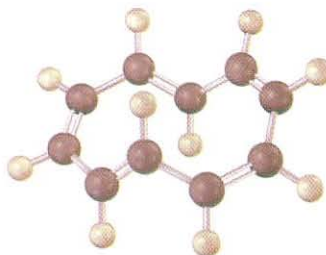
Richard Willstätter

Richard Willstätter (1872–1942) was born in Karlsruhe, Germany, and obtained his Ph.D. from the Technische Hochschule, Munich (1895). He was professor of chemistry at the universities of Zurich, Berlin, and then Munich (1916–1924). In 1915, he won the Nobel Prize in chemistry for his work on elucidating the structure of chlorophyll. Nevertheless, as a Jew, he was subjected to anti-Semitic pressure that caused him to resign his position at Munich in 1924. He continued to work privately.

Chemists in the early 1900s believed that the only requirement for aromaticity was the presence of a cyclic conjugated system. It was therefore expected that cyclooctatetraene, as a close analog of benzene, would also prove to be unusually stable. The facts, however, proved otherwise. When cyclooctatetraene was first prepared in 1911 by the German chemist Richard Willstätter, it was found not to be particularly stable but to resemble an open-chain polyene in its reactivity.

Cyclooctatetraene reacts readily with Br_2 , KMnO_4 , and HCl , just as other alkenes do. In fact, cyclooctatetraene is not even conjugated. It is tub-shaped rather than planar and has no cyclic conjugation because neighboring p orbitals don't have the necessary parallel alignment for overlap. The π electrons are localized in four discrete $\text{C}=\text{C}$ bonds rather than delocalized around the ring. X-ray studies show that the $\text{C}-\text{C}$ single bonds are 147 pm long and the double bonds are 134 pm long. In addition, the ^1H NMR spectrum shows a single sharp resonance line at 5.7 δ , a value characteristic of an alkene rather than an aromatic molecule.

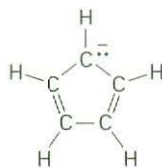
Problem 15.5 To be aromatic, a molecule must have $4n + 2 \pi$ electrons and must have cyclic conjugation. 1,3,5,7,9-Cyclodecapentaene fulfills one of these criteria but not the other and has resisted all attempts at synthesis. Explain.



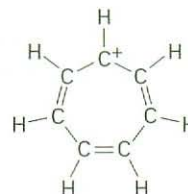
15.4 Aromatic Ions

ThomsonNOW Click *Organic Interactive* to learn to recognize and identify aromatic systems.

According to the Hückel criteria for aromaticity, a molecule must be cyclic, conjugated (that is, be nearly planar and have a p orbital on each carbon) and have $4n + 2 \pi$ electrons. Nothing in this definition says that the number of p orbitals and the number of π electrons in those orbitals must be the same. In fact, they can be different. The $4n + 2$ rule is broadly applicable to many kinds of molecules and ions, not just to neutral hydrocarbons. For example, both the cyclopentadienyl *anion* and the cycloheptatrienyl *cation* are aromatic.



Cyclopentadienyl anion



Cycloheptatrienyl cation

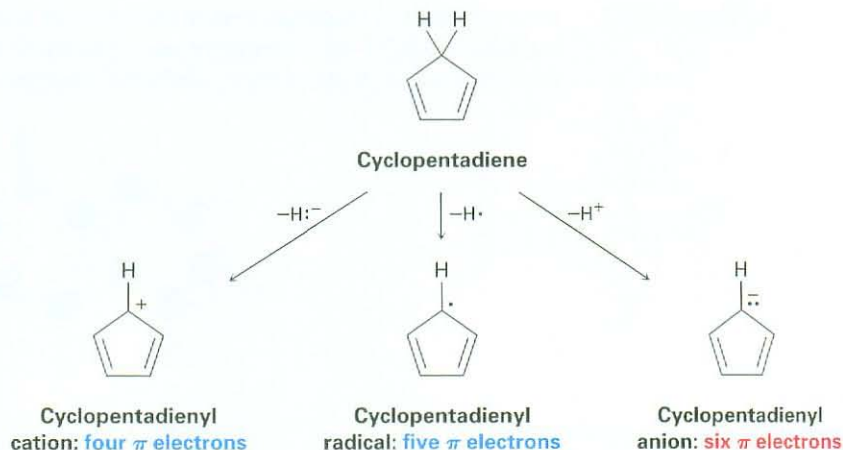
Six π electrons; aromatic ions

Let's look first at the cyclopentadienyl anion. Cyclopentadiene itself is not aromatic because it is not fully conjugated. The $-\text{CH}_2-$ carbon in the ring is sp^3 -hybridized, thus preventing complete cyclic conjugation. Imagine, though, that we remove one hydrogen from the saturated CH_2 group so that the carbon becomes sp^2 -hybridized. The resultant species would have five p orbitals, one on each of the five carbons, and would be fully conjugated.

There are three ways the hydrogen might be removed, as shown in Figure 15.4.

- We could remove the hydrogen atom and *both* electrons (H^-) from the C–H bond, leaving a cyclopentadienyl cation.
- We could remove the hydrogen and *one* electron ($\text{H}\cdot$) from the C–H bond, leaving a cyclopentadienyl radical.
- We could remove a hydrogen ion with *no* electrons (H^+), leaving a cyclopentadienyl anion.

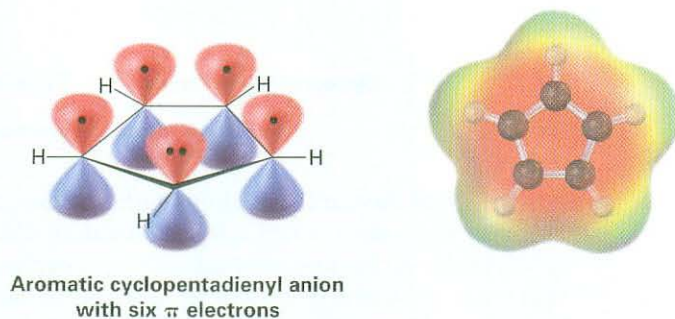
Active Figure 15.4 Generating the cyclopentadienyl cation, radical, and anion by removing a hydrogen from cyclopentadiene. Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.



Although five equivalent resonance structures can be drawn for all three species, Hückel's rule predicts that *only the six- π -electron anion should be aromatic*. The four- π -electron cyclopentadienyl carbocation and the five- π -electron cyclopentadienyl radical are predicted to be unstable and antiaromatic.

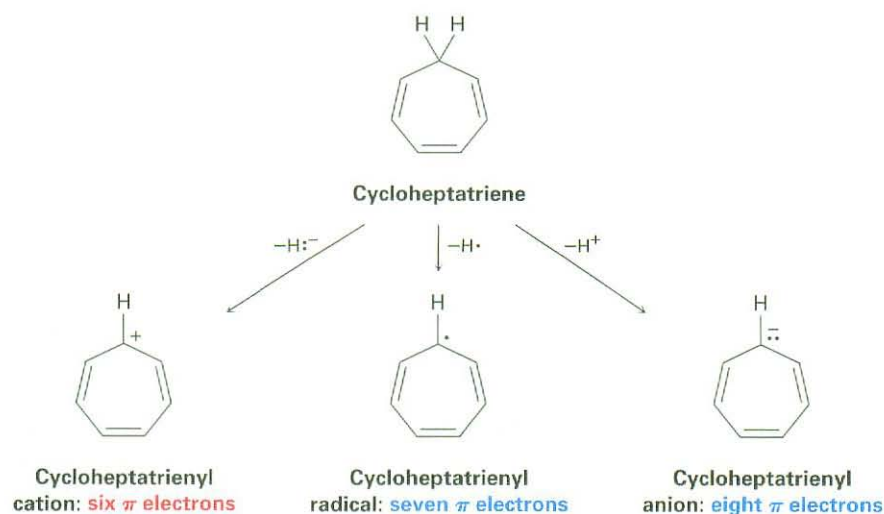
In practice, both the cyclopentadienyl cation and the radical are highly reactive and difficult to prepare. Neither shows any sign of the stability expected for an aromatic system. The six- π -electron cyclopentadienyl anion, by contrast, is easily prepared and remarkably stable. In fact, cyclopentadiene is one of the most acidic hydrocarbons known, with $\text{p}K_{\text{a}} = 16$, a value comparable to that of water! Cyclopentadiene is acidic because the anion formed by loss of H^+ is so stable (Figure 15.5).

Active Figure 15.5 An orbital view of the aromatic cyclopentadienyl anion, showing the cyclic conjugation and six π electrons in five p orbitals. The electrostatic potential map further indicates that the ion is symmetrical and that all five carbons are electron-rich (red). Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.



Similar arguments can be used to predict the relative stabilities of the cycloheptatrienyl cation, radical, and anion. Removal of a hydrogen from cycloheptatriene can generate the six- π -electron cation, the seven- π -electron radical, or the eight- π -electron anion (Figure 15.6). All three species again have numerous resonance forms, but Hückel's rule predicts that only the six- π -electron cycloheptatrienyl cation should be aromatic. The seven- π -electron cycloheptatrienyl radical and the eight- π -electron anion are antiaromatic.

Figure 15.6 Generation of the cycloheptatrienyl cation, radical, and anion. Only the six- π -electron cation is aromatic.



Both the cycloheptatrienyl radical and the anion are reactive and difficult to prepare. The six- π -electron cation, however, is extraordinarily stable. In fact, the cycloheptatrienyl cation was first prepared more than a century ago by reaction of Br_2 with cycloheptatriene (Figure 15.7), although its structure was not recognized at the time.

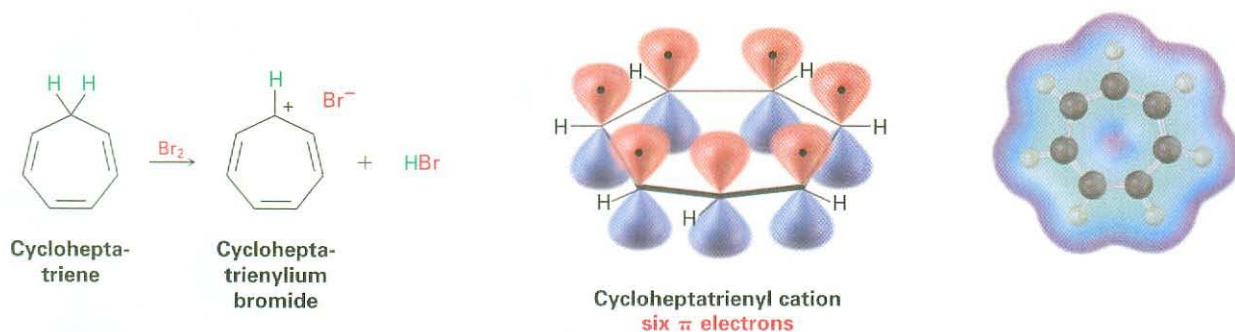
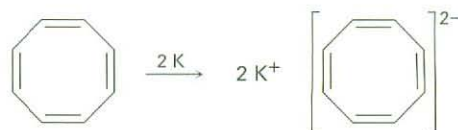


Figure 15.7 Reaction of cycloheptatriene with bromine yields cycloheptatrienyl bromide, an ionic substance containing the cycloheptatrienyl cation. The electrostatic potential map shows that all seven carbon atoms are equally charged and electron-poor (blue).

Problem 15.6 Draw the five resonance structures of the cyclopentadienyl anion. Are all carbon-carbon bonds equivalent? How many absorption lines would you expect to see in the ^1H NMR and ^{13}C NMR spectra of the anion?

Problem 15.7 Cyclooctatetraene readily reacts with potassium metal to form the stable cyclooctatetraene dianion, $\text{C}_8\text{H}_8^{2-}$. Why do you suppose this reaction occurs so easily? What geometry do you expect for the cyclooctatetraene dianion?

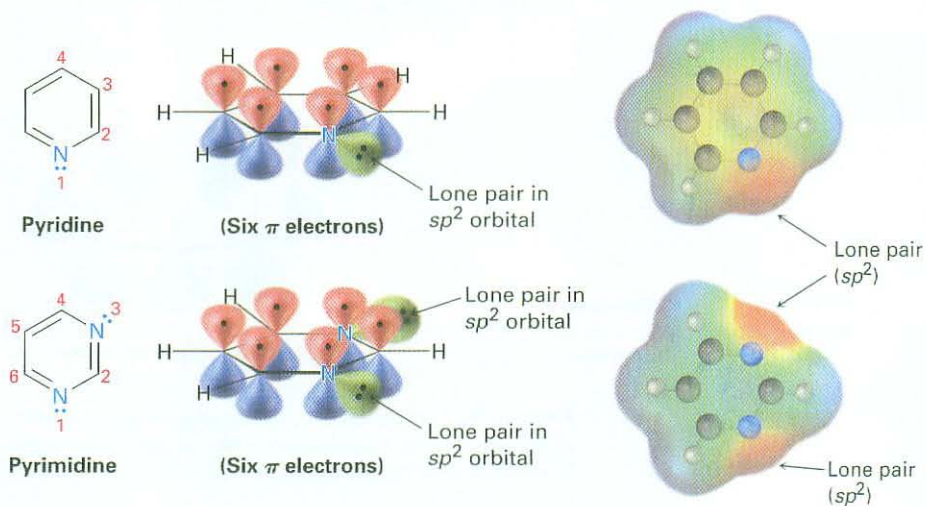


15.5 Aromatic Heterocycles: Pyridine and Pyrrole

Look back once again at the definition of aromaticity in Section 15.4: . . . a cyclic, conjugated molecule containing $4n + 2 \pi$ electrons. Nothing in this definition says that the atoms in the ring must be *carbon*. In fact, *heterocyclic* compounds can also be aromatic. A **heterocycle** is a cyclic compound that contains atoms of two or more elements in its ring, usually carbon along with nitrogen, oxygen, or sulfur. Pyridine and pyrimidine, for example, are six-membered heterocycles with nitrogen in their rings.

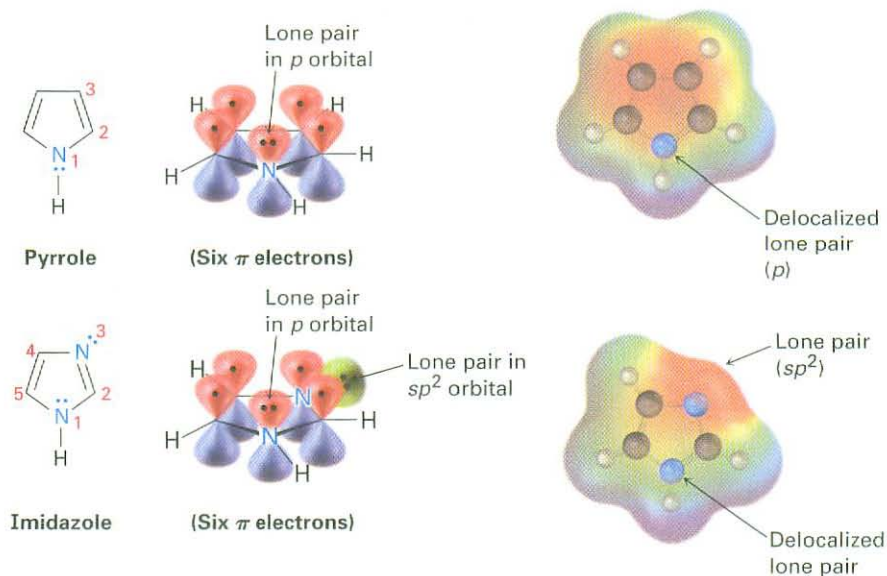
Pyridine is much like benzene in its π electron structure. Each of the five sp^2 -hybridized carbons has a p orbital perpendicular to the plane of the ring, and each p orbital contains one π electron. The nitrogen atom is also sp^2 -hybridized and has one electron in a p orbital, bringing the total to six π electrons. The nitrogen lone-pair electrons (red in an electrostatic potential map) are in an sp^2 orbital in the plane of the ring and are not part of the aromatic π system (Figure 15.8). Pyrimidine, also shown in Figure 15.8, is a benzene analog that has two nitrogen atoms in a six-membered, unsaturated ring. Both nitrogens are sp^2 -hybridized, and each contributes one electron to the aromatic π system.

Figure 15.8 Pyridine and pyrimidine are nitrogen-containing aromatic heterocycles with π electron arrangements much like that of benzene. Both have a lone pair of electrons on nitrogen in an sp^2 orbital in the plane of the ring.



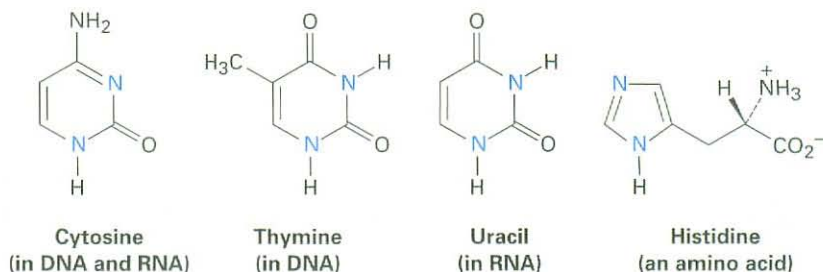
Pyrrole (two *r*'s, one *l*) and imidazole are *five*-membered heterocycles, yet both have *six* π electrons and are aromatic. In pyrrole, each of the four sp^2 -hybridized carbons contributes one π electron, and the sp^2 -hybridized nitrogen atom contributes the two from its lone pair, which occupies a p orbital (Figure 15.9). Imidazole, also shown in Figure 15.9, is an analog of pyrrole that has two nitrogen atoms in a five-membered, unsaturated ring. Both nitrogens are sp^2 -hybridized, but one is in a double bond and contributes only one electron to the aromatic π system, while the other is not in a double bond and contributes two from its lone pair.

Figure 15.9 Pyrrole and imidazole are five-membered, nitrogen-containing heterocycles but have six π electron arrangements, much like that of the cyclopentadienyl anion. Both have a lone pair of electrons on nitrogen in a p orbital perpendicular to the ring.



Note that nitrogen atoms have different roles depending on the structure of the molecule. The nitrogen atoms in pyridine and pyrimidine are both in double bonds and contribute only *one* π electron to the aromatic sextet, just as a carbon atom in benzene does. The nitrogen atom in pyrrole, however, is not in a double bond and contributes *two* π electrons (its lone pair) to the aromatic sextet. In imidazole, both kinds of nitrogen are present in the same molecule—a double-bonded “pyridine-like” nitrogen that contributes one π electron and a “pyrrole-like” nitrogen that contributes two.

Pyrimidine and imidazole rings are particularly important in biological chemistry. Pyrimidine, for instance, is the parent ring system in cytosine, thymine, and uracil, three of the five heterocyclic amine bases found in nucleic acids. An aromatic imidazole ring is present in histidine, one of the twenty amino acids found in proteins.



WORKED EXAMPLE 15.1

Accounting for the Aromaticity of a Heterocycle

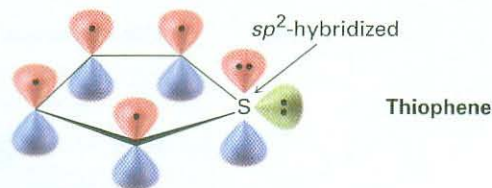
Thiophene, a sulfur-containing heterocycle, undergoes typical aromatic substitution reactions rather than addition reactions. Why is thiophene aromatic?



Thiophene

Strategy Recall the requirements for aromaticity—a planar, cyclic, conjugated molecule with $4n + 2 \pi$ electrons—and see how these requirements apply to thiophene.

Solution Thiophene is the sulfur analog of pyrrole. The sulfur atom is sp^2 -hybridized and has a lone pair of electrons in a p orbital perpendicular to the plane of the ring. Sulfur also has a second lone pair of electrons in the ring plane.



Problem 15.8 Draw an orbital picture of furan to show how the molecule is aromatic.



Problem 15.9 Thiamin, or vitamin B₁, contains a positively charged five-membered nitrogen-sulfur heterocycle called a *thiazolium* ring. Explain why the thiazolium ring is aromatic.



15.6 Why $4n + 2$?

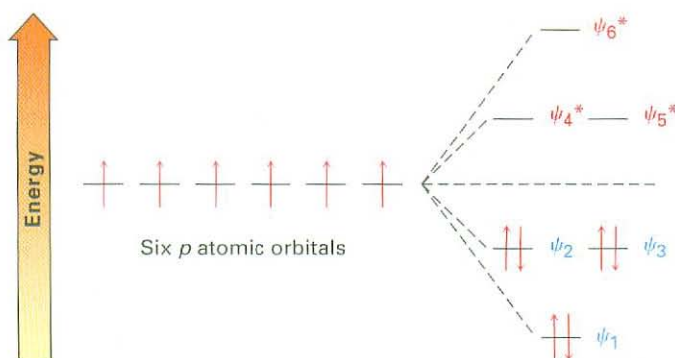
Key IDEAS

Test your knowledge of Key Ideas by using resources in ThomsonNOW or by answering end-of-chapter problems marked with ▲.

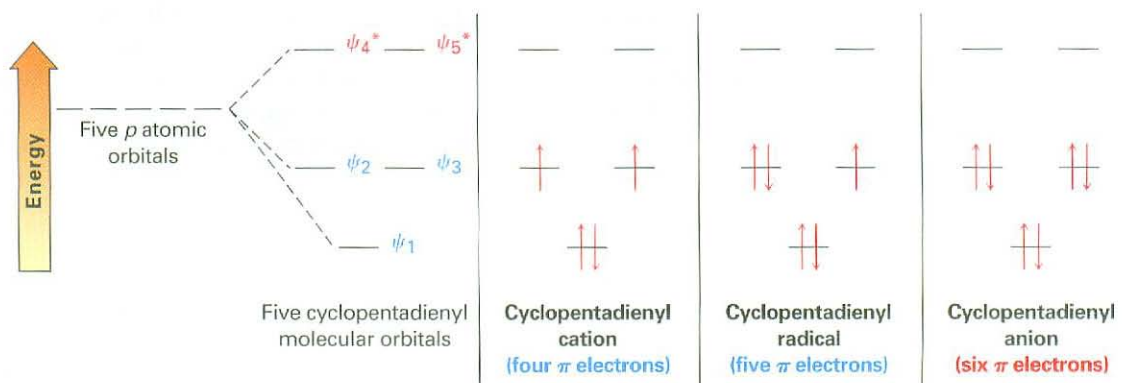
What's so special about $4n + 2 \pi$ electrons? Why do 2, 6, 10, 14 . . . π electrons lead to aromatic stability, while other numbers of electrons do not? The answer comes from molecular orbital theory. When the energy levels of molecular orbitals for cyclic conjugated molecules are calculated, it turns out that there is always a single lowest-lying MO, above which the MOs come in degenerate pairs. Thus, when electrons fill the various molecular orbitals, it takes two electrons, or one pair, to fill the lowest-lying orbital and four electrons, or two pairs, to fill each of n succeeding energy levels—a total of $4n + 2$. Any other number would leave an energy level partially filled.

The six π molecular orbitals of benzene were shown previously in Figure 15.3, and their relative energies are shown again in Figure 15.10. The lowest-energy MO, ψ_1 , occurs singly and contains two electrons. The next two lowest-energy orbitals, ψ_2 and ψ_3 , are degenerate, and it therefore takes four electrons to fill both. The result is a stable six- π -electron aromatic molecule with filled bonding orbitals.

Figure 15.10 Energy levels of the six benzene π molecular orbitals. There is a single, lowest-energy orbital, above which the orbitals come in degenerate pairs.



A similar line of reasoning carried out for the cyclopentadienyl cation, radical, and anion is shown in Figure 15.11. The five atomic p orbitals combine to give five π molecular orbitals, with a single lowest-energy orbital and degenerate pairs of higher-energy orbitals. In the four- π -electron cation, there are two electrons in ψ_1 but only one electron each in ψ_2 and ψ_3 . Thus, the cation has two orbitals that are only partially filled, and it is therefore unstable and antiaromatic. In the five- π -electron radical, ψ_1 and ψ_2 are filled but ψ_3 is still only half full. Only in the six- π -electron cyclopentadienyl anion are all the bonding orbitals filled. Similar analyses can be carried out for all other aromatic compounds.



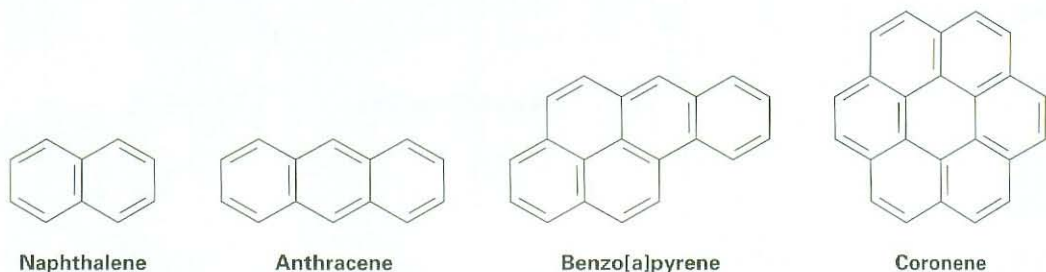
Active Figure 15.11 Energy levels of the five cyclopentadienyl molecular orbitals. Only the six- π -electron cyclopentadienyl anion has a filled-shell configuration leading to aromaticity. Sign in at www.thomsonedu.com to see a simulation based on this figure and to take a short quiz.

Problem 15.10 Show the relative energy levels of the seven π molecular orbitals of the cycloheptatrienyl system. Tell which of the seven orbitals are filled in the cation, radical, and anion, and account for the aromaticity of the cycloheptatrienyl cation.

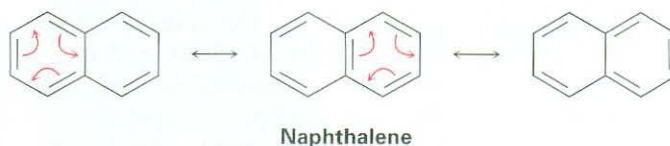
15.7 Polycyclic Aromatic Compounds

The Hückel rule is strictly applicable only to monocyclic compounds, but the general concept of aromaticity can be extended beyond simple monocyclic compounds to include *polycyclic* aromatic compounds. Naphthalene, with two

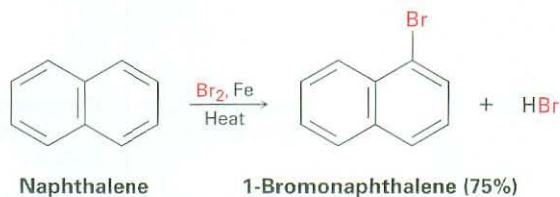
benzene-like rings fused together; anthracene, with three rings; benzo[a]pyrene, with five rings; and coronene, with six rings are all well-known aromatic hydrocarbons. Benzo[a]pyrene is particularly interesting because it is one of the cancer-causing substances found in tobacco smoke.



All polycyclic aromatic hydrocarbons can be represented by a number of different resonance forms. Naphthalene, for instance, has three.

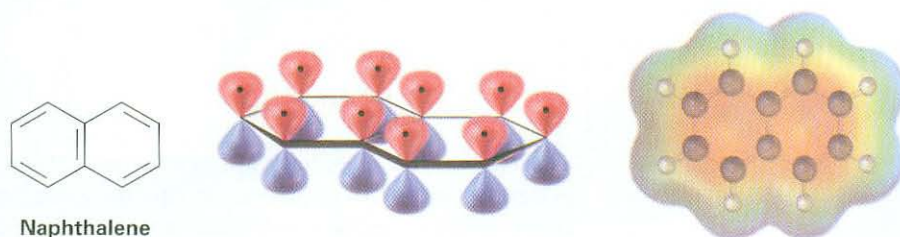


Naphthalene and other polycyclic aromatic hydrocarbons show many of the chemical properties associated with aromaticity. Thus, measurement of its heat of hydrogenation shows an aromatic stabilization energy of approximately 250 kJ/mol (60 kcal/mol). Furthermore, naphthalene reacts slowly with electrophiles such as Br_2 to give substitution products rather than double-bond addition products.



The aromaticity of naphthalene is explained by the orbital picture in Figure 15.12. Naphthalene has a cyclic, conjugated π electron system, with p orbital overlap both around the ten-carbon periphery of the molecule and across the central bond. Since ten π electrons is a Hückel number, there is π electron delocalization and consequent aromaticity in naphthalene.

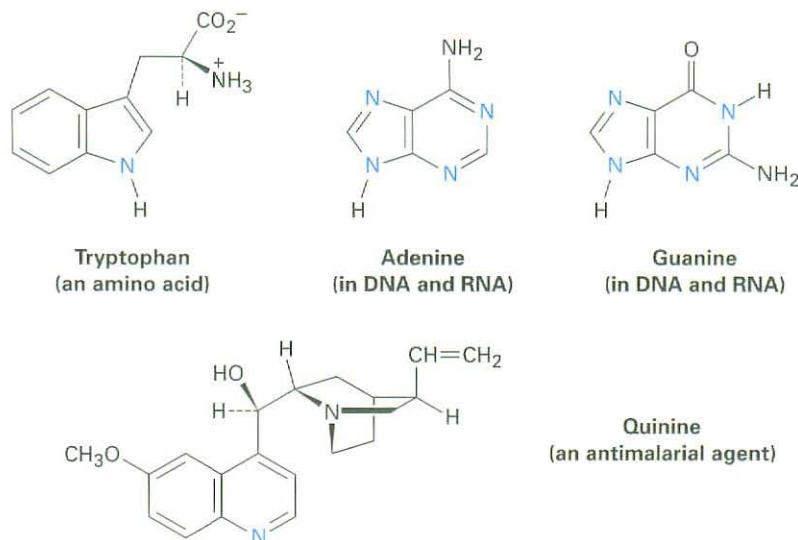
Figure 15.12 An orbital picture and electrostatic potential map of naphthalene, showing that the ten π electrons are fully delocalized throughout both rings.



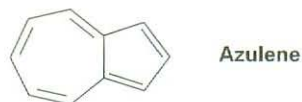
Just as there are heterocyclic analogs of benzene, there are also many heterocyclic analogs of naphthalene. Among the most common are quinoline, isoquinoline, indole, and purine. Quinoline, isoquinoline, and purine all contain pyridine-like nitrogens that are part of a double bond and contribute one electron to the aromatic π system. Indole and purine both contain pyrrole-like nitrogens that contribute two π electrons.



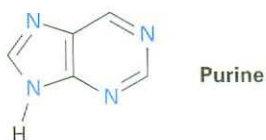
Among the many biological molecules that contain polycyclic aromatic rings, the amino acid tryptophan contains an indole ring, and the antimalarial drug quinine contains a quinoline ring. Adenine and guanine, two of the five heterocyclic amine bases found in nucleic acids, have rings based on purine.



Problem 15.11 Azulene, a beautiful blue hydrocarbon, is an isomer of naphthalene. Is azulene aromatic? Draw a second resonance form of azulene in addition to that shown.



Problem 15.12 How many electrons does each of the four nitrogen atoms in purine contribute to the aromatic π system?



15.8 Spectroscopy of Aromatic Compounds

Infrared Spectroscopy

Aromatic rings show a characteristic C–H stretching absorption at 3030 cm^{-1} and a series of peaks in the 1450 to 1600 cm^{-1} range of the infrared spectrum. The aromatic C–H band at 3030 cm^{-1} generally has low intensity and occurs just to the left of a typical saturated C–H band. As many as four absorptions are sometimes observed in the 1450 to 1600 cm^{-1} region because of complex molecular motions of the ring itself. Two bands, one at 1500 cm^{-1} and one at 1600 cm^{-1} , are usually the most intense. In addition, aromatic compounds show weak absorptions in the 1660 to 2000 cm^{-1} region and strong absorptions in the 690 to 900 cm^{-1} range due to C–H out-of-plane bending. The exact position of both sets of absorptions is diagnostic of the substitution pattern of the aromatic ring.

Monosubstituted:	690–710 cm^{-1}	<i>m</i>-Disubstituted:	690–710 cm^{-1}
	730–770 cm^{-1}		810–850 cm^{-1}
<i>o</i>-Disubstituted:	735–770 cm^{-1}	<i>p</i>-Disubstituted:	810–840 cm^{-1}

The IR spectrum of toluene in Figure 15.13 shows these characteristic absorptions.

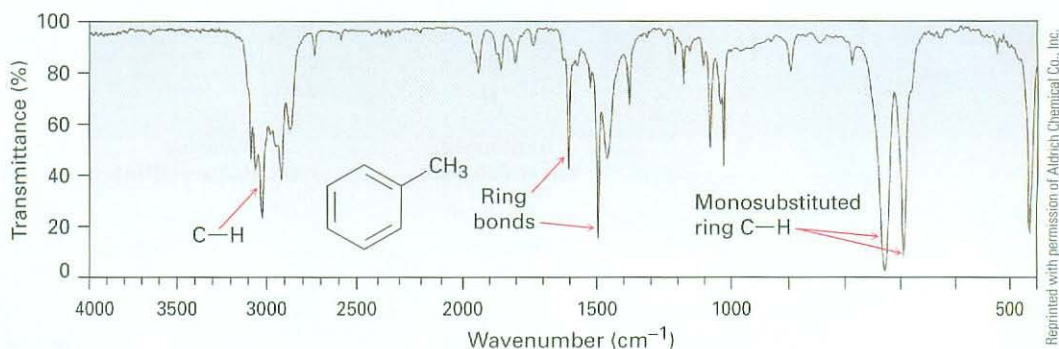


Figure 15.13 The infrared spectrum of toluene.

Ultraviolet Spectroscopy

Aromatic rings are detectable by ultraviolet spectroscopy because they contain a conjugated π electron system. In general, aromatic compounds show a series of bands, with a fairly intense absorption near 205 nm and a less intense absorption in the 255 to 275 nm range. The presence of these bands in the ultraviolet spectrum of a molecule is a sure indication of an aromatic ring.

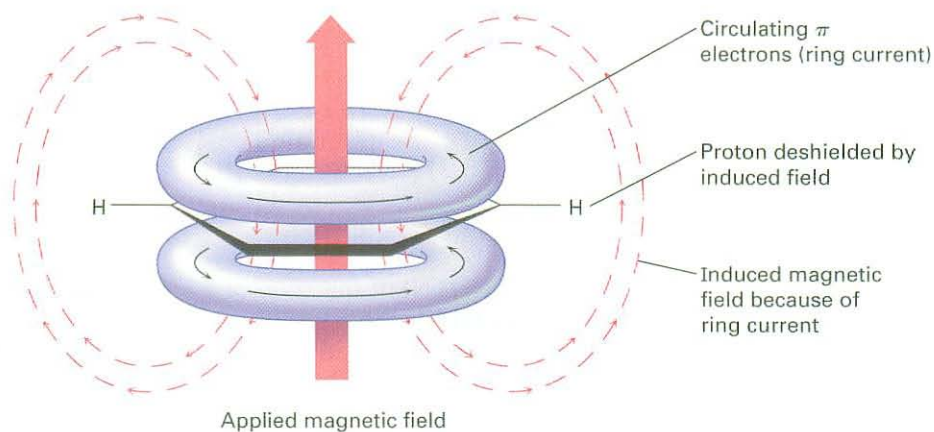
Nuclear Magnetic Resonance Spectroscopy

Hydrogens directly bonded to an aromatic ring are easily identifiable in the ^1H NMR spectrum. Aromatic hydrogens are strongly deshielded by the ring and absorb between 6.5 and $8.0\ \delta$. The spins of nonequivalent aromatic protons on substituted rings often couple with each other, giving rise to spin-spin splitting patterns that can identify the substitution of the ring.

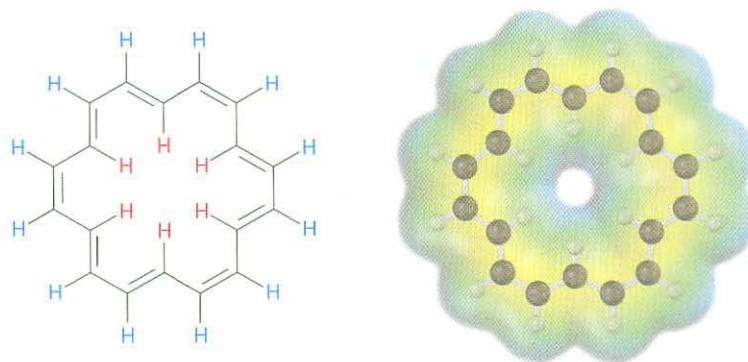
Much of the difference in chemical shift between aromatic protons (6.5 – $8.0\ \delta$) and vinylic protons (4.5 – $6.5\ \delta$) is due to a property of aromatic

rings called *ring-current*. When an aromatic ring is oriented perpendicular to a strong magnetic field, the delocalized π electrons circulate around the ring, producing a small local magnetic field. This induced field *opposes* the applied field in the middle of the ring but *reinforces* the applied field outside the ring (Figure 15.14). Aromatic protons therefore experience an effective magnetic field greater than the applied field and come into resonance at a lower applied field.

Figure 15.14 The origin of aromatic ring-current. Aromatic protons are deshielded by the induced magnetic field caused by delocalized π electrons circulating in the molecular orbitals of the aromatic ring.



Note that the aromatic ring-current produces different effects inside and outside the ring. If a ring were large enough to have both “inside” and “outside” protons, those protons on the outside would be deshielded and absorb at a field lower than normal, but those protons on the inside would be shielded and absorb at a field higher than normal. This prediction has been strikingly verified by studies on [18]annulene, an 18- π -electron cyclic conjugated polyene that contains a Hückel number of electrons ($4n + 2 = 18$ when $n = 4$). The 6 inside protons of [18]annulene are strongly shielded by the aromatic ring-current and absorb at -3.0δ (that is, 3.0 ppm *upfield* from TMS), while the 12 outside protons are strongly deshielded and absorb in the typical aromatic region at 9.3 ppm downfield from TMS.



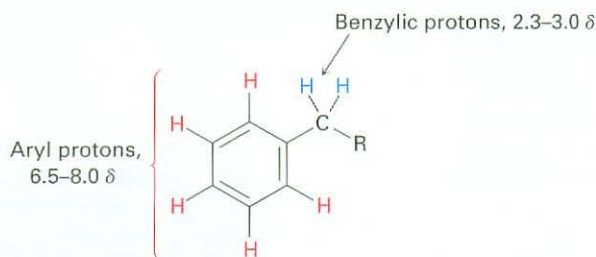
[18]Annulene

Inside H: -3.0δ

Outside H: 9.3 δ

The presence of a ring-current is characteristic of all Hückel aromatic molecules and is a good test of aromaticity. For example, benzene, a six- π -electron aromatic molecule, absorbs at 7.37 δ , but cyclooctatetraene, an eight- π -electron nonaromatic molecule, absorbs at 5.78 δ .

Hydrogens on carbon next to aromatic rings also show distinctive absorptions in the NMR spectrum. Benzylic protons normally absorb downfield from other alkane protons in the region from 2.3 to 3.0 δ .



The ^1H NMR spectrum of *p*-bromotoluene, shown in Figure 15.15, displays many of the features just discussed. The aromatic protons appear as two doublets at 7.02 and 7.45 δ , and the benzylic methyl protons absorb as a sharp singlet at 2.29 δ . Integration of the spectrum shows the expected 2:2:3 ratio of peak areas.

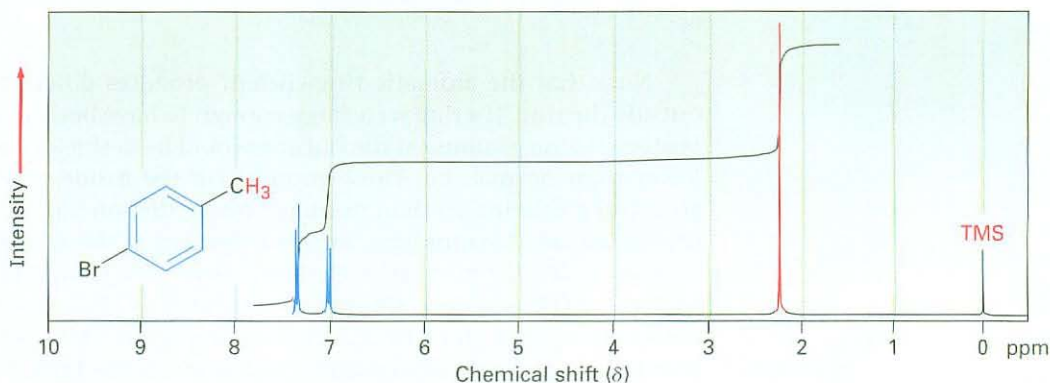
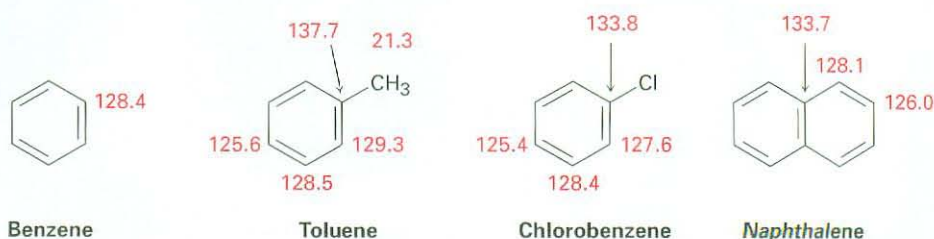


Figure 15.15 The ^1H NMR spectrum of *p*-bromotoluene.

Carbon atoms of an aromatic ring absorb in the range 110 to 140 δ in the ^{13}C NMR spectrum, as indicated by the examples in Figure 15.16. These resonances are easily distinguished from those of alkane carbons but occur in the same range as alkene carbons. Thus, the presence of ^{13}C absorptions at 110 to 140 δ does not in itself establish the presence of an aromatic ring. Confirming evidence from infrared, ultraviolet, or ^1H NMR is needed.

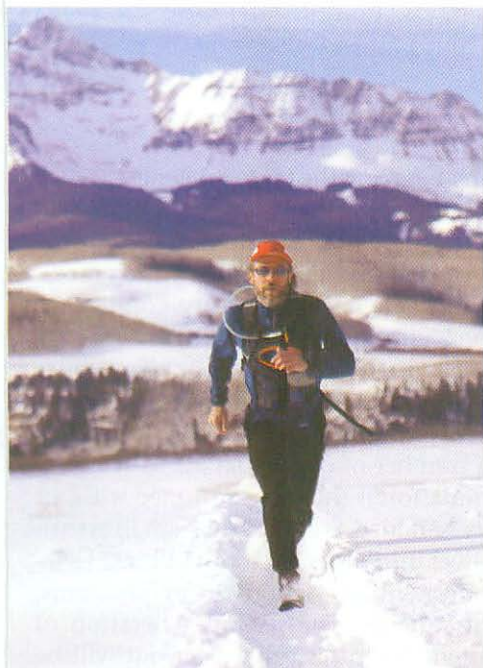
Figure 15.16 Some ^{13}C NMR absorptions of aromatic compounds (δ units).



Focus On . . .



Aspirin, NSAIDs, and COX-2 Inhibitors



© Doug Berry/Corbis

Many athletes rely on NSAIDs to help with pain and soreness.

Whatever the cause—tennis elbow, a sprained ankle, or a wrenched knee—pain and inflammation seem to go together. They are, however, different in their origin, and powerful drugs are available for treating each separately. Codeine, for example, is a powerful *analgesic*, or pain reliever, used in the management of debilitating pain, while cortisone and related steroids are potent *anti-inflammatory* agents, used for treating arthritis and other crippling inflammations. For minor pains and inflammation, both problems are often treated at the same time by using a common over-the-counter medication called an *NSAID*, or *nonsteroidal anti-inflammatory drug*.

The most common NSAID is aspirin, or acetylsalicylic acid, whose use goes back to the late 1800s. It had been known from before the time of Hippocrates in 400 BC that fevers could be lowered by chewing the bark of willow trees. The active agent in willow bark was found in 1827 to be an aromatic compound called *salicin*, which could be converted by reaction with water into salicyl alcohol and then oxidized to give salicylic acid. Salicylic acid turned out to be even more effective than salicin for reducing fevers and to have analgesic and anti-inflammatory action as well. Unfortunately, it also turned out to be too corrosive to the walls of the stomach for everyday use. Conversion of the phenol

—OH group into an acetate ester, however, yielded acetylsalicylic acid, which proved just as potent as salicylic acid but less corrosive to the stomach.

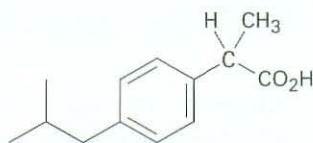


Although extraordinary in its powers, aspirin is also more dangerous than commonly believed. Only about 15 g can be fatal to a small child, and aspirin can cause stomach bleeding and allergic reactions in long-term users. Even more serious is a condition called *Reye's syndrome*, a potentially fatal reaction to aspirin sometimes seen in children recovering from the flu. As a result of these problems, numerous other NSAIDs have been developed in the last several decades, most notably ibuprofen and naproxen.

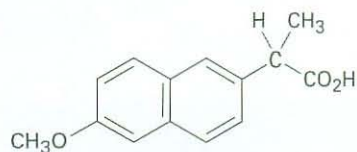
Like aspirin, both ibuprofen and naproxen are relatively simple aromatic compounds containing a side-chain carboxylic acid group. Ibuprofen, sold

(continued)

under the names Advil, Nuprin, Motrin, and others, has roughly the same potency as aspirin but is less prone to cause stomach upset. Naproxen, sold under the names Aleve and Naprosyn, also has about the same potency as aspirin but remains active in the body six times longer.



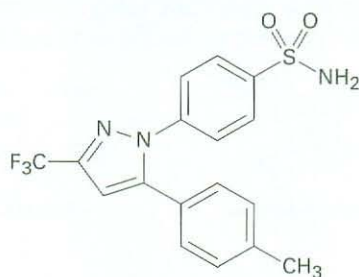
Ibuprofen
(Advil, Nuprin, Motrin)



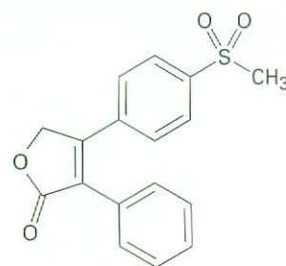
Naproxen
(Aleve, Naprosyn)

Aspirin and other NSAIDs function by blocking the cyclooxygenase (COX) enzymes that carry out the body's synthesis of prostaglandins (Sections 7.11 and 27.4). There are two forms of the enzyme, COX-1, which carries out the normal physiological production of prostaglandins, and COX-2, which mediates the body's response to arthritis and other inflammatory conditions. Unfortunately, both COX-1 and COX-2 enzymes are blocked by aspirin, ibuprofen, and other NSAIDs, thereby shutting down not only the response to inflammation but also various protective functions, including the control mechanism for production of acid in the stomach.

Medicinal chemists have devised a number of drugs that act as selective inhibitors of the COX-2 enzyme. Inflammation is thereby controlled without blocking protective functions. Originally heralded as a breakthrough in arthritis treatment, the first generation of COX-2 inhibitors, including Vioxx, Celebrex, and Bextra, turned out to cause potentially serious heart problems, particularly in elderly or compromised patients. The second generation of COX-2 inhibitors now under development promises to be safer but will be closely scrutinized for side effects before gaining approval.



Celecoxib
(Celebrex)



Rofecoxib
(Vioxx)

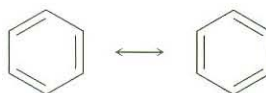
SUMMARY AND KEY WORDS

antiaromatic, 523
arene, 518
aromatic, 516
benzyl, 518
heterocycle, 528

The term **aromatic** is used for historical reasons to refer to the class of compounds related structurally to benzene. Aromatic compounds are systematically named according to IUPAC rules, but many common names are also used. Disubstituted benzenes are named as **ortho** (1,2 disubstituted), **meta** (1,3 disubstituted), or **para** (1,4 disubstituted) derivatives. The C_6H_5- unit itself is referred to as a **phenyl group**, and the $C_6H_5CH_2-$ unit is a **benzyl group**.

Hückel $4n + 2$ rule, 523
 meta (*m*), 519
 ortho (*o*), 519
 para (*p*), 519
 phenyl, 518

Benzene is described by valence-bond theory as a resonance hybrid of two equivalent structures.



Benzene is described by molecular orbital theory as a planar, cyclic, conjugated molecule with six π electrons. According to the **Hückel rule**, a molecule must have $4n + 2$ π electrons, where $n = 0, 1, 2, 3$, and so on, to be aromatic. Planar, cyclic, conjugated molecules with other numbers of π electrons are **antiaromatic**.

Other kinds of substances besides benzene-like compounds can also be aromatic. For example, the cyclopentadienyl anion and the cycloheptatrienyl cation are aromatic ions. Pyridine, a six-membered, nitrogen-containing **heterocycle**, is aromatic and resembles benzene electronically. Pyrrole, a five-membered heterocycle, resembles the cyclopentadienyl anion.

Aromatic compounds have the following characteristics:

- Aromatic compounds are cyclic, planar, and conjugated.
- Aromatic compounds are unusually stable. Benzene, for instance, has a heat of hydrogenation 150 kJ/mol less than we might expect for a cyclic triene.
- Aromatic compounds react with electrophiles to give substitution products, in which cyclic conjugation is retained, rather than addition products, in which conjugation is destroyed.
- Aromatic compounds have $4n + 2$ π electrons, which are delocalized over the ring.

EXERCISES

Organic KNOWLEDGE TOOLS

ThomsonNOW Sign in at www.thomsonedu.com to assess your knowledge of this chapter's topics by taking a pre-test. The pre-test will link you to interactive organic chemistry resources based on your score in each concept area.

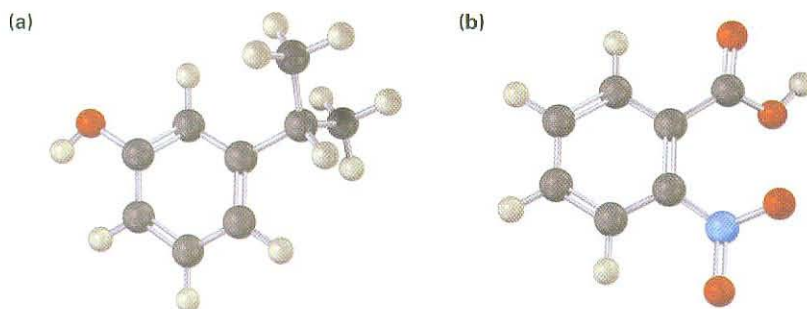
 Online homework for this chapter may be assigned in Organic OWL.

- indicates problems assignable in Organic OWL.
- ▲ denotes problems linked to Key Ideas of this chapter and testable in ThomsonNOW.

VISUALIZING CHEMISTRY

(Problems 15.1–15.12 appear within the chapter.)

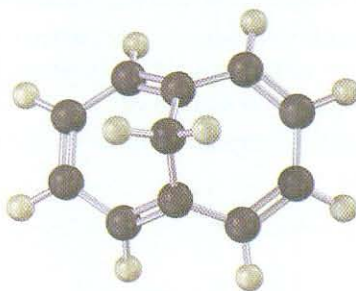
15.13 ■ Give IUPAC names for the following substances (red = O, blue = N):



- 15.14 ■ ▲ All-cis cyclodecapentaene is a stable molecule that shows a single absorption in its ^1H NMR spectrum at 5.67δ . Tell whether it is aromatic, and explain its NMR spectrum.

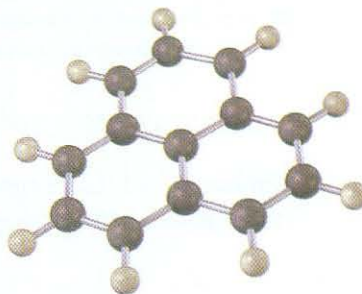


- 15.15 ■ ▲ 1,6-Methanonaphthalene has an interesting ^1H NMR spectrum in which the eight hydrogens around the perimeter absorb at 6.9 to 7.3δ , while the two CH_2 protons absorb at -0.5δ . Tell whether it is aromatic, and explain its NMR spectrum.

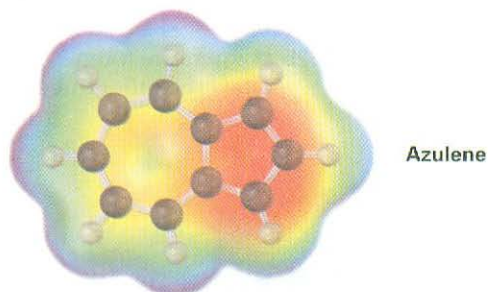


1,6-Methanonaphthalene

- 15.16 ■ The following molecular model is that of a carbocation. Draw two resonance structures for the carbocation, indicating the positions of the double bonds.

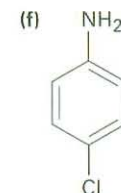
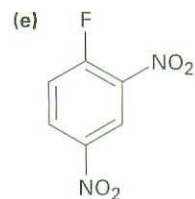
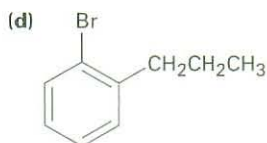
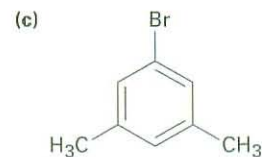
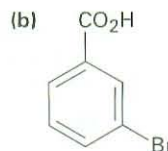
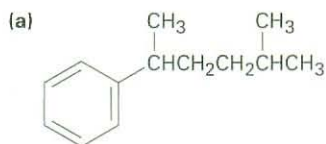


- 15.17 Azulene, an isomer of naphthalene, has a remarkably large dipole moment for a hydrocarbon ($\mu = 1.0$ D). Explain, using resonance structures.



ADDITIONAL PROBLEMS

- 15.18 ■ Give IUPAC names for the following compounds:

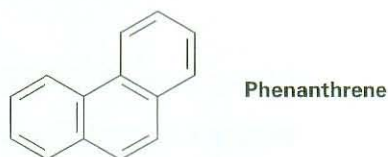


- 15.19 ■ Draw structures corresponding to the following names:
- (a) 3-Methyl-1,2-benzenediamine (b) 1,3,5-Benzenetriol
 (c) 3-Methyl-2-phenylhexane (d) *o*-Aminobenzoic acid
 (e) *m*-Bromophenol (f) 2,4,6-Trinitrophenol (picric acid)
- 15.20 ■ Draw and name all possible isomers of the following:
- (a) Dinitrobenzene (b) Bromodimethylbenzene (c) Trinitrophenol
- 15.21 ■ Draw and name all possible aromatic compounds with the formula C_7H_7Cl .
- 15.22 Draw and name all possible aromatic compounds with the formula C_8H_9Br . (There are 14.)
- 15.23 ■ ▲ Propose structures for aromatic hydrocarbons that meet the following descriptions:
- (a) C_9H_{12} ; gives only one $C_9H_{11}Br$ product on substitution with bromine
 (b) $C_{10}H_{14}$; gives only one $C_{10}H_{13}Cl$ product on substitution with chlorine
 (c) C_8H_{10} ; gives three C_8H_9Br products on substitution with bromine
 (d) $C_{10}H_{14}$; gives two $C_{10}H_{13}Cl$ products on substitution with chlorine

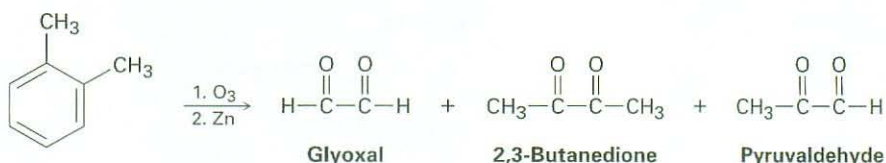
- 15.24** Look at the three resonance structures of naphthalene shown in Section 15.7, and account for the fact that not all carbon-carbon bonds have the same length. The C1-C2 bond is 136 pm long, whereas the C2-C3 bond is 139 pm long.
- 15.25** ■ There are four resonance structures for anthracene, one of which is shown. Draw the other three.



- 15.26** ■ There are five resonance structures of phenanthrene, one of which is shown. Draw the other four.



- 15.27** Look at the five resonance structures for phenanthrene (Problem 15.26) and predict which of its carbon-carbon bonds is shortest.
- 15.28** In 1932, A. A. Levine and A. G. Cole studied the ozonolysis of *o*-xylene and isolated three products: glyoxal, 2,3-butanedione, and pyruvaldehyde:



In what ratio would you expect the three products to be formed if *o*-xylene is a resonance hybrid of two structures? The actual ratio found was 3 parts glyoxal, 1 part 2,3-butanedione, and 2 parts pyruvaldehyde. What conclusions can you draw about the structure of *o*-xylene?

- 15.29** ■ 3-Chlorocyclopropene, on treatment with AgBF_4 , gives a precipitate of AgCl and a stable solution of a product that shows a single ^1H NMR absorption at 11.04 δ . What is a likely structure for the product, and what is its relation to Hückel's rule?

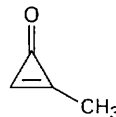


- 15.30** Draw an energy diagram for the three molecular orbitals of the cyclopropenyl system (C_3H_3). How are these three molecular orbitals occupied in the cyclopropenyl anion, cation, and radical? Which of the three substances is aromatic according to Hückel's rule?

- 15.31** Cyclopropanone is highly reactive because of its large amount of angle strain, but methylcyclopropanone, although even more strained than cyclopropanone, is nevertheless quite stable and can even be distilled. Explain, taking the polarity of the carbonyl group into account.

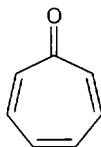


Cyclopropanone

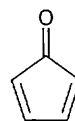


Methylcyclopropanone

- 15.32** Cycloheptatrienone is stable, but cyclopentadienone is so reactive that it can't be isolated. Explain, taking the polarity of the carbonyl group into account.

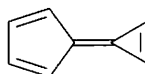


Cycloheptatrienone



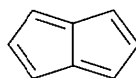
Cyclopentadienone

- 15.33** Which would you expect to be most stable, cyclononatetraenyl radical, cation, or anion?
- 15.34** How might you convert 1,3,5,7-cyclononatetraene to an aromatic substance?
- 15.35** Calicene, like azulene (Problem 15.17), has an unusually large dipole moment for a hydrocarbon. Explain, using resonance structures.

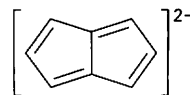


Calicene

- 15.36** Pentalene is a most elusive molecule and has never been isolated. The pentalene dianion, however, is well known and quite stable. Explain.

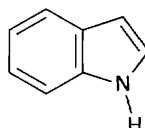


Pentalene



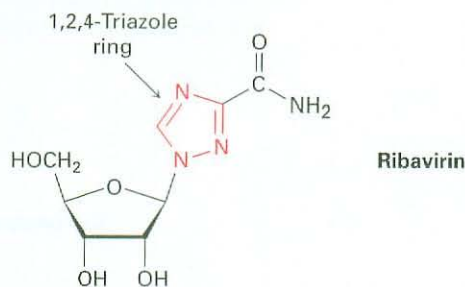
Pentalene dianion

- 15.37** Indole is an aromatic heterocycle that has a benzene ring fused to a pyrrole ring. Draw an orbital picture of indole.
- (a) How many π electrons does indole have?
- (b) What is the electronic relationship of indole to naphthalene?



Indole

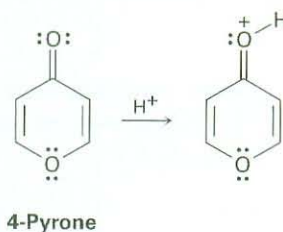
- 15.38 ■ Ribavirin, an antiviral agent used against hepatitis C and viral pneumonia, contains a 1,2,4-triazole ring. Why is the ring aromatic?



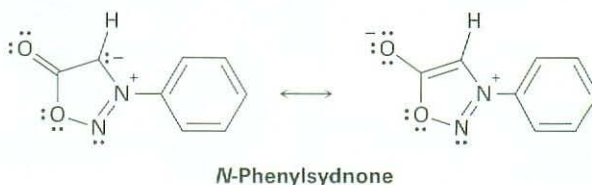
- 15.39 ■ Bextra, a COX-2 inhibitor used in the treatment of arthritis, contains an isoxazole ring. Why is the ring aromatic?



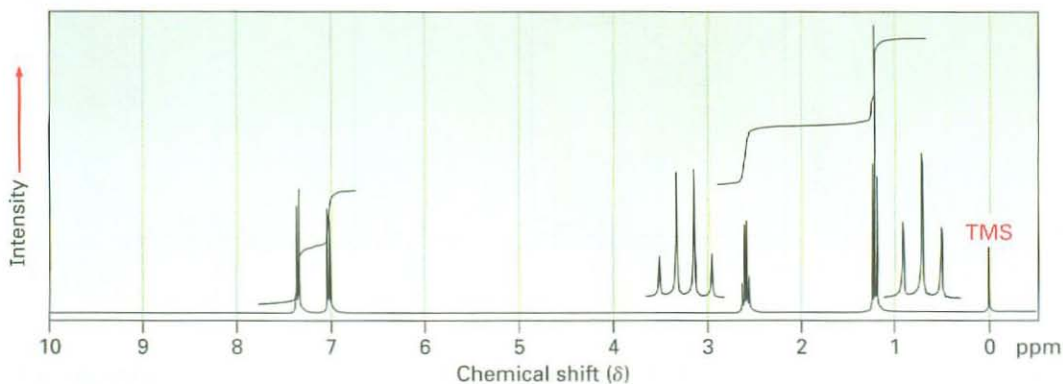
- 15.40 ■ On reaction with acid, 4-pyrone is protonated on the carbonyl-group oxygen to give a stable cationic product. Using resonance structures and the Hückel $4n + 2$ rule, explain why the protonated product is so stable.



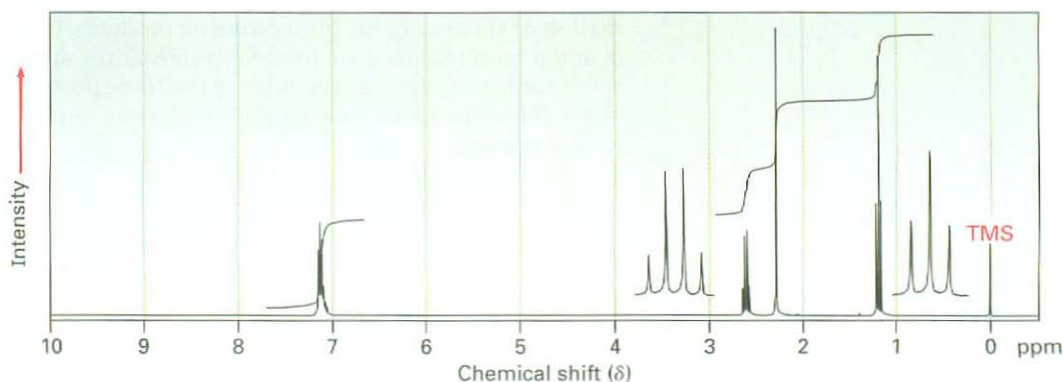
- 15.41 Compound A, C_8H_{10} , yields three substitution products, C_8H_9Br , on reaction with Br_2 . Propose two possible structures for A. The 1H NMR spectrum of A shows a complex four-proton multiplet at 7.0δ and a six-proton singlet at 2.30δ . What is the structure of A?
- 15.42 *N*-Phenylsydnone, so-named because it was first studied at the University of Sydney, Australia, behaves like a typical aromatic molecule. Explain, using the Hückel $4n + 2$ rule.



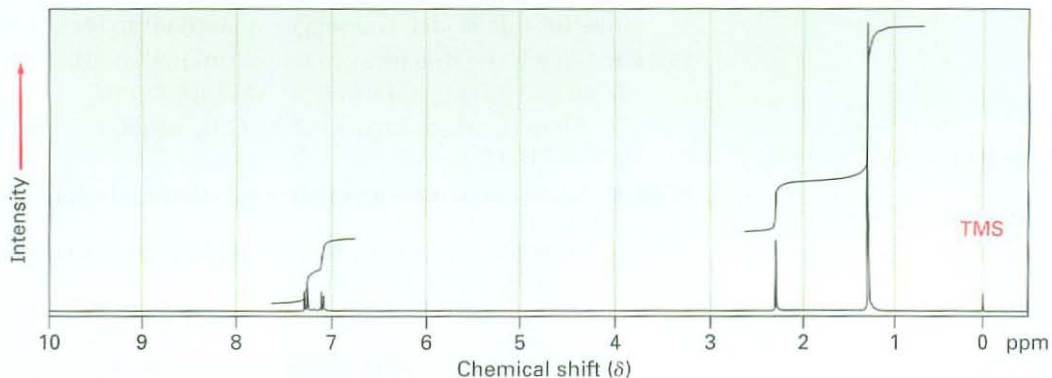
- 15.43 1-Phenyl-2-butene has an ultraviolet absorption at $\lambda_{\max} = 208 \text{ nm}$ ($\epsilon = 8000$). On treatment with a small amount of strong acid, isomerization occurs and a new substance with $\lambda_{\max} = 250 \text{ nm}$ ($\epsilon = 15,800$) is formed. Propose a structure for this isomer, and suggest a mechanism for its formation.
- 15.44 ■ What is the structure of a hydrocarbon that has $M^+ = 120$ in its mass spectrum and has the following ^1H NMR spectrum?
 7.25 δ (5 H, broad singlet); 2.90 δ (1 H, septet, $J = 7 \text{ Hz}$); 1.22 δ (6 H, doublet, $J = 7 \text{ Hz}$)
- 15.45 ■ Propose structures for compounds that fit the following descriptions:
- (a) $\text{C}_{10}\text{H}_{14}$
 H NMR: 7.18 δ (4 H, broad singlet); 2.70 δ (4 H, quartet, $J = 7 \text{ Hz}$); 1.20 δ (6 H, triplet, $J = 7 \text{ Hz}$)
 IR: 745 cm^{-1}
- (b) $\text{C}_{10}\text{H}_{14}$
 H NMR: 7.0 δ (4 H, broad singlet); 2.85 δ (1 H, septet, $J = 8 \text{ Hz}$); 2.28 δ (3 H, singlet); 1.20 δ (6 H, doublet, $J = 8 \text{ Hz}$)
 IR: 825 cm^{-1}
- 15.46 ■ Propose structures for aromatic compounds that have the following ^1H NMR spectra:
- (a) $\text{C}_8\text{H}_9\text{Br}$
 IR: 820 cm^{-1}



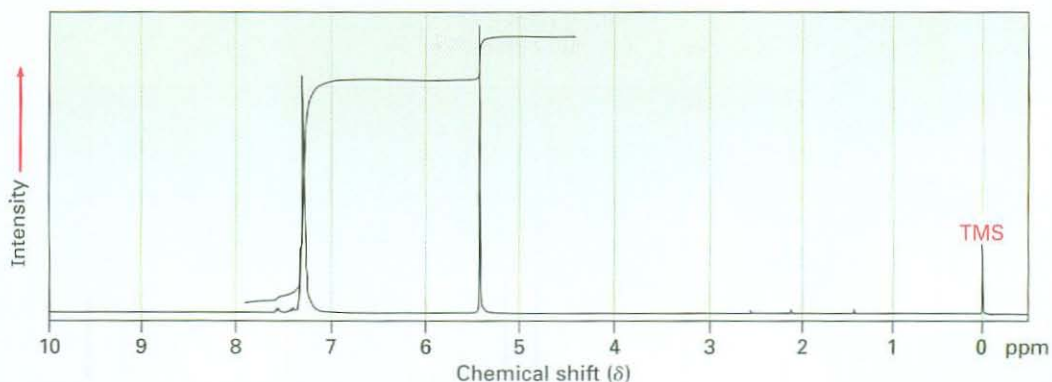
- (b) C_9H_{12}
 IR: 750 cm^{-1}



(c) $C_{11}H_{16}$
IR: 820 cm^{-1}



15.47 ■ Propose a structure for a molecule $C_{14}H_{12}$ that has the following 1H NMR spectrum and has IR absorptions at 700 , 740 , and 890 cm^{-1} :



15.48 Aromatic substitution reactions occur by addition of an electrophile such as Br^+ to the aromatic ring to yield an allylic carbocation intermediate, followed by loss of H^+ . Show the structure of the intermediate formed by reaction of benzene with Br^+ .

15.49 The substitution reaction of toluene with Br_2 can, in principle, lead to the formation of three isomeric bromotoluene products. In practice, however, only *o*- and *p*-bromotoluene are formed in substantial amounts. The meta isomer is not formed. Draw the structures of the three possible carbocation intermediates (Problem 15.48), and explain why ortho and para products predominate over meta.