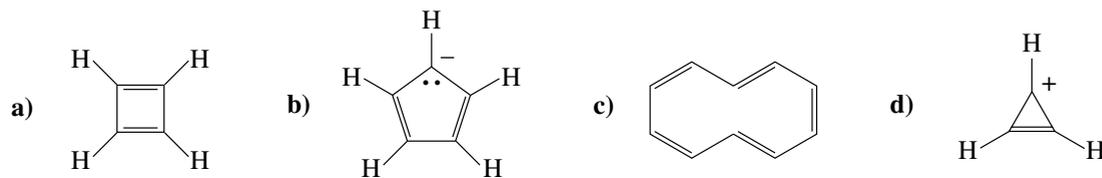


arranged about zero energy, it is necessary for one degenerate pair,  $\pi_4^{\text{nb}}$  and  $\pi_5^{\text{nb}}$ , to be located at zero energy. MOs at zero energy are termed nonbonding.) If the total number of MOs is odd, the pattern is the same with the exception that the highest-energy MO is absent. In this case the MOs can no longer be symmetrically arranged about zero energy. This arrangement is also illustrated in Figure 16.3 for the seven MOs of the cycloheptatrienyl carbocation. The exact energy of each MO is not as important as is the pattern of one lowest-energy MO and degenerate pairs with increasing energy.

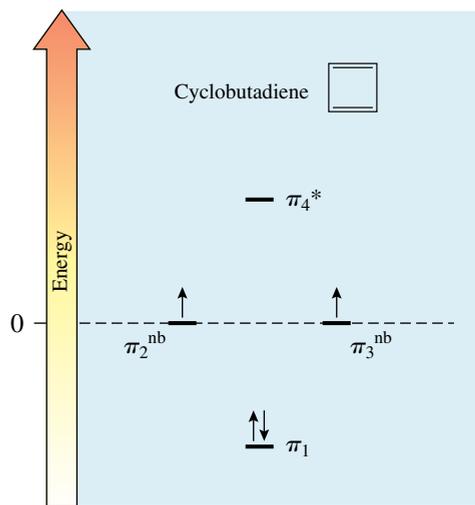
### PROBLEM 16.3

Show the patterns for the pi MO energy levels for these compounds:



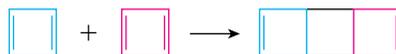
## 16.4 CYCLOBUTADIENE

Let's now examine the MO picture for cyclobutadiene and see whether we can discern why it is so much less stable than benzene. There are four  $p$  orbitals in cyclobutadiene, so there are four pi MOs. These must be arranged with one MO at lowest energy, two degenerate MOs at zero energy, and one MO at highest energy. There are four electrons in these MOs. Two of these electrons occupy the lowest-energy MO. According to Hund's rule, the two remaining electrons have the same spin and each occupies a different member of the degenerate pair of nonbonding MOs.



The difference between the electron arrangement in benzene and that in cyclobutadiene is the key to whether a cyclic, conjugated compound will be especially stable, like benzene, or especially unstable, like cyclobutadiene. Benzene has its **highest occupied molecular orbitals** (the highest-energy MOs that contain electrons, also known as **HOMOs**) completely filled with electrons. Cyclic compounds, completely conjugated around the ring, with filled HOMOs, such as benzene, are especially stable and are aromatic. In contrast, cyclobutadiene has only enough electrons that its HOMOs are half filled. Compounds with half-filled HOMOs such as cyclobutadiene are found to be especially unstable and are termed **antiaromatic**.

Cyclobutadiene is a highly reactive compound. As mentioned previously, numerous attempts to prepare it failed because of this high reactivity. However, it can be prepared and studied at very low temperatures, below 35 K. Such studies indicate that it does not have a square geometry, as would be suggested by the resonance structures shown on page 646. Rather, it has a rectangular geometry, with shorter double bonds alternating with longer single bonds. Such bond alternation relieves some of the antiaromatic destabilization by decreasing the overlap between the *p* orbitals where the longer bonds occur and is characteristic of compounds that are not aromatic. When a sample of cyclobutadiene is allowed to warm above 35 K, the molecules react rapidly to form dimers that are no longer conjugated and therefore are no longer antiaromatic.

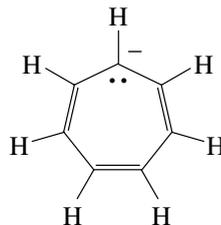


#### PROBLEM 16.4

Add the appropriate number of electrons to the MO energy level diagram for cyclooctatetraene in Figure 16.3. Is this compound aromatic or antiaromatic?

#### PROBLEM 16.5

Add the appropriate number of electrons to the MO energy level diagram for the cycloheptatrienyl cation in Figure 16.3. Is this ion aromatic or antiaromatic? The cycloheptatrienyl anion has two more electrons than the cation. Do you expect this anion to be a stable species? Explain.



Cycloheptatrienyl anion

#### PROBLEM 16.6

Add electrons to the MO energy level diagrams for the compounds in parts b, c, and d of Problem 16.3, and predict whether each is aromatic or antiaromatic.

## 16.5 HÜCKEL'S RULE

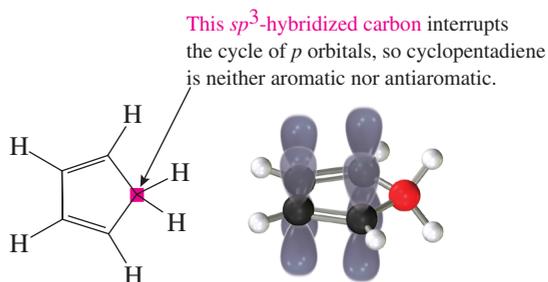
All cyclic, conjugated molecules have one lowest-energy pi MO and pairs of degenerate MOs at higher energies. Whether a compound is aromatic or antiaromatic depends on the number of electrons occupying these MOs. An aromatic compound has its HOMOs completely filled with electrons. Therefore, it must have two electrons in the lowest-energy MO plus some multiple of four electrons so that the HOMOs are filled. (Another way of stating this is that it must have an odd number of pairs of electrons, one pair for the lowest-energy MO and an even number of pairs to fill the occupied degenerate MOs.)

The criteria for a compound to be aromatic were developed by Erich Hückel.

### ▶ HÜCKEL'S RULE

Cyclic, fully conjugated, planar molecules with  $4n + 2$  pi electrons ( $n = \text{any integer including zero}$ ) are aromatic.

Let's analyze each aspect of this rule. First, the molecule must have a ring with a series of conjugated  $p$  orbitals that extends completely around the cycle, like benzene. If the cycle of conjugated orbitals is interrupted, as in the case of cyclopentadiene, then the compound is neither aromatic nor antiaromatic. It is just an alkene.



Second, the ring must be planar so that the  $p$  orbitals overlap in pi fashion completely around the cycle. If the ring is not planar, the  $p$  orbitals are twisted so that they are not parallel, resulting in a decrease in overlap. This decreases or even eliminates the aromatic or antiaromatic effect of the conjugation.

Finally, the number of pi electrons must equal 2 plus a multiple of 4 (or  $4n + 2$  pi electrons). Some of the possible numbers are as follows:

$n$	$4n + 2$	Number of pairs
0	2	1
1	6	3
2	10	5
3	14	7

As we have seen, benzene, with its six pi electrons (sometimes called an aromatic sextet), is the prototypical aromatic compound.

The criteria for an antiaromatic compound can be generalized in a similar manner. The requisite number of electrons to have the HOMOs half filled is a multiple of four (an even number of pairs). Therefore, cyclic, fully conjugated, planar molecules with  $4n$  pi electrons are antiaromatic. Some of the possible numbers of electrons are as follows:

$n$	$4n$	Number of pairs
1	4	2
2	8	4
3	12	6

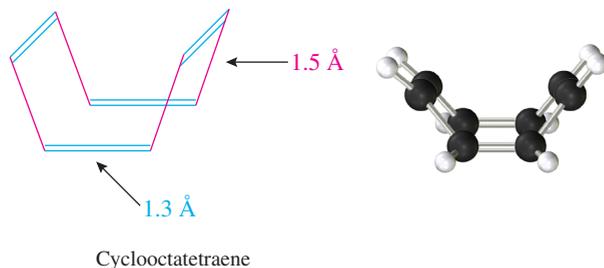
Some additional examples will help clarify this concept and illustrate its usefulness in predicting and explaining experimental observations.

### PROBLEM 16.7

Use Hückel's rule to predict whether each of the compounds in problem 16.3 is aromatic or not.

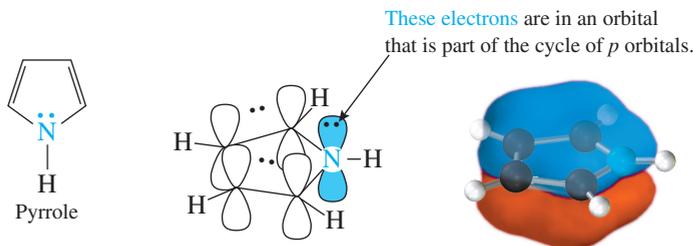
## 16.6 CYCLOOCTATETRAENE

Cyclooctatetraene has four double bonds, so it has eight pi electrons. This is a multiple of 4, so cyclooctatetraene would be antiaromatic if it were planar. However, planar cyclooctatetraene would have considerable angle strain because its bond angles would be  $135^\circ$  rather than the trigonal planar bond angle of  $120^\circ$ . To relieve both antiaromatic destabilization and angle strain, cyclooctatetraene adopts a nonplanar, tub-shaped geometry. Each double bond is twisted relative to the adjacent double bonds so that the  $p$  orbitals of one are nearly perpendicular to those of the adjacent double bonds. Therefore, cyclooctatetraene behaves as a normal, nonconjugated alkene. It can be readily prepared and isolated, and it does not show any of the special instability associated with antiaromatic compounds. Nor does it have any features of the special stability associated with aromatic compounds. It exhibits bond alternation—that is, shorter double bonds alternating with longer single bonds—and reacts with bromine to give addition products. It is said to be nonaromatic.

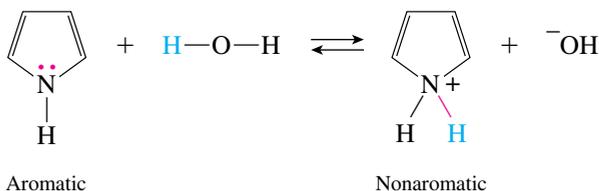


## 16.7 HETEROCYCLIC AROMATIC COMPOUNDS

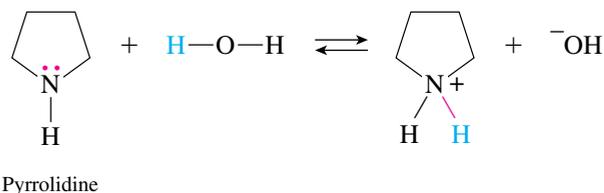
A heterocyclic compound is one that has an atom other than carbon as one of the ring atoms. The compound with a five-membered ring that has two double bonds and a nitrogen atom is called pyrrole.



It is a planar molecule, and the pair of electrons on the nitrogen is in a  $p$  orbital that is parallel to the  $p$  orbitals of the ring double bonds. Therefore, pyrrole has a series of conjugated  $p$  orbitals that extend completely around the ring and that contain a total of six electrons: two from the nitrogen and four from the double bonds. It is an aromatic compound. On the basis of its heat of combustion, its aromatic resonance energy is calculated to be 21 kcal/mol (88 kJ/mol). It undergoes substitution reactions like benzene, rather than addition reactions like alkenes. Furthermore, it is much less basic than other amines. As can be seen in the following equation, the nitrogen of its conjugate acid does not have an electron pair to contribute to the cycle, so it is no longer aromatic. In other words, the electrons on the nitrogen of pyrrole are part of an aromatic sextet. If they are used to form a bond to a proton in an acid–base reaction, the aromatic stabilization of pyrrole is lost.

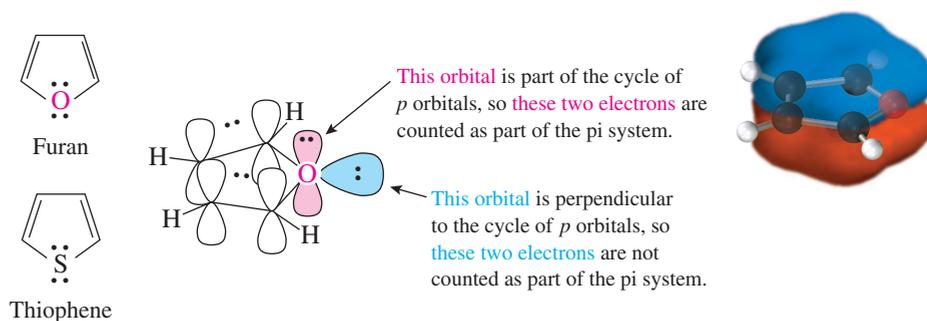


Pyrrole is about  $10^{14}$  times weaker as a base than is pyrrolidine, the five-membered nitrogen heterocycle that has no double bonds, because the basic pair of electrons on the nitrogen of pyrrolidine is not part of an aromatic cycle.



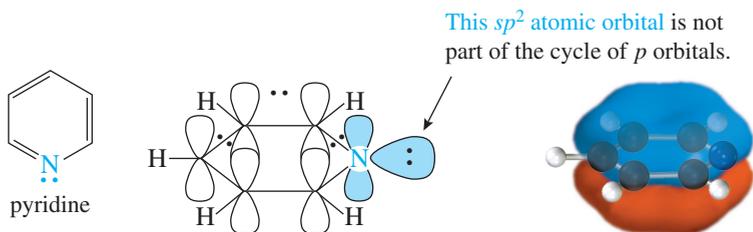
The oxygen analog of pyrrole is furan. In this case, one pair of electrons on the oxygen is part of an aromatic sextet while the other is in an  $sp^2$  hybrid AO that lies in the plane of the ring and is not part of the aromatic cycle. The sulfur analog, thiophene, has a similar structure. Both furan and thiophene are aromatic compounds that exhibit sub-

stitution reactions. From their heats of combustion the resonance energies of furan and thiophene are calculated to be 16 kcal/mol (67 kJ/mol) and 29 kcal/mol (121 kJ/mol), respectively.



The differing amounts of aromatic stabilization for benzene, pyrrole, furan, and thiophene demonstrate that aromatic stabilization occurs in varying degrees, depending on the structure of the compound. Some compounds have a large aromatic stabilization that dramatically affects their stabilities and chemical reactions. Others may have only a small stabilization and have stabilities and reactions that are more comparable to a normal alkene.

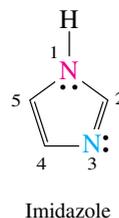
Pyridine has a six-membered ring containing a nitrogen atom and is the nitrogen analog of benzene. The electrons on the nitrogen are in an  $sp^2$  orbital in the plane of the ring like the electrons of the carbon–hydrogen bonds and are not part of the cycle of pi electrons. Pyridine has six electrons in its pi MOs and is aromatic.



Because the unshared electron pair on the nitrogen is not part of the aromatic pi electron system, pyridine is a much stronger base than pyrrole. Recall that pyridine is used as a basic solvent in a number of reactions.

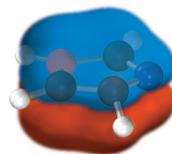
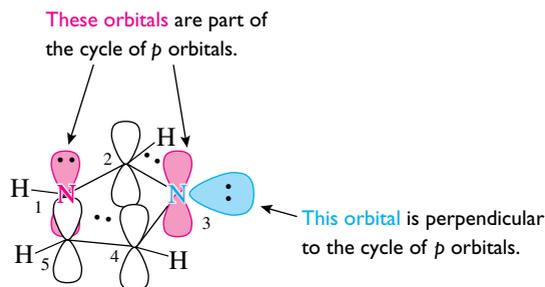
### PRACTICE PROBLEM 16.1

Determine which electrons of imidazole are in orbitals that are part of the conjugated cycle of  $p$  orbitals and which are not. Explain whether imidazole is aromatic or not.

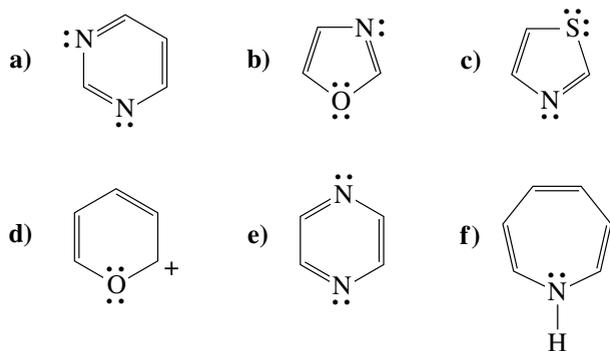


**Solution**

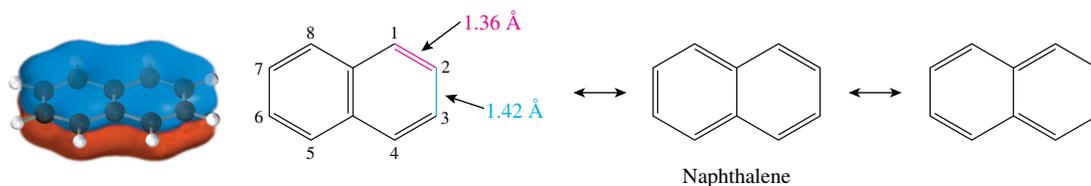
Nitrogen 1 (red) is like the nitrogen of pyrrole. Its electron pair is in a  $p$  orbital that is part of the conjugated cycle. In contrast, nitrogen 3 (blue) is like the nitrogen of pyridine. Its electron pair is in an  $sp^2$  hybrid AO that is perpendicular to the conjugated cycle of  $p$  orbitals, so these electrons are not counted. (Only one orbital on an atom can be part of the conjugated cycle. Because the  $p$  orbital of the double bond is part of the cycle, the other orbital on N-3 cannot be part of the cycle.) Overall imidazole has six electrons in the cycle, the four electrons of the two double bonds, and the two electrons on N-1, so it is aromatic.

**PROBLEM 16.8**

Explain whether each of these compounds is aromatic, antiaromatic, or nonaromatic:

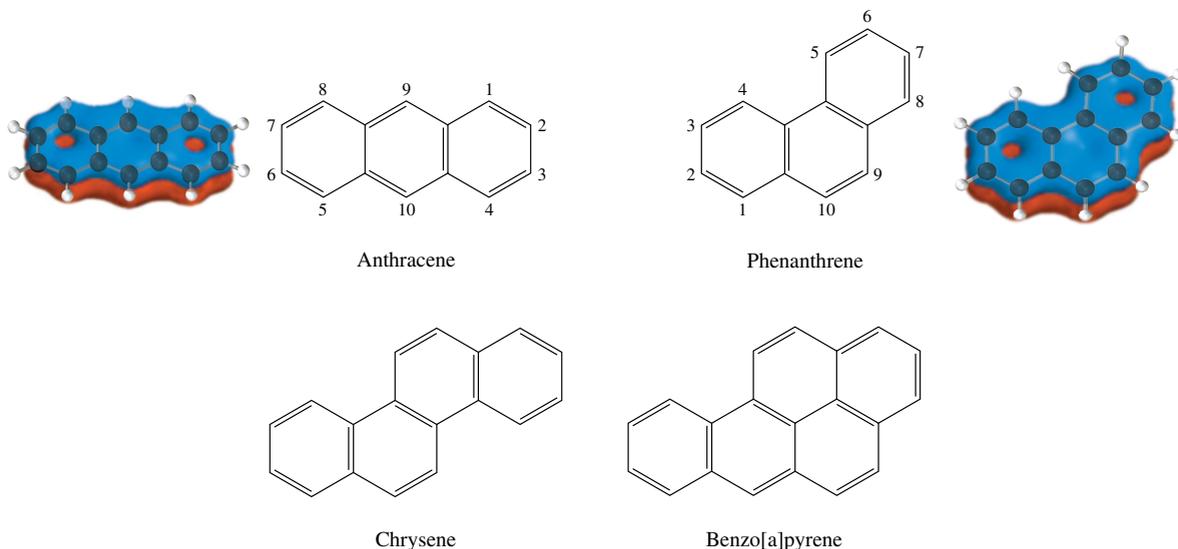
**16.8 POLYCYCLIC AROMATIC HYDROCARBONS**

Polycyclic aromatic hydrocarbons have two or more benzene rings fused together. The simplest example is naphthalene. Hückel's rule does not apply to such fused ring systems. However, if the individual rings that are fused to form the polycyclic compound are aromatic, then the fused compound is also considered to be aromatic. Naphthalene, formed by fusing two benzene rings, is aromatic, although it is not expected to have as much resonance stabilization as two benzenes. This is confirmed experimentally. On the basis of its heat of combustion, the resonance energy for naphthalene has been calculated to be 61 kcal/mol (255 kJ/mol), a value that is larger than that of benzene (36 kcal/mol [151 kJ/mol]), although not twice as large.



Three resonance structures can be written for naphthalene. Note that the C-1—C-2 bond is a double bond in two of these structures and a single bond in one, while the C-2—C-3 bond is a single bond in two structures and a double bond in one. This explains why the C-1—C-2 bond is shorter than the C-2—C-3 bond.

Anthracene and phenanthrene are isomeric compounds with three fused benzene rings. Their resonance energies are calculated to be 84 kcal/mol (352 kJ/mol) and 92 kcal/mol (385 kJ/mol), respectively. Many other polycyclic aromatic hydrocarbons are known. Chrysene and benzo[a]pyrene are typical examples.



These compounds all possess considerable aromatic stabilization. They undergo substitution reactions like benzene, although some of them have pi bonds that are more reactive than those of benzene.

### PROBLEM 16.9

Draw the five resonance structures for phenanthrene. Based on examination of these structures, which carbon–carbon bond of phenanthrene should be the shortest?

### PROBLEM 16.10

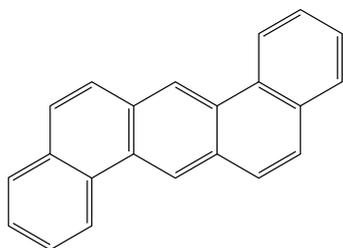
Reaction of phenanthrene with  $\text{Br}_2$  produces  $\text{C}_{14}\text{H}_{10}\text{Br}_2$ . This reaction occurs at the bond with the most double bond character. Show the structure of this product. Qualitatively compare the amount of resonance energy lost on formation of this product to the amount that would be lost if the addition were to occur at a different bond.

## Focus On

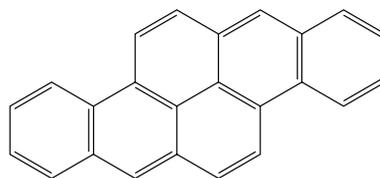
### Carcinogenic Polycyclic Aromatic Hydrocarbons

The first case of an environmental carcinogen was identified by an English surgeon, Percivall Pott, in 1775. He recognized a high incidence of scrotal cancer among chimney sweeps and correctly identified the causative agent as the coal soot to which they were continuously exposed. In the 1930s, some of the polycyclic aromatic hydrocarbons (PAH) found in coal soot were proved to be carcinogenic.

Incomplete combustion of carbonaceous material produces a wide variety of polycyclic aromatic hydrocarbons because these compounds are relatively stable and have a high ratio of carbon to hydrogen. Some of the highly carcinogenic compounds that are produced are benzo[*a*]pyrene, dibenz[*a,h*]anthracene, and dibenz[*a,h*]pyrene. These compounds are produced by the combustion of fossil fuels and are also found in tobacco smoke and automobile exhaust.



Dibenz[*a,h*]anthracene

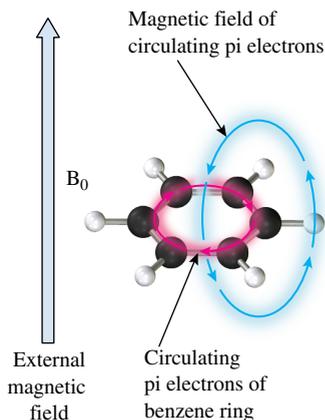


Dibenz[*a,h*]pyrene

Although the mode of action of these compounds is not completely known, one idea is that they bind to DNA by sliding between its aromatic bases. Then oxidation of a reactive double bond in the PAH produces an epoxide intermediate that reacts with the DNA to initiate the carcinogenic process.

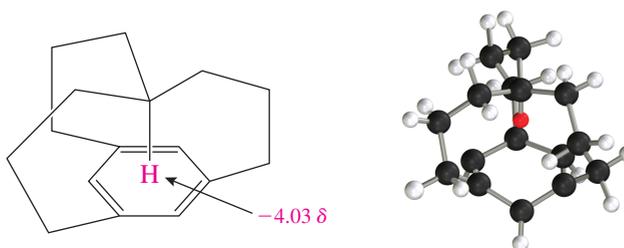
## 16.9 NMR AND AROMATICITY

It can be difficult to determine whether some compounds have any aromatic character or not based on their chemical reactions, especially if the amount of aromatic stabilization is small. In such situations, NMR spectroscopy provides another useful criterion for aromaticity. As discussed in Chapter 14, the hydrogens on a benzene ring usually appear in the region of 7 to 8  $\delta$  in the  $^1\text{H}$ -NMR spectrum, significantly downfield from the position for hydrogens on alkene double bonds. This downfield shift is a result of a “ring current” that results from circulation of the pi electrons when the molecule is placed in the external magnetic field of the NMR instrument. The circulating electrons generate



a magnetic field that is opposed to the external magnetic field in the center of the ring but is parallel to the external magnetic field outside the ring in the region where the hydrogens are located.

Because the induced field is parallel to the external field where the hydrogens are located, less external field is needed to reach the total field required for the absorption of the electromagnetic radiation and the hydrogens appear at a downfield position. Of course, if a hydrogen is held near the center of the ring, an upfield shift is observed. As an example, the bridges in the following compound force the red proton to sit directly above the benzene ring. This hydrogen appears upfield from TMS at the extremely high field position of  $-4.03 \delta$ !



This ring current in benzene is termed **diamagnetic** and is characteristic of aromatic compounds in general. The presence of a diamagnetic ring current provides a useful experimental criterion for the presence of aromaticity in a compound. Other examples of the use of this method are provided in Section 16.10.

Antiaromatic compounds exhibit a different ring current, termed **paramagnetic**, that induces a magnetic field that is parallel to the external magnetic field in the center of the ring and opposed to it outside the ring. This causes hydrogens on the outside of the ring to appear upfield from the position of normal alkene hydrogen, a result that is exactly the opposite of the effect found with aromatic compounds.

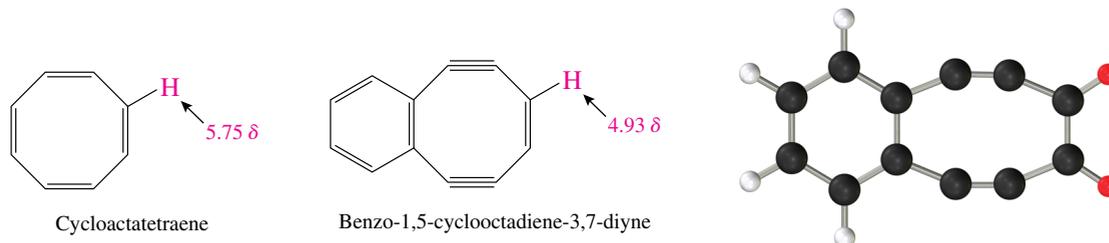
An example of this effect is provided by tri-*tert*-butylcyclobutadiene. This compound is stable at room temperature for a brief time because the bulky *tert*-butyl groups retard the dimerization reaction that destroys less hindered cyclobutadienes. The ring hydrogen of this compound appears at  $5.38 \delta$ , a position somewhat upfield from that of the hydrogens of a nonaromatic model compound such as cyclobutene ( $5.95 \delta$ ).



Tri-*tert*-butylcyclobutadiene

Because of its nonplanar geometry, cyclooctatetraene is not antiaromatic and its hydrogens appear at  $5.75 \delta$ , a value typical for alkenes. However, the triple bonds of the compound called benzo-1,5-cyclooctadiene-3,7-diyne force this molecule to assume a nearly planar geometry. The pi system of its eight-membered ring contains eight electrons. (Only two of the electrons of each triple bond are part of the conjugated system.)

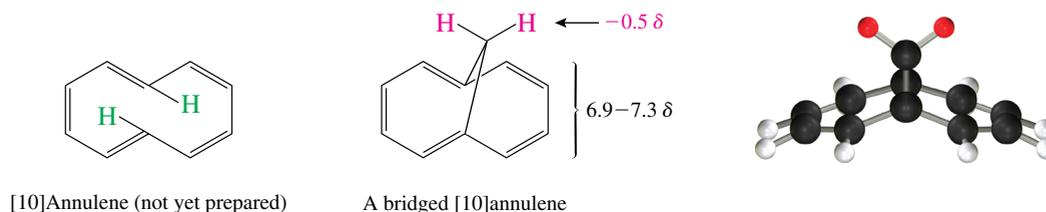
The hydrogens on the double bond of the eight-membered ring appear upfield at  $4.93 \delta$ , indicating that this compound has some antiaromatic character.



## 16.10 ANNULENES

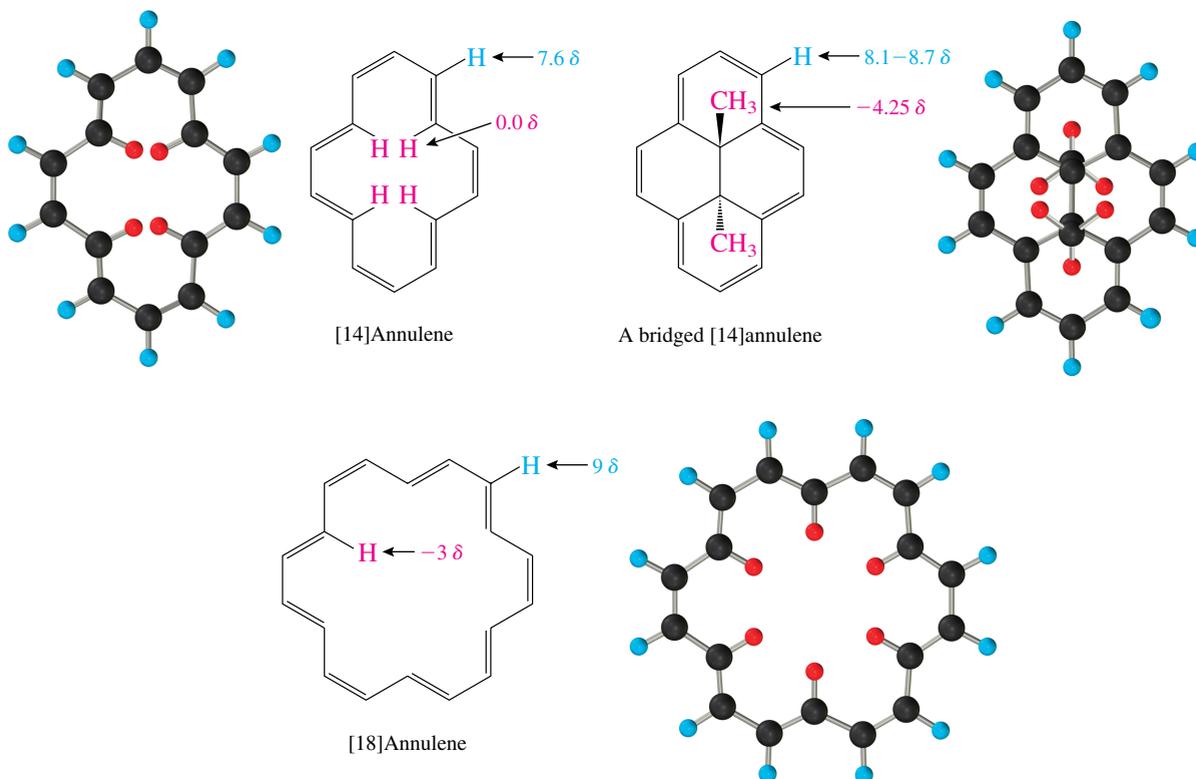
The general name **annulene** is sometimes given to rings that contain alternating single and double bonds in a single Lewis structure. Thus, benzene can be called [6]annulene, and cyclooctatetraene can be called [8]annulene. A number of larger annulenes have been prepared to determine whether they follow Hückel's rule and are aromatic when they have  $4n + 2$  electrons in the cycle.

The larger members of this series would have considerable angle strain if they were planar and had only cis double bonds. The incorporation of trans double bonds provides a way to relieve this angle strain, although this often introduces steric strain resulting from atoms on opposite sides of the ring being forced into the same region of space. Consider, for example, [10]annulene. With two trans double bonds it has no angle strain, but **the two hydrogens that point into the interior of the ring** cause so much steric strain that attempts to prepare this compound have not yet been successful. However, the compound with a  $\text{CH}_2$  bridge in place of the offending hydrogens has been prepared. Although the bridge causes the ring to be somewhat distorted from planarity, the compound does show the presence of a diamagnetic ring current typical of an aromatic compound. The hydrogens on the periphery of the ring appear at  $6.9$  to  $7.3 \delta$ , and the hydrogens on the bridge, which are held over the face of the ring, appear at the substantially upfield position of  $-0.5 \delta$ . (The hydrogens of a typical  $\text{CH}_2$  group attached to a carbon-carbon double bond appear near  $2 \delta$ .)



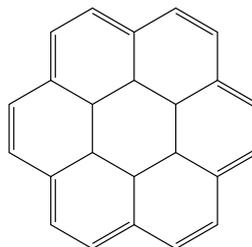
The hydrogens inside the ring of the [14]annulene with four trans double bonds appear at  $0.0 \delta$  and the hydrogens on the outside of the ring appear at  $7.6 \delta$ , indicating the presence of a diamagnetic ring current. However, the steric strain caused by the hydrogens inside the ring makes this compound quite reactive. The bridged [14]annulene, where these steric interactions are absent, is stable and has many characteristics of an

aromatic compound. The bond distances are all near 1.4 Å, it undergoes substitution reactions rather than addition reactions, the outer hydrogens appear at 8.1 to 8.7  $\delta$ , and the hydrogens of the methyl groups appear at  $-4.25 \delta$ . As a final example, the hydrogens on the inside of the ring of [18]annulene appear at  $-3 \delta$  and the outside hydrogens appear at 9  $\delta$ .



### PROBLEM 16.11

The  $^1\text{H-NMR}$  spectrum of this compound shows absorptions in the region of 9.5  $\delta$  and other absorptions in the region of  $-7 \delta$ . Explain which hydrogens are responsible for each of these absorptions.

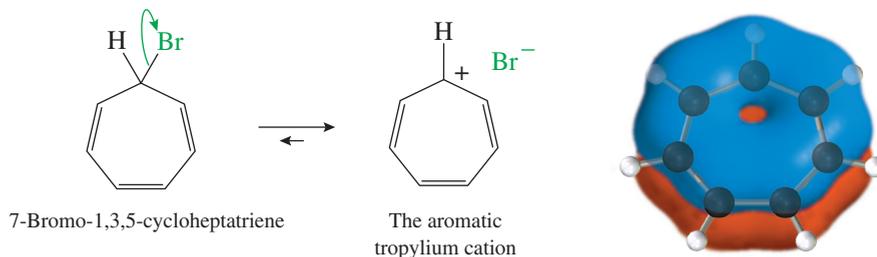


### MODEL BUILDING PROBLEM 16.1

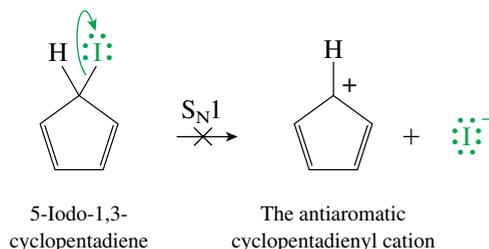
Build models of [10]annulene and the bridged [10]annulene discussed on the previous page and examine the strain and planarity of each.



The cycloheptatrienyl carbocation, also known as the tropylium cation, has six pi electrons. It is also aromatic and is quite stable. In fact, 7-bromo-1,3,5-cycloheptatriene actually exists as an ionic compound.



In contrast, the cyclopentadienyl carbocation, which has four pi electrons and is antiaromatic, is quite unstable. Thus, 5-iodo-1,3-cyclopentadiene is unreactive under conditions in which iodocyclopentane reacts rapidly by an S<sub>N</sub>1 mechanism.

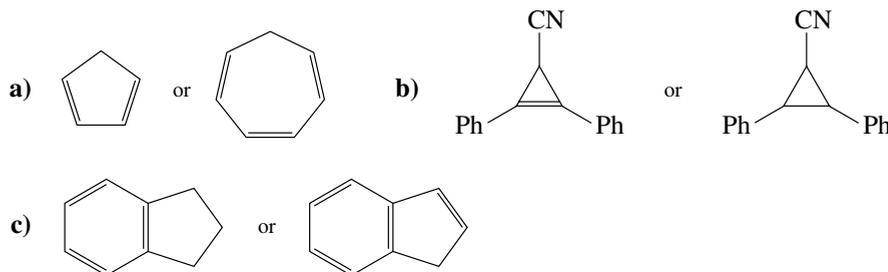


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**Chemistry Now™**  
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for additional practice  
identifying **Aromatic  
Compounds.**

The concept of aromaticity is very important in understanding the chemical behavior of cyclic, conjugated compounds. It is most important with benzene and its derivatives, but it also has applications to many other types of compounds. Whenever a reactant, product, or intermediate contains a planar cycle of *p* orbitals, the effect of aromaticity (or antiaromaticity) on the reaction must be considered.

### PROBLEM 16.12

Explain which of these compounds is a stronger acid:



### PROBLEM 16.13

Explain which of these compounds has the faster rate of substitution by the S<sub>N</sub>1 mechanism:

