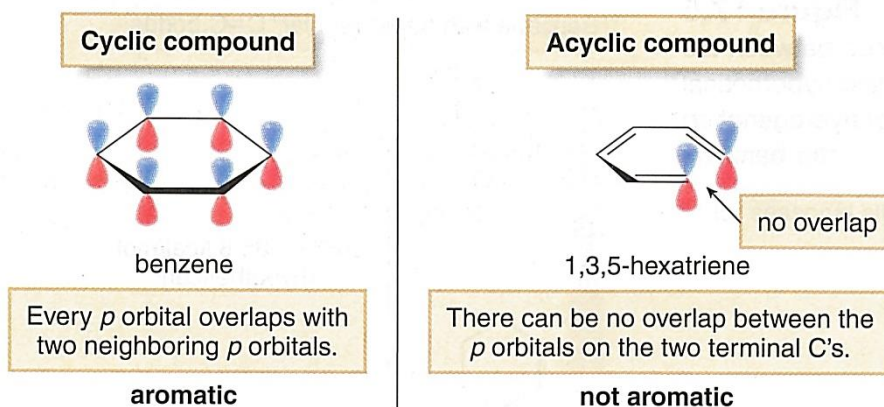# 17.7 The Criteria for Aromaticity—Hückel's Rule

Four structural criteria must be satisfied for a compound to be aromatic:

- A molecule must be cyclic, planar, completely conjugated, and contain a particular number of π electrons.

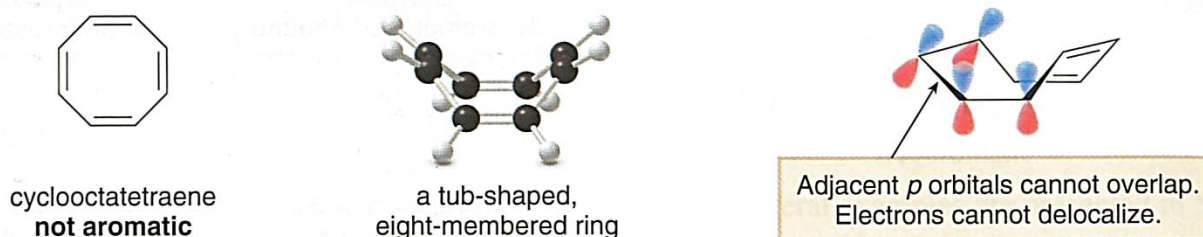**[1]** A molecule must be cyclic.

- To be aromatic, each p orbital must overlap with p orbitals on two adjacent atoms.

The p orbitals on all six carbons of benzene continuously overlap, so benzene is aromatic. 1,3,5-Hexatriene has six p orbitals, too, but the two on the terminal carbons cannot overlap with each other, so **1,3,5-hexatriene is not aromatic.**
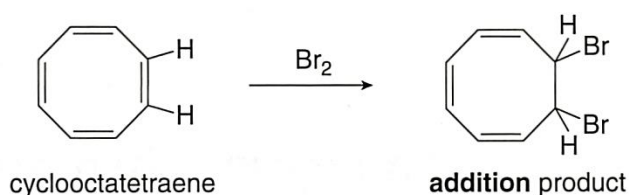
Cyclic compound	Acyclic compound

benzene — 1,3,5-hexatriene — no overlap

Every p orbital overlaps with two neighboring p orbitals.	There can be no overlap between the p orbitals on the two terminal C's.
aromatic	**not aromatic**

[2] A molecule must be planar.

- All adjacent p orbitals must be aligned so that the π electron density can be delocalized.

cyclooctatetraene
not aromatic

a tub-shaped, eight-membered ring

Adjacent p orbitals cannot overlap. Electrons cannot delocalize.
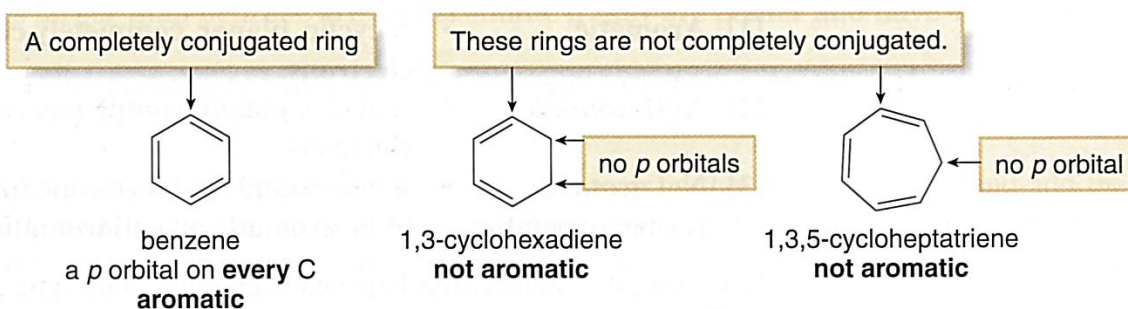
For example, cyclooctatetraene resembles benzene in that it is a cyclic molecule with alternating double and single bonds. Cyclooctatetraene is tub shaped, however, **not planar,** so overlap between adjacent π bonds is impossible. **Cyclooctatetraene, therefore, is *not* aromatic,** so it undergoes addition reactions like those of other alkenes.

cyclooctatetraene — Br$_2$ → **addition** product

[3] A molecule must be completely conjugated.

- Aromatic compounds must have a *p* orbital on every atom.

A completely conjugated ring

These rings are not completely conjugated.

benzene
a *p* orbital on **every** C
aromatic

no *p* orbitals

1,3-cyclohexadiene
not aromatic

no *p* orbital

1,3,5-cycloheptatriene
not aromatic

Both 1,3-cyclohexadiene and 1,3,5-cycloheptatriene contain at least one carbon atom that does not have a *p* orbital, and so they are not completely conjugated and therefore *not* **aromatic.**

[4] A molecule must satisfy Hückel's rule, and contain a particular number of π electrons.

Some compounds satisfy the first three criteria for aromaticity, but still they show none of the stability typical of aromatic compounds. For example, **cyclobutadiene** is so highly reactive that it can only be prepared at extremely low temperatures.

cyclobutadiene

a planar, cyclic, completely conjugated molecule
that is *not* aromatic
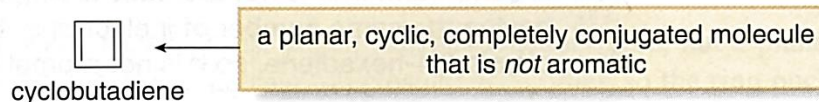
It turns out that in addition to being cyclic, planar, and completely conjugated, a compound needs a particular number of π electrons to be aromatic. Erich Hückel first recognized in 1931 that the following criterion, expressed in two parts and now known as **Hückel's rule,** had to be satisfied, as well:

- An aromatic compound must contain $4n + 2$ π electrons ($n = 0, 1, 2$, and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n$ π electrons are especially unstable, and are said to be *antiaromatic.*

Thus, compounds that contain 2, 6, 10, 14, 18, and so forth π electrons are aromatic, as shown in Table 17.2. **Benzene is aromatic and especially stable because it contains 6 π electrons. Cyclobutadiene is antiaromatic and especially unstable because it contains 4 π electrons.**
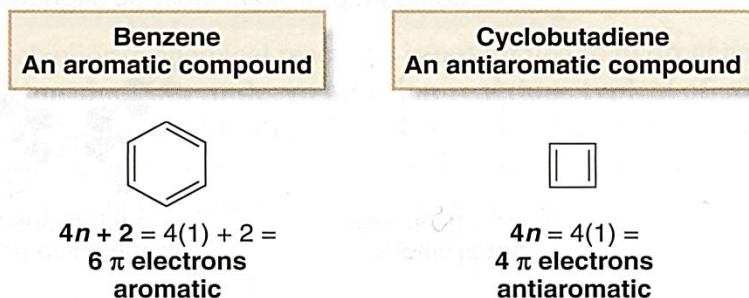
Benzene	Cyclobutadiene
An aromatic compound	An antiaromatic compound

$4n + 2 = 4(1) + 2 =$
6 π electrons
aromatic

$4n = 4(1) =$
4 π electrons
antiaromatic

Table 17.2	The Number of π Electrons That Satisfy Hückel's Rule	
	n	**$4n + 2$**
	0	2
	1	6
	2	10
	3	14
	4, etc.	18

Considering aromaticity, all compounds can be classified in one of three ways:

[1] **Aromatic**   • **A cyclic, planar, completely conjugated compound with $4n + 2$ π electrons.**

[2] **Antiaromatic**   • **A cyclic, planar, completely conjugated compound with $4n$ π electrons.**

[3] **Not aromatic (or nonaromatic)**   • **A compound that lacks one (or more) of the four requirements to be aromatic or antiaromatic.**

Note, too, the relationship between each compound type and a similar open-chained molecule having the same number of π electrons.

• An aromatic compound is *more* stable than a similar acyclic compound having the same number of π electrons. Benzene is more stable than 1,3,5-hexatriene.

• An antiaromatic compound is *less* stable than an acyclic compound having the same number of π electrons. Cyclobutadiene is less stable than 1,3-butadiene.

• A compound that is not aromatic is *similar* in stability to an acyclic compound having the same number of π electrons. 1,3-Cyclohexadiene is similar in stability to *cis,cis*-2,4-hexadiene, so it is not aromatic.

nonaromatic

benzene   and   1,3,5-hexatriene   cyclobutadiene   and   1,3-butadiene   1,3-cyclohexadiene   and   *cis,cis*-2,4-hexadiene

more stable
aromatic

less stable
antiaromatic

similar stability
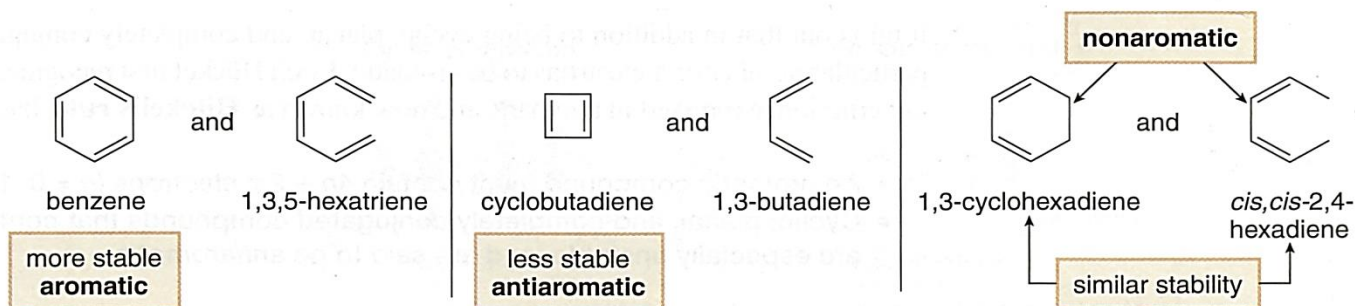
^{1}H NMR spectroscopy readily indicates whether a compound is aromatic. The protons on sp^2 hybridized carbons in aromatic hydrocarbons are highly deshielded and absorb at 6.5–8 ppm,

whereas hydrocarbons that are not aromatic absorb at 4.5–6 ppm, typical of protons bonded to the C=C of an alkene. Thus, benzene absorbs at 7.3 ppm, whereas cyclooctatetraene, which is not aromatic, absorbs farther upfield, at 5.8 ppm for the protons on its sp^2 hybridized carbons.

benzene
H ← 7.3 ppm
Ph–H region
aromatic

cyclooctatetraene
H ← 5.8 ppm
C_{sp^2}–H region
not aromatic
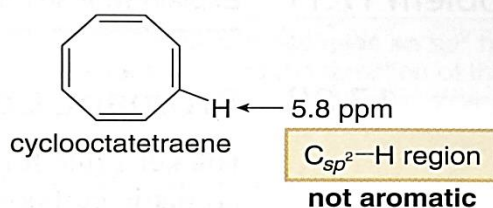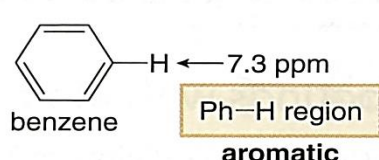
Many compounds in addition to benzene are aromatic. Several examples are presented in Section 17.8.

Estimate where the protons bonded to sp^2 hybridized carbons will absorb in the ^{1}H NMR spectrum of each compound.

a.   b.   c.
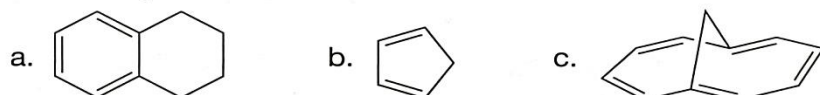
Examples of Aromatic Compounds

In Section 17.8 we look at many different types of aromatic compounds.

Aromatic Compounds with a Single Ring

Benzene is the most common aromatic compound having a single ring. **Completely conjugated rings larger than benzene are also aromatic if they are planar and have $4n + 2$ π electrons.**

- **Hydrocarbons containing a single ring with alternating double and single bonds are called** *annulenes.*

To name an annulene, indicate the number of atoms in the ring in brackets and add the word *annulene*. Thus, benzene is [6]-annulene. Both **[14]-annulene** and **[18]-annulene** are cyclic, planar, completely conjugated molecules that follow Hückel's rule, and so they are aromatic.
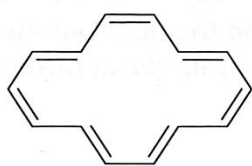
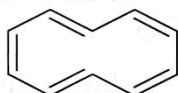[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic
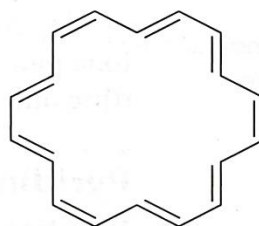
[18]-annulene
$4n + 2 = 4(4) + 2 =$
18 π electrons
aromatic

[10]-Annulene has 10 π electrons, which satisfies Hückel's rule, but a planar molecule would place the two H atoms inside the ring too close to each other, so the ring puckers to relieve this strain. Because **[10]-annulene is not planar,** the 10 π electrons can't delocalize over the entire ring and it is **not aromatic.**

[10]-Annulene fits Hückel's rule, but it's **not planar.**

The molecule puckers to keep these H's farther away from each other.

[10]-annulene
10 π electrons
not aromatic

=
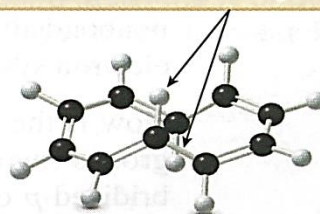
3-D representation

Would [16]-, [20]- or [22]-annulene be aromatic if each ring is planar?

Explain why an annulene cannot have an odd number of carbon atoms in the ring.

Aromatic Compounds with More Than One Ring

Hückel's rule for determining aromaticity can be applied only to monocyclic systems, but many aromatic compounds containing several benzene rings joined together are also known. Two or more six-membered rings with alternating double and single bonds can be fused together to form **polycyclic aromatic hydrocarbons (PAHs).** Joining two benzene rings together forms **naphthalene.** There are two different ways to join three rings together, forming **anthracene** and **phenanthrene,** and many more complex hydrocarbons are known.

| naphthalene | anthracene | phenanthrene |
| 10 π electrons | 14 π electrons | 14 π electrons |
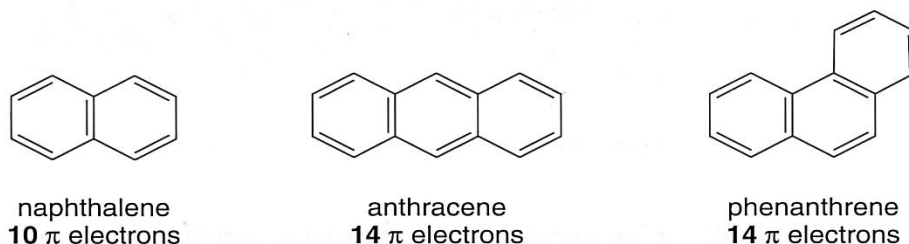
As the number of fused benzene rings increases, the number of resonance structures increases as well. Although two resonance structures can be drawn for benzene, naphthalene is a hybrid of three resonance structures.
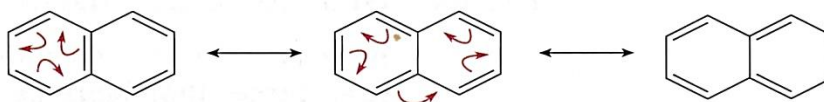
Draw the four resonance structures for anthracene.

Aromatic Heterocycles

Heterocycles containing oxygen, nitrogen, or sulfur—atoms that also have at least one lone pair of electrons—can also be aromatic. With heteroatoms, we must always determine whether the lone pair is localized on the heteroatom or part of the delocalized π system. Two examples, **pyridine** and **pyrrole,** illustrate these different possibilities.
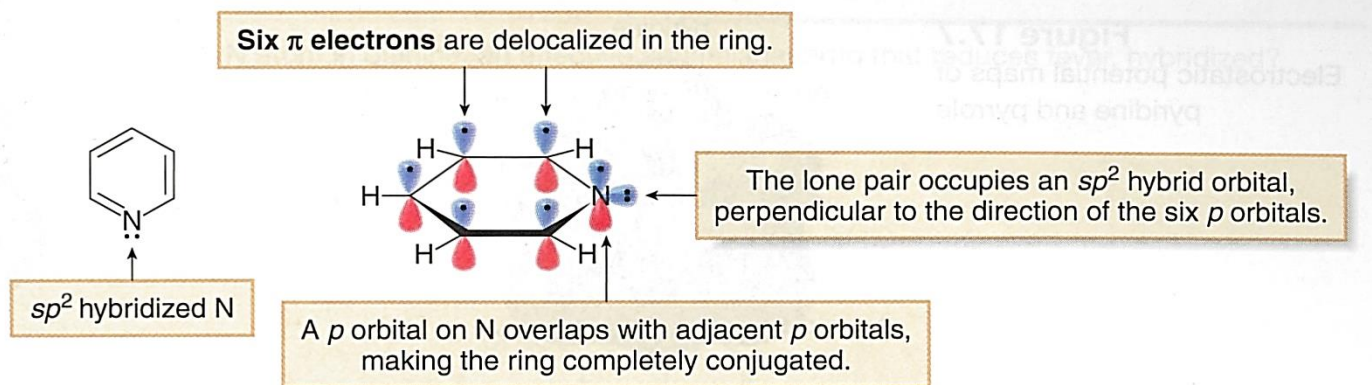
Pyridine

Pyridine is a heterocycle containing a six-membered ring with three π bonds and one nitrogen atom. Like benzene, two resonance structures can be drawn.


two resonance structures for pyridine
6 π electrons

Pyridine is cyclic, planar, and completely conjugated, because the three single and double bonds alternate around the ring. **Pyridine has six π electrons, two from each π bond, thus satisfying Hückel's rule and making pyridine aromatic.** The nitrogen atom of pyridine also has a nonbonded electron pair, which is localized on the N atom, so it is *not* part of the delocalized π electron system of the aromatic ring.

How is the nitrogen atom of the pyridine ring hybridized? The N atom is surrounded by three groups (two atoms and a lone electron pair), making it sp^2 **hybridized,** and leaving one unhybridized p orbital with one electron that overlaps with adjacent p orbitals. The lone pair on N resides in an sp^2 hybrid orbital that is perpendicular to the delocalized π electrons.

Six π electrons are delocalized in the ring.

The lone pair occupies an sp^2 hybrid orbital, perpendicular to the direction of the six p orbitals.

sp^2 hybridized N

A p orbital on N overlaps with adjacent p orbitals, making the ring completely conjugated.

Pyrrole

Pyrrole contains a five-membered ring with two π bonds and one nitrogen atom. The N atom also has a lone pair of electrons.
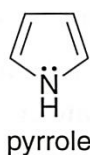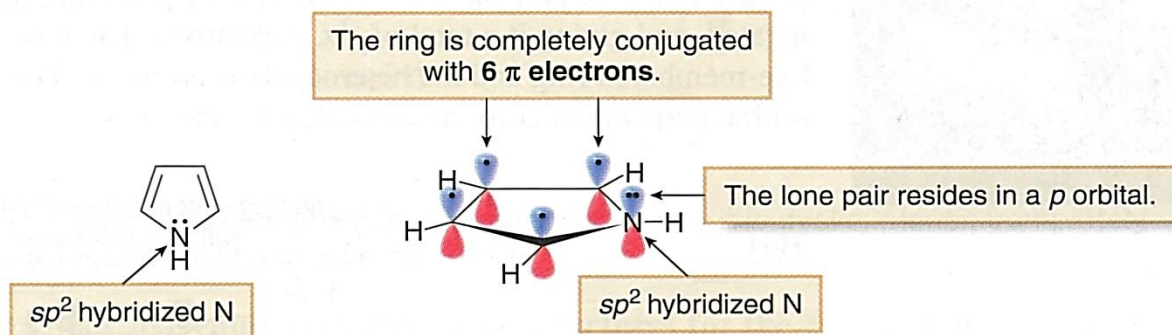

pyrrole

Pyrrole is cyclic and planar, with a total of four π electrons from the two π bonds. Is the non-bonded electron pair localized on N or part of a delocalized π electron system? The lone pair on N is *adjacent* to a double bond. Recall the following general rule from Section 16.5:

- In any system X=Y−Z:, Z is sp^2 hybridized and the lone pair occupies a p orbital to make the system conjugated.

If the lone pair on the N atom occupies a p orbital:

- **Pyrrole has a p orbital on every adjacent atom, so it is completely conjugated.**
- **Pyrrole has six π electrons—four from the π bonds and two from the lone pair.**

The ring is completely conjugated with **6 π electrons**.

The lone pair resides in a p orbital.

sp^2 hybridized N

sp^2 hybridized N

Because pyrrole is cyclic, planar, completely conjugated, and has $4n + 2$ π electrons, **pyrrole is aromatic. The number of electrons—not the size of the ring—determines whether a compound is aromatic.**

Electrostatic potential maps, shown in Figure 17.7 for pyridine and pyrrole, confirm that the **nonbonded electron pair in pyridine is localized on N,** whereas the **lone pair in pyrrole is part of the delocalized π system.** Thus, a fundamental difference exists between the N atoms in pyridine and pyrrole.

- When a heteroatom is already part of a double bond (as in the N of pyridine), its lone pair cannot occupy a p orbital and so it cannot be delocalized over the ring.
- When a heteroatom is *not* part of a double bond (as in the N of pyrrole), its lone pair can be located in a p orbital and delocalized over a ring to make it aromatic.