

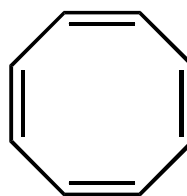
6.15 AROMATICITY AND HÜCKEL'S RULE

Benzene, as we have seen, is an aromatic hydrocarbon. It is called **aromatic** because it has certain properties that are associated with benzene and benzene-like molecules. Aromatic compounds typically are planar, have special chemical stability, tend to undergo substitution rather than addition, and show a **ring current** in their nuclear magnetic resonance spectrum. The chemical properties of benzene will be discussed in Chapter 22; nuclear magnetic resonance spectra will be described in Chapter 13.

Ever since the special properties of benzene were first discovered, organic chemists have wondered whether these characteristics were peculiar only to benzene, or whether other molecules might also be aromatic. In particular, might cyclobutadiene and cyclooctatetraene be four- or eight-membered analogues of benzene? Might they also be aromatic? Or, is there something about benzene that sets it off from other molecules?



Cyclobutadiene



Cyclooctatetraene

Research has shown that cyclobutadiene and cyclooctatetraene are clearly *not* aromatic. In fact, particularly in the case of cyclobutadiene, they can even be called **antiaromatic**, meaning that they are actually *less stable* than predicted. They have negative resonance energies. Cyclobutadiene is very unstable; it is not found in nature, and its synthesis is exceedingly difficult. Cyclooctatetraene is also quite unstable; it is found rarely in nature. Cyclooctatetraene is not planar, and its four double bonds behave independently of one another.

Systems such as benzene, cyclobutadiene, and cyclooctatetraene, which are cyclic, conjugated polyenes, are known as **annulenes**. Benzene might be considered an example of a **[6]annulene**, which cyclobutadiene and cyclooctatetraene might be called **[4]annulene** and **[8]annulene**, respectively.

Molecular orbital calculations on the annulenes have shown that when the number of π -electrons is predicted by the arithmetic series, $4n+2$, the annulene will be aromatic. When the number of π -electrons falls into the arithmetic series, $4n$, the annulene will not be aromatic. The $4n+2$ rule is known as **Hückel's Rule**.

Hückel's Rule							
$4n+2$:	2	6	10	14	18	22	26
$4n$:	4	8	12	16	20	24	28

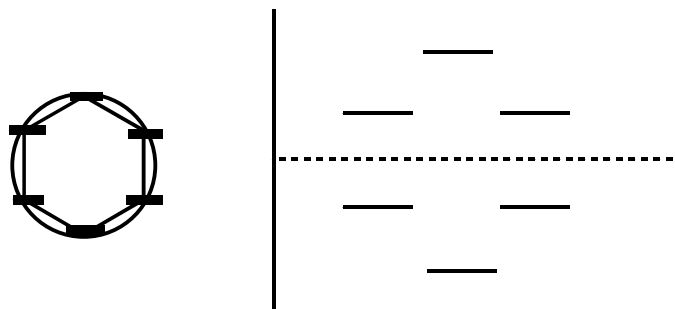
Benzene, with six π -electrons, clearly falls into the aromatic series, while cyclobutadiene, with four π -electrons, and cyclooctatetraene, with eight π -electrons, are not predicted to be aromatic according to Hückel's Rule.

A discussion of Hückel's Rule requires us to examine the orbital array diagram for the annulene under consideration. A simple mnemonic device can be used to show how the orbital array for an annulene can be drawn. In using this drawing device, the assumption is made that the annulene behaves as a cyclic conjugated system. The method for this mnemonic device follows the steps:

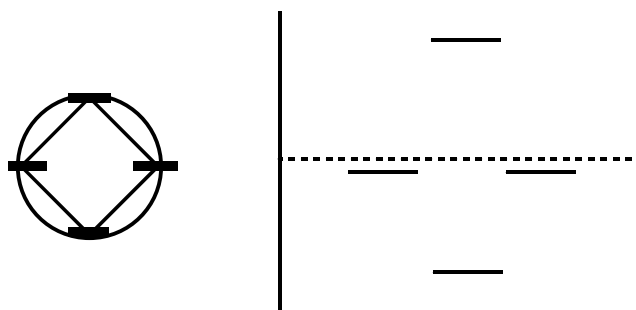
- 1) Draw a circle
- 2) Inscribe the polygon that represents the annulene within the circle, with the polygon arranged so that one of its points is aimed directly downward.
- 3) Each point where the polygon touches the circle represents an energy level in the orbital array.

The examples of benzene and cyclobutadiene illustrate how this method is applied.

Benzene



Cyclobutadiene



PROBLEM 6-17: Using the circle method, derive orbital arrays for the following annulene systems:

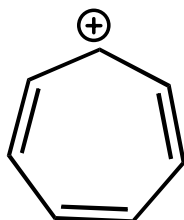
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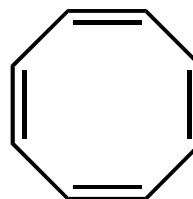
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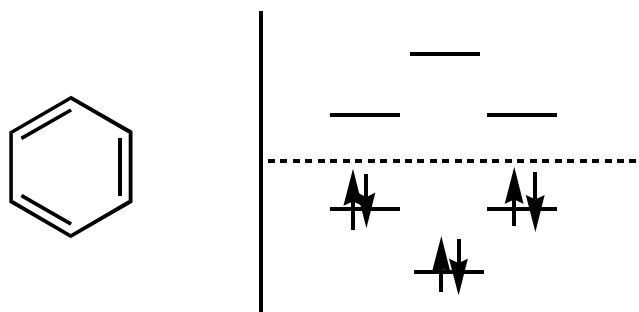
c)



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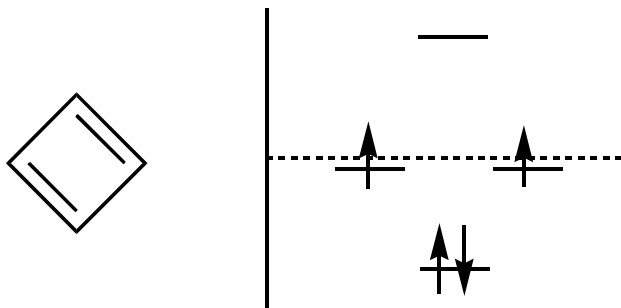


We can see why Hückel's Rule applies to these annulenes. If we treat benzene ([6]annulene) as an aromatic system, the following orbital array can be drawn.



When the six electrons are added to this array, the final electronic configuration shows paired electrons in each of the bonding molecular orbitals. This is a stable electronic configuration. Since the orbitals in the highest occupied energy level are filled with *paired* electrons, this is known as a **closed-shell** electronic configuration. Any annulene system that has six π -electrons will thus have a similar electronic configuration, and it will also have aromatic properties.

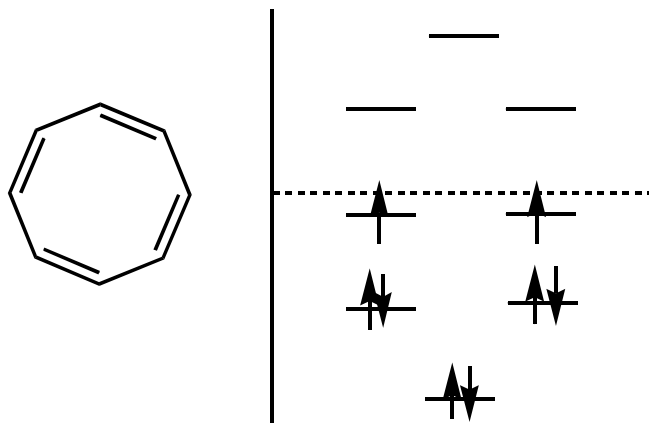
If cyclobutadiene is treated as an aromatic system, the following orbital array should apply.



When the four electrons are placed in this array, two of the orbitals will contain unpaired electrons. We recall from general chemistry that **Hund's Rule** requires that, for a set of degenerate orbitals, each orbital must accept a single electron before any of the orbitals can accept an electron pair. For this reason, two of the orbitals in cyclobutadiene must contain unpaired electrons. The result is an unstable electronic configuration, and we find that cyclobutadiene is clearly not aromatic. In this case, the orbitals in the highest occupied energy level contain *unpaired* electrons; this is known as an **open-shell** electronic configuration.

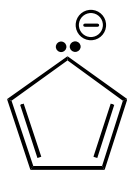
Cyclobutadiene can assume a closed-shell electronic configuration, but only if the two double bonds are treated as *independent* double bonds. An orbital array that resembles an unconjugated diene would have paired electrons in each orbital and would be a more stable electronic configuration.

A similar analysis of cyclooctatetraene shows that eight π -electrons do not form a stable electronic configuration.

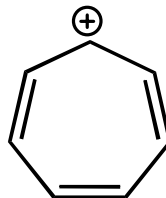


This analysis shows that, even if cyclooctatetraene were planar and conjugated, it could not be aromatic. With an unstable (open-shell) electronic configuration, there is no energy advantage to a planar molecule. An alternative electronic configuration, with each of the four π -bonds behaving independently of the others, is a closed-shell configuration. The actual cyclooctatetraene molecule assumes a puckered, non-planar conformation, where there is no interaction among the π -bonds.

Other six-electron annulene-based systems, besides benzene, have also been shown to have aromatic properties. Two cases in particular are the **cyclopentadienyl anion** and the **cycloheptatrienyl cation**. The cycloheptatrienyl cation is better known as the **tropylium ion**.



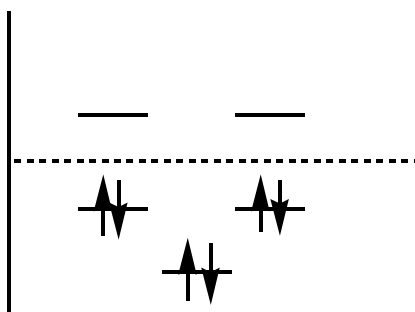
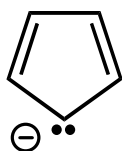
Cyclopentadienyl anion



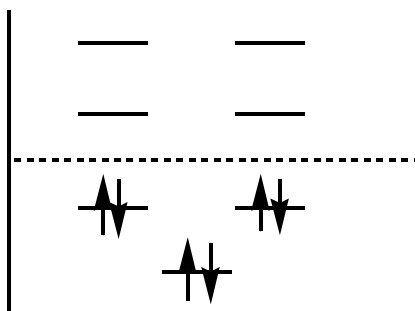
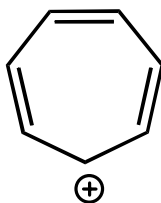
Cycloheptatrienyl cation
(Tropylium ion)

Each of these ions has six π -electrons. Orbital arrays for each of the ions show stable (closed-shell) electronic configurations.

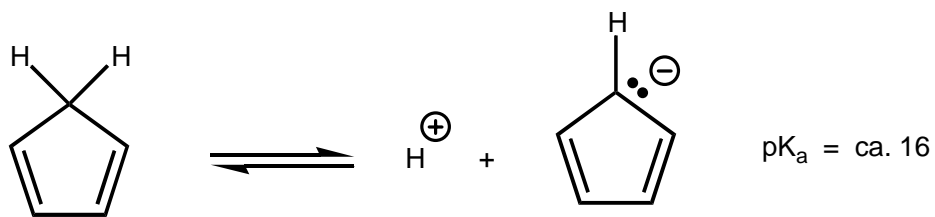
Cyclopentadienyl anion



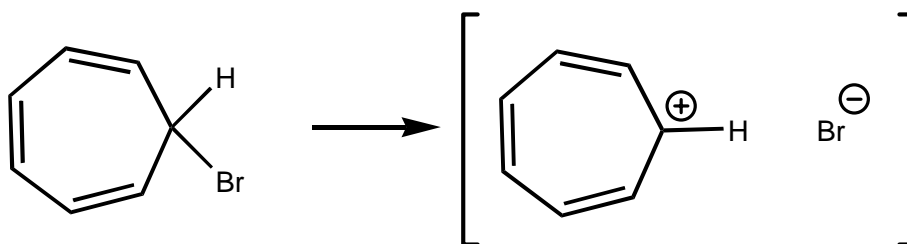
Cycloheptatrienyl cation



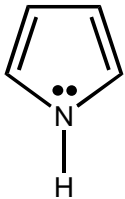
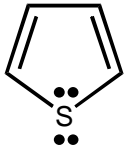
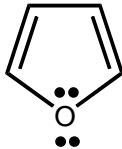
The special stability of the cyclopentadienyl anion accounts for the enhanced acidity of the methylene hydrogens of cyclopentadiene. These hydrogens are more acidic than the typical C-H bond by a factor of about 10^{30} . When cyclopentadiene loses a proton, the cyclopentadienyl anion, which is aromatic, is formed.



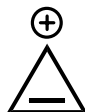
The tropylium ion is a very stable carbocation. The special stability of the tropylium ion can be demonstrated by observing that 7-bromo-1,3,5-cycloheptatriene actually exists as **tropylium bromide**, a completely ionic compound.



The same principles apply to heterocyclic molecules as well. The unshared electron pairs on the heteroatoms of compounds such as pyrrole, thiophene, and furan can occupy bonding molecular orbitals and be included in the six π -electrons of an aromatic system. The resonance energies of these compounds are similar in magnitude to those found in benzene.

			
	Pyrrole	Thiophene	Furan
Resonance Energy (kJ/mole):	88	121	67

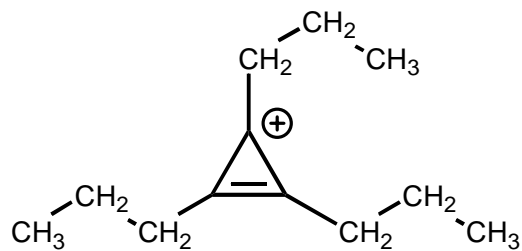
If Hückel's Rule can be applied to systems with six π -electrons, can it also be applied to systems with *two* π -electrons? Would the **cyclopropenyl cation** be expected to show aromatic properties?



Cyclopropenyl cation

At first glance, one might not expect this ion to have any stability at all. Angle strain in this ion should be very high, indeed. Nevertheless, the cyclopropenyl cation has been prepared,

and substituted cyclopropenyl cations, such as the tripropyl derivative shown here, are so stable that they can be identified in aqueous solution.

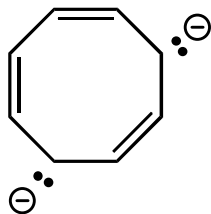


Tripropylcyclopropenyl cation

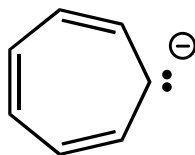
As predicted by Hückel's Rule, annulenes with 10, 14, and 18 π -electrons have also been prepared. The predictions of Hückel's Rule have been confirmed with these systems. Large resonance energies, a preference for aromatic substitution, and significant nuclear magnetic resonance ring currents have been demonstrated for these systems.

PROBLEM 6-18:

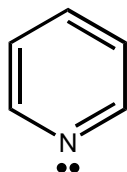
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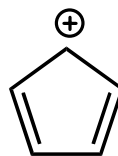
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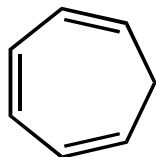
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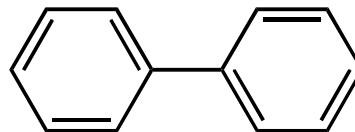
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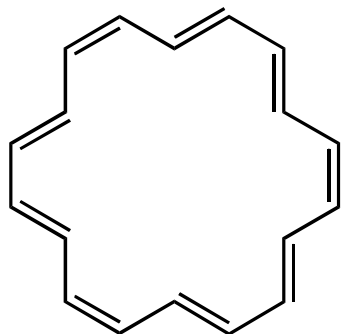
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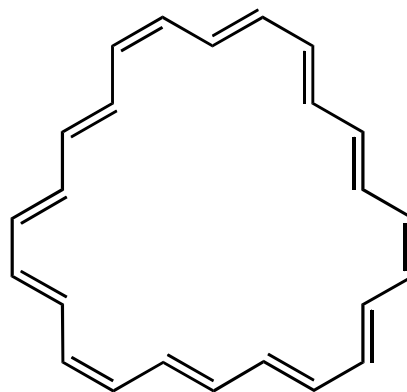
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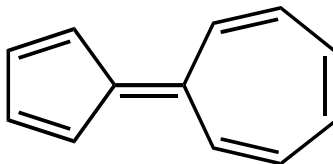
g)



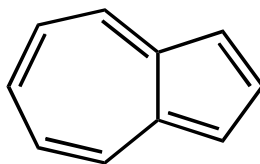
h)



PROBLEM 6-19: The following compound has been shown to have aromatic properties. Draw resonance forms to show that both rings can be aromatic.



PROBLEM 6-20: The following compound has been shown to have aromatic properties. Draw resonance forms to show that both rings can be aromatic.



Azulene

