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Cyclobutadiene and Cyclooctatetraene
Requirements for Aromaticity

cyclic conjugation is necessary, *but not sufficient*

- not aromatic
- aromatic
- not aromatic
Heat of hydrogenation of benzene is 152 kJ/mol.

Heats of hydrogenation to give cyclohexane (kJ/mol):
- 120
- 231
- 208

Heat of hydrogenation of benzene is 152 kJ/mol less than 3 times heat of hydrogenation of cyclohexene.
Heats of Hydrogenation

to give cyclooctane (kJ/mol)

heat of hydrogenation of cyclooctatetraene is more than 4 times heat of hydrogenation of cyclooctene

97  205  303  410
The structure of a stabilized derivative is characterized by alternating short bonds and long bonds.

Structure of Cyclobutadiene

![Cyclobutadiene Structure](image)

- (CH$_3$)$_3$C
- C(CH$_3$)$_3$
- 138 pm
- 151 pm
- CO$_2$CH$_3$
Structure of Cyclooctatetraene

cyclooctatetraene is not planar

has alternating long (146 pm) and short (133 pm) bonds
there must be some factor in addition to cyclic conjugation that determines whether a molecule is aromatic or not
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Hückel's Rule:
Annulenes

the additional factor that influences aromaticity is the number of $\pi$ electrons
among planar, monocyclic, completely conjugated polyenes, only those with $4n + 2$ π electrons possess special stability (are aromatic)

<table>
<thead>
<tr>
<th>$n$</th>
<th>$4n+2$</th>
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<tbody>
<tr>
<td>0</td>
<td>2</td>
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<tr>
<td>1</td>
<td>6</td>
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<td>2</td>
<td>10</td>
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<td>3</td>
<td>14</td>
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benzene!
Hückel restricted his analysis to planar, completely conjugated, monocyclic polyenes. He found that the \( \pi \) molecular orbitals of these compounds had a distinctive pattern. One \( \pi \) orbital was lowest in energy, another was highest in energy, and the others were arranged in pairs between the highest and the lowest.
$\pi$-MOs of Benzene

6 $p$ orbitals give 6 $\pi$ orbitals
3 orbitals are bonding; 3 are antibonding
6 $\pi$ electrons fill all of the bonding orbitals
all $\pi$ antibonding orbitals are empty
\[ \pi\text{-MOs of Cyclobutadiene} \]

(square planar)

- antibonding
- bonding

4 \( p \) orbitals give 4\( \pi \) orbitals
1 orbital is bonding, one is antibonding, and 2 are nonbonding
Cyclobutadiene

$\pi$-MOs of Cyclobutadiene (square planar)

4 $\pi$ electrons; bonding orbital is filled; other 2 $\pi$ electrons singly occupy two nonbonding orbitals
8 $p$ orbitals give 8 $\pi$ orbitals
3 orbitals are bonding, 3 are antibonding, and 2 are nonbonding

$\pi$-MOs of Cyclooctatetraene
(square planar)
π-MOs of Cyclooctatetraene (square planar)

Cyclooctatetraene

8 π electrons; 3 bonding orbitals are filled; 2 nonbonding orbitals are each half-filled
\( \pi \)-Electron Requirement for Aromaticity

- 4 \( \pi \) electrons: not aromatic
- 6 \( \pi \) electrons: aromatic
- 8 \( \pi \) electrons: not aromatic
Completely Conjugated Polyenes

6 \pi electrons; completely conjugated

6 \pi electrons; not completely conjugated

aromatic

not aromatic
Annulenes are planar, monocyclic, completely conjugated polyenes. That is, they are the kind of hydrocarbons treated by Hückel's rule.
predicted to be aromatic by Hückel's rule, but too much angle strain when planar and all double bonds are cis.

10-sided regular polygon has angles of 144°.
incorporating two trans double bonds into the ring relieves angle strain but introduces van der Waals strain into the structure and causes the ring to be distorted from planarity
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**[10]Annulene**

van der Waals strain between these two hydrogens
14 $\pi$ electrons satisfies Hückel's rule
van der Waals strain between hydrogens inside the ring
16 \pi \text{ electrons does not satisfy Hückel's rule}
alternating short (134 pm) and long (146 pm) bonds
not aromatic

[16] Annulene
18 $\pi$ electrons satisfies Hückel's rule

resonance energy = 418 kJ/mol

bond distances range between 137-143 pm
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Aromatic Ions
Cycloheptatrienyl Cation

6 \pi\text{ electrons delocalized}
over 7 carbons

positive charge dispersed
over 7 carbons

very stable carbocation
also called tropylium cation
Cycloheptatrienyl Cation
Tropylium cation is so stable that tropylium bromide is ionic rather than covalent.

mp 203 °C; soluble in water; insoluble in diethyl ether
Cyclopentadienide Anion

6 π electrons delocalized over 5 carbons
negative charge dispersed over 5 carbons
stabilized anion
Cyclopentadienide Anion
Acidity of Cyclopentadiene

Cyclopentadiene is unusually acidic for a hydrocarbon. Increased acidity is due to stability of cyclopentadienide anion.

$pK_a = 16$

$K_a = 10^{-16}$

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Electron Delocalization in Cyclopentadienide Anion
Electron Delocalization in Cyclopentadienide Anion
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Electron Delocalization in Cyclopentadienide Anion
Electron Delocalization in Cyclopentadienide Anion
Compare Acidities of Cyclopentadiene and Cycloheptatriene

\[ \text{p}K_a = 16 \]
\[ K_a = 10^{-16} \]

\[ \text{p}K_a = 36 \]
\[ K_a = 10^{-36} \]
Compare Acidities of Cyclopentadiene and Cycloheptatriene

Aromatic anion
6 $\pi$ electrons

Anion not aromatic
8 $\pi$ electrons
Cyclopropenyl Cation

Also written as

\[ n = 0 \]

\[ 4n + 2 = 2 \pi \text{ electrons} \]
Cyclooctatetraene Dianion

\[ n = 2 \]
\[ 4n + 2 = 10 \pi \text{ electrons} \]

also written as
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Heterocyclic Aromatic Compounds
Examples

Pyridine

Pyrrole

Furan

Thiophene
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Heterocyclic Aromatic Compounds
and
Hückel's Rule
Pyridine

6 $\pi$ electrons in ring

lone pair on nitrogen is in an $sp^2$ hybridized orbital;
not part of $\pi$ system of ring
Pyrrole

lone pair on nitrogen must be part of ring $\pi$ system if ring is to have 6 $\pi$ electrons

lone pair must be in a $p$ orbital in order to overlap with ring $\pi$ system
Furan

two lone pairs on oxygen
one pair is in a $p$ orbital and is part of ring $\pi$ system; other is in an $sp^2$ hybridized orbital and is not part of ring $\pi$ system