Aromatic Hydrocarbons

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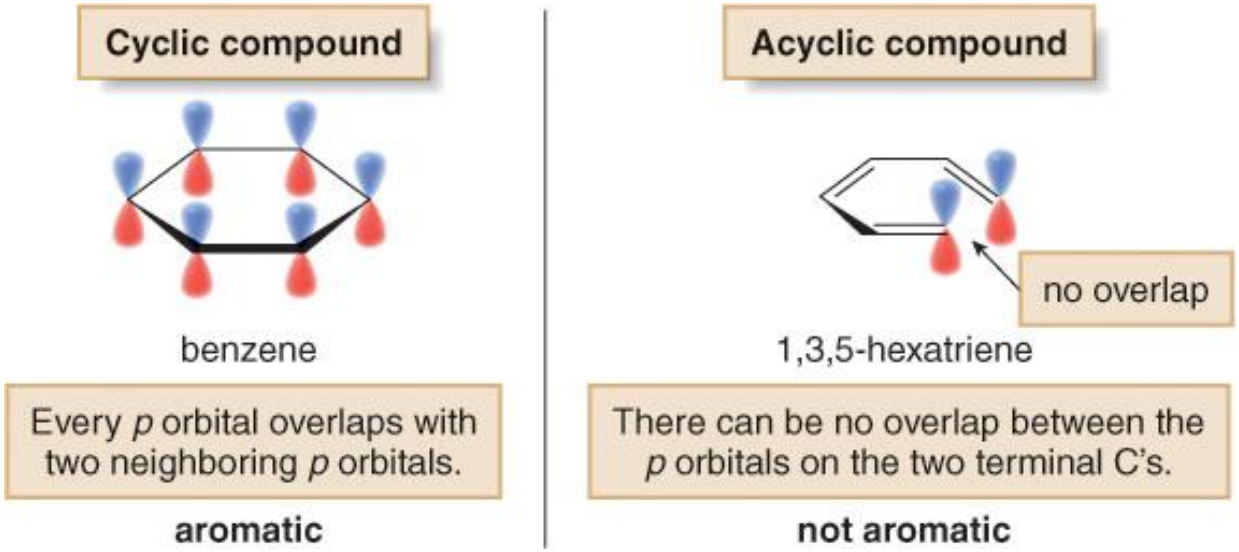
AROMATICITY

The Criteria for Aromaticity:

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

[1] A molecule must be cyclic.

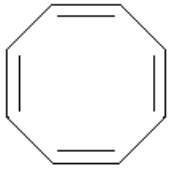


To be aromatic, each *p* orbital must overlap with *p* orbitals on adjacent atoms.

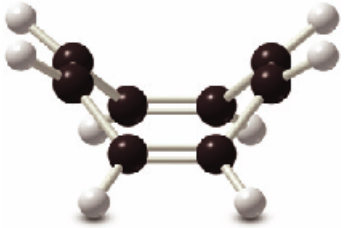
The Criteria for Aromaticity:

[2] A molecule must be planar.

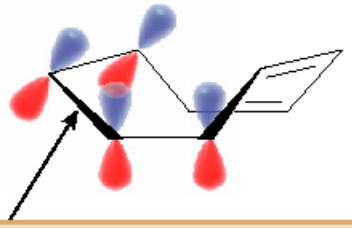
All adjacent *p* orbitals must be aligned so that the π electron density can be delocalized.



cyclooctatetraene
not aromatic

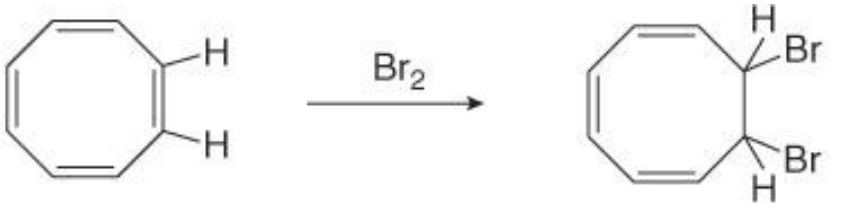


a tub-shaped,
eight-membered ring



Adjacent *p* orbitals cannot overlap.
Electrons cannot delocalize.

Since cyclooctatetraene is non-planar, it is not aromatic, and it undergoes addition reactions just like those of other alkenes.

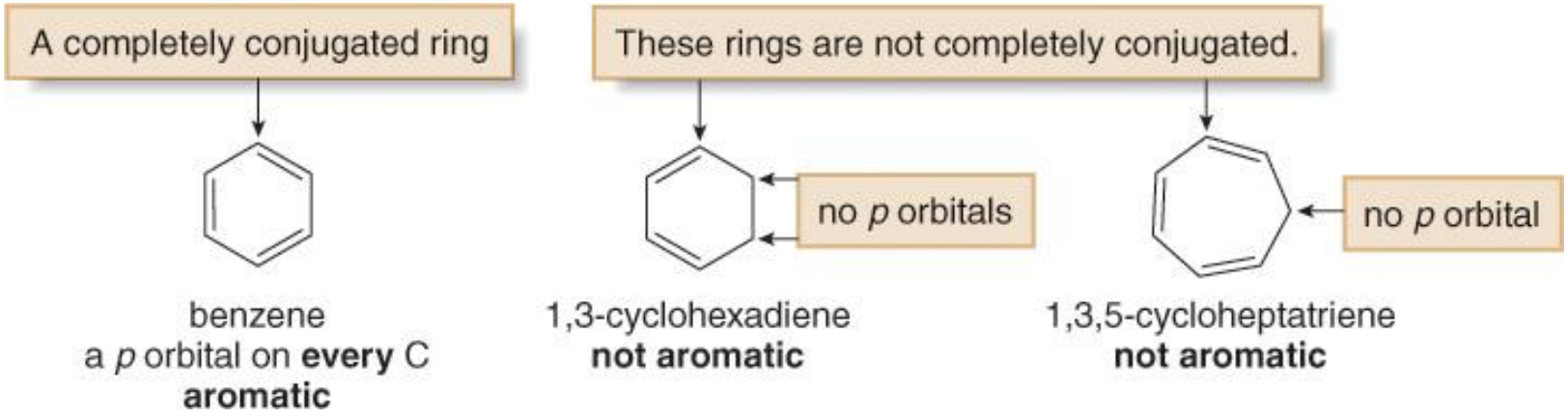


cyclooctatetraene **addition** product

The Criteria for Aromaticity:

[3] A molecule must be completely conjugated.

Aromatic compounds must have a *p* orbital on every atom and each must overlap with adjacent p orbitals.

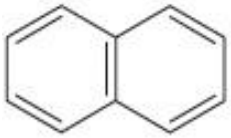


The Criteria for Aromaticity:

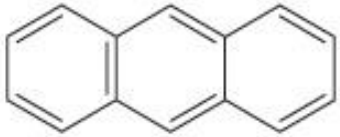
[4] A molecule must satisfy Hückel's rule, which requires a particular number of π electrons.

Hückel's rule:

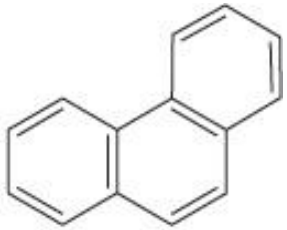
- An aromatic compound must contain $4n + 2$ π electrons ($n = 0, 1, 2$, and so forth).
- Cyclic, planar, and completely conjugated compounds that contain $4n$ π electrons are especially unstable, and are said to be *antiaromatic.*



naphthalene
10 π electrons



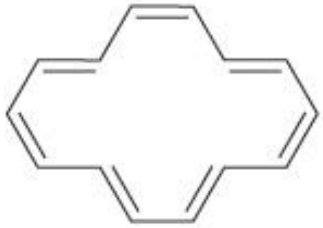
anthracene
14 π electrons



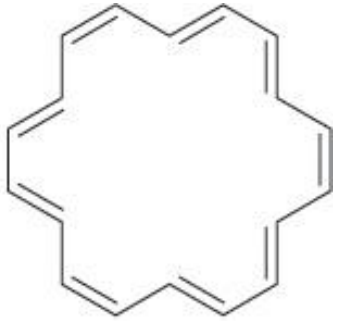
phenanthrene
14 π electrons

Annulene

- An annulene is a monocyclic hydrocarbon with alternating double and single bonds.
- To name an annulene, indicate the number of atoms in the ring in brackets and add the word annulene.



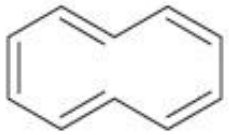
[14]-annulene
$4n + 2 = 4(3) + 2 =$
14 π electrons
aromatic



[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. Thus, the ring puckers to relieve this strain.
- Since [10]-annulene is not planar, the 10 π electrons can't delocalize over the entire ring and it is not aromatic.

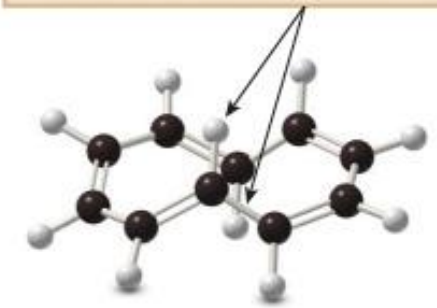
[10]-Annulene fits Hückel's rule, but it's **not planar**.



[10]-annulene
10 π electrons
not aromatic

=

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



3-D representation

Heterocycle: Cyclic compound that comprises atoms of two or more elements in its ring

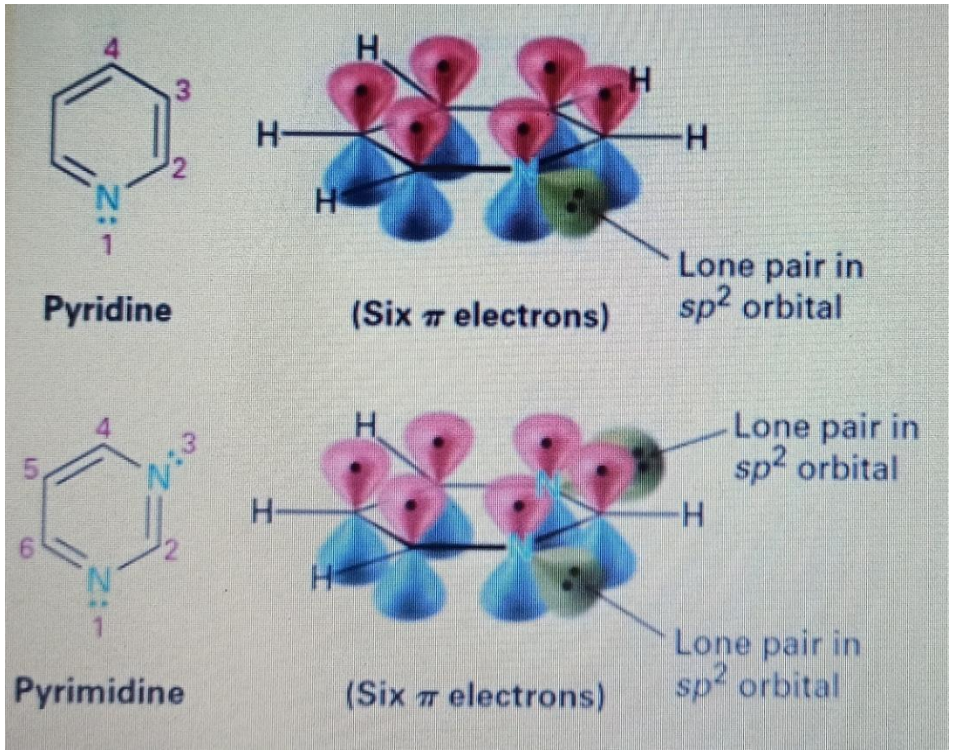
Pyridine

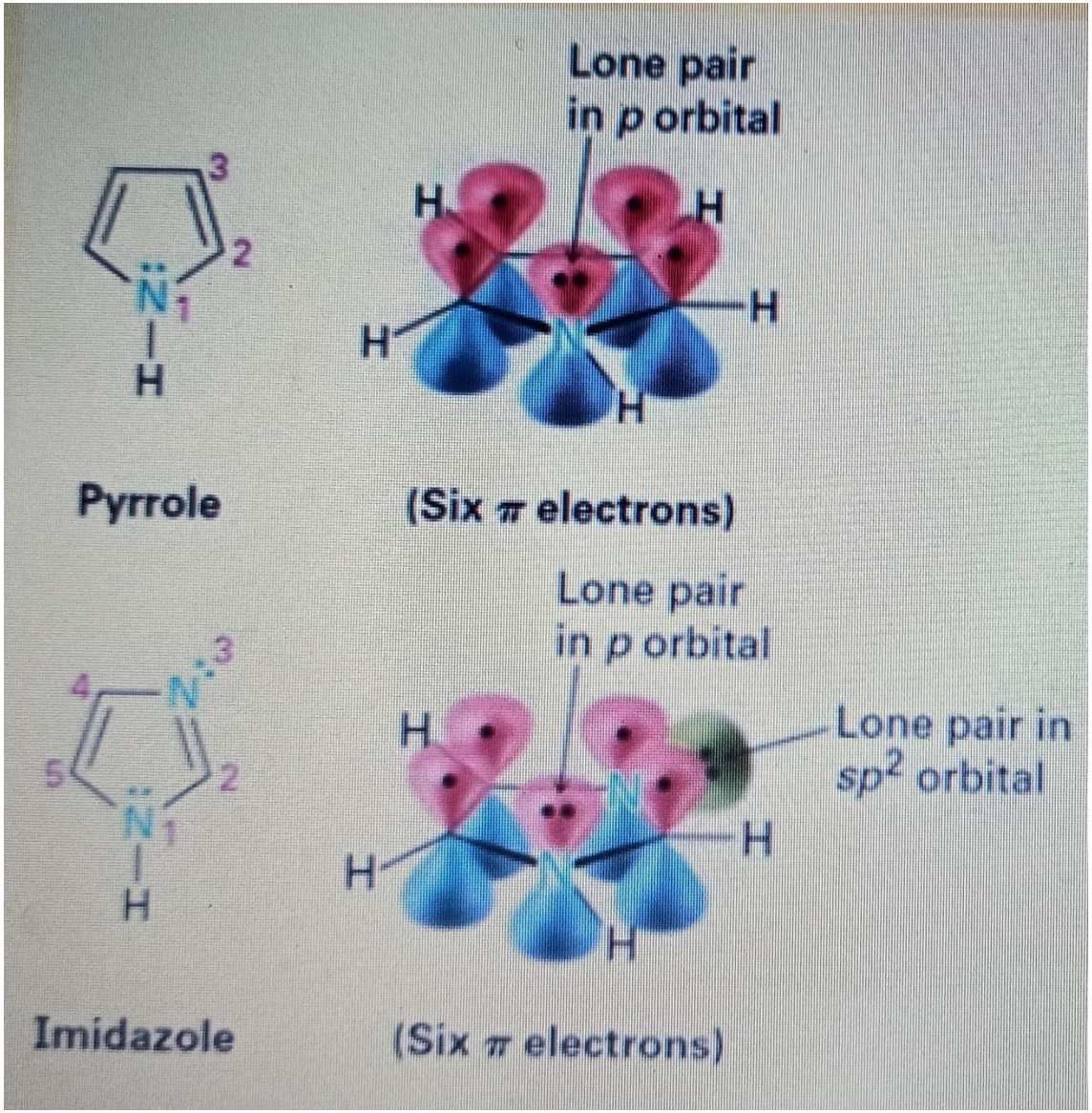
- Six-membered heterocycle with a nitrogen atom in its ring
- π electron structure resembles benzene (6 electrons)
- The nitrogen lone pair electrons are not part of the aromatic system (perpendicular orbital)

- The π structure of pyridine is quite similar to that of benzene
  - All five sp^2-hybridized ions possess a p orbital perpendicular with one to the plane of the ring
  - Each p orbital comprises one π electron
  - The nitrogen atom is also sp^2-hybridized and possesses one electron in a p orbital

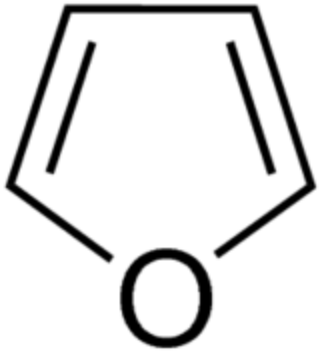
Pyrimidine comprises two nitrogen atoms in a six-membered, unsaturated ring

- The sp^2-hybridized nitrogen atoms share an electron each to the aromatic π system

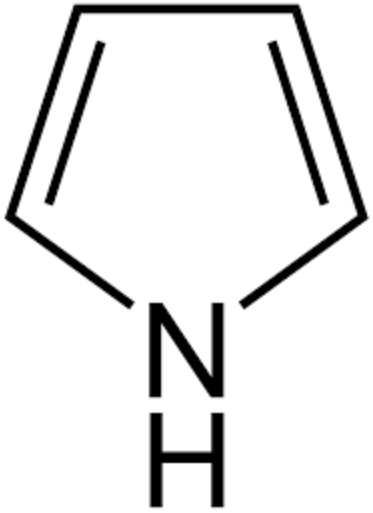



Lone pair
in p orbital
Pyrrole
(Six π electrons)
Lone pair
in p orbital
Lone pair in
sp2 orbital
Imidazole
(Six π electrons)

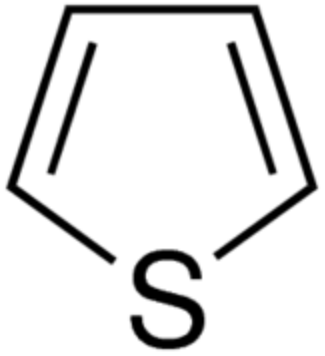
Work example



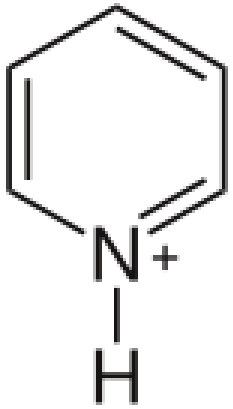
Furan



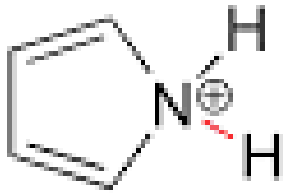
Pyrrole



Thiophene



Pyridinium ion

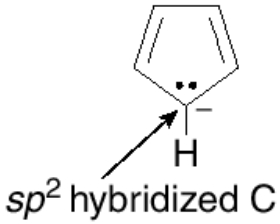


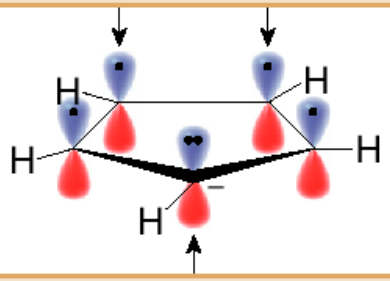
Protonated Pyrrole

Both negatively and positively charged ions can be aromatic if they possess all the necessary elements.

The cyclopentadienyl anion

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





The lone pair resides in a *p* orbital.

- **The cyclopentadienyl anion is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons.**

One can draw five equivalent resonance structures for the cyclopentadienyl anion.

- Having the "right" number of electrons is necessary for a species to be unusually stable by virtue of aromaticity.
- Thus, although five resonance structures can also be drawn for the cyclopentadienyl cation and radical, only the cyclopentadienyl anion has 6 π electrons, a number that satisfies Hückel's rule.

cyclopentadienyl anion
- **6** π electrons
- contains $4n + 2$ π electrons

aromatic

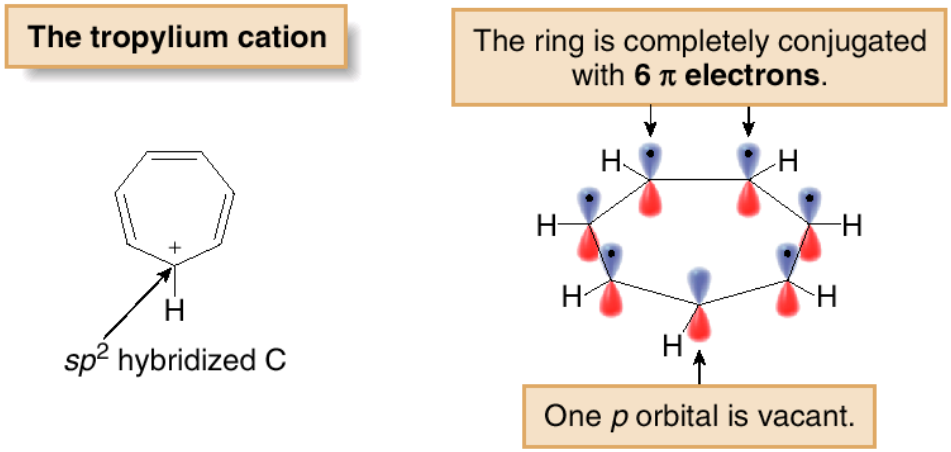
cyclopentadienyl cation
- **4** π electrons
- contains $4n$ π electrons

antiaromatic

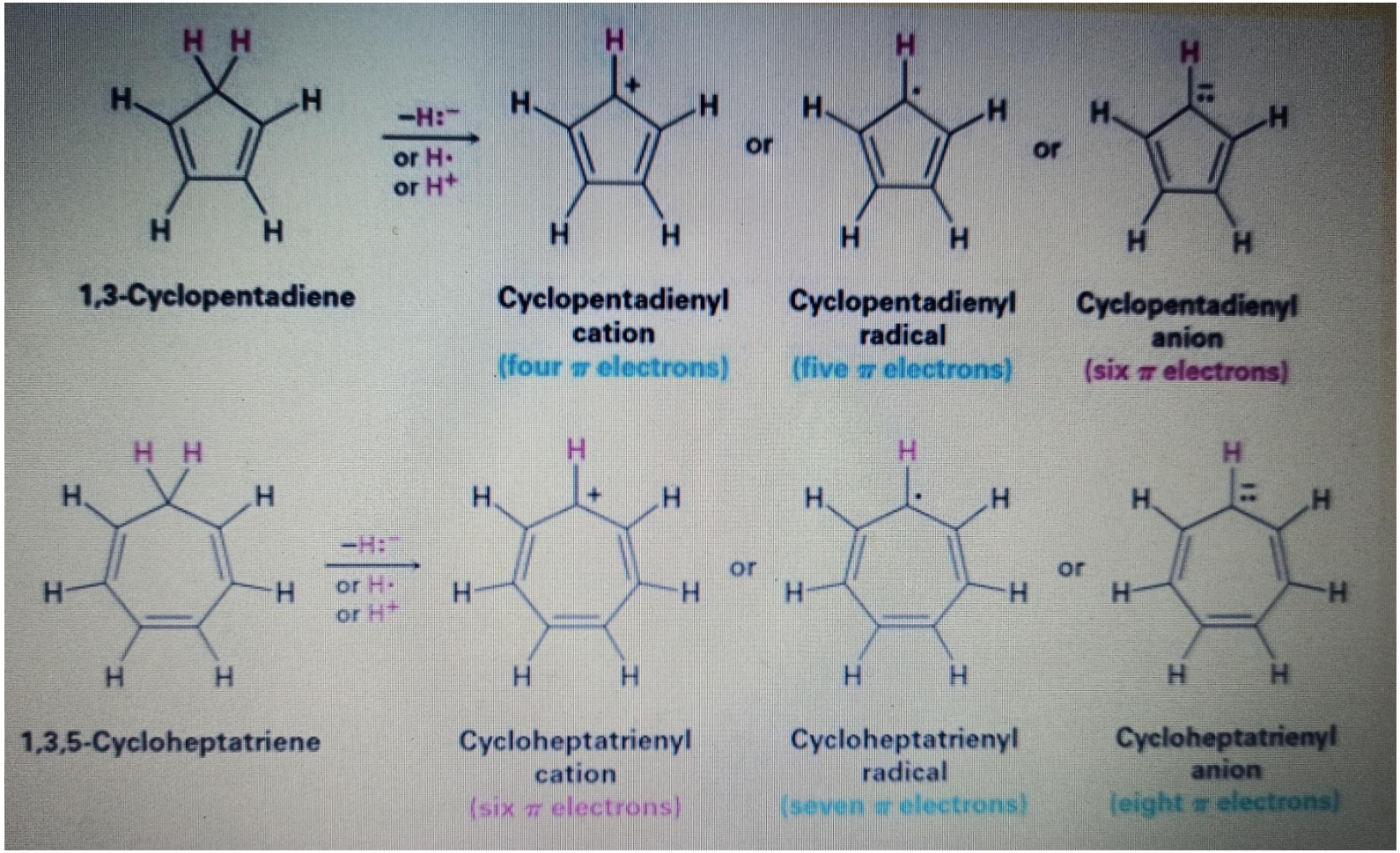
cyclopentadienyl radical
- **5** π electrons
- does not contain either $4n$ or $4n + 2$ π electrons

nonaromatic

- The tropylium cation is a planer carbocation with three double bonds and a positive charge contained in a seven-membered ring.
- Because the tropylium cation has three π bonds and no other nonbonded electron pairs, it contains six π electrons, thereby satisfying Hückel's rule.



- The tropylium cation is aromatic because it is cyclic, planar, completely conjugated, and has six π electrons delocalized over the seven atoms of the ring.


1,3-Cyclopentadiene
−H:⁻
or H·
or H⁺
Cyclopentadienyl cation
(four π electrons)
or
Cyclopentadienyl radical
(five π electrons)
or
Cyclopentadienyl anion
(six π electrons)
1,3,5-Cycloheptatriene
−H:⁻
or H·
or H⁺
Cycloheptatrienyl cation
(six π electrons)
or
Cycloheptatrienyl radical
(seven π electrons)
or
Cycloheptatrienyl anion
(eight π electrons)

Aromatic, Antiaromatic and Nonaromatic Compounds

Note 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.