Organic Chemistry I

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Organic Chemistry, (9th edition)

By *John McMurry*, Cengage Learning, 2016

Aromaticity and the Hückel 4*n*+2 Rule

For benzene-like aromatic molecules:

- Benzene is **cyclic** and **conjugated**.
- Benzene is unusually stable, having a heat of hydrogenation 150 kJ/mol less negative than the expected for a conjugated cyclic triene.
- Benzene is **planar** and has the shape of a regular hexagon. All bond angles are 120°, all carbon atoms are ***sp*^{2}-hybridized**, and all carbon–carbon bond lengths are 139 pm.
- Benzene undergoes substitution reactions that retain the cyclic conjugation rather than electrophilic addition reactions that would destroy it.
- Benzene can be described as a resonance hybrid whose structure is intermediate between two line-bond structures.

Something else, called the **Hückel 4*n*+2 rule**, is needed to complete a description of aromaticity.

According to a theory devised in 1931 by the German physicist Erich Hückel, a molecule is aromatic only if it has a **planar**, **monocyclic** system of conjugation and contains a total of ***4n*+2 π *electrons***, where *n* is an integer (*n* = 0, 1, 2, 3, . . .). In other words, only molecules with 2, 6, 10, 14, 18, . . . π electrons can be aromatic.

If they are cyclic, planar, and apparently conjugated with 4*n* π electrons (4, 8, 12, 16, . . .), it is said to be **antiaromatic** because delocalization of their π electrons would lead to their destabilization.

Cyclobutadiene has four π electrons and is antiaromatic. The π electrons are localized in two double bonds rather than delocalized around the ring.

Cyclobutadiene is highly reactive and shows none of the properties associated with aromaticity. Even at -78 °C, it dimerizes by a Diels–Alder reaction. One molecule behaves as a diene and the other as a dienophile.

Cyclobutadiene

Two double bonds;
four π electrons

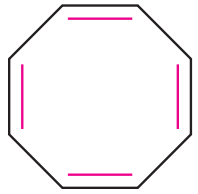
Benzene has six π electrons ($4n+2 = 6$ when $n=1$) and is aromatic.

Benzene

Three double bonds;
six π electrons

Cyclooctatetraene has eight π electrons and is not aromatic. The π electrons are localized into four double bonds rather than delocalized around the ring, and the molecule is tub-shaped rather than planar.

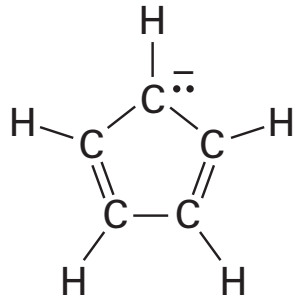
It has no cyclic conjugation because neighboring *p* orbitals don't have the necessary parallel alignment for overlap, and it resembles an open-chain polyene in its reactivity.



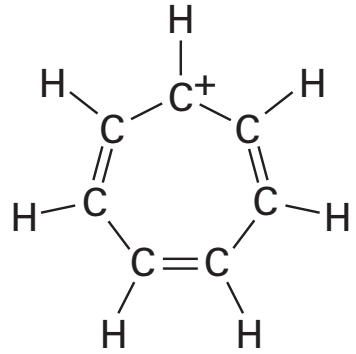
Cyclooctatetraene

Four double bonds;
eight π electrons

The number of π electrons must be the same as the number of atoms in the ring or that the substance must be neutral. The numbers can differ and the substance can be an ion. Cyclopentadienyl anion and cycloheptatrienyl cation are aromatic and contains a six-membered ring.



Cyclopentadienyl anion



Cycloheptatrienyl cation

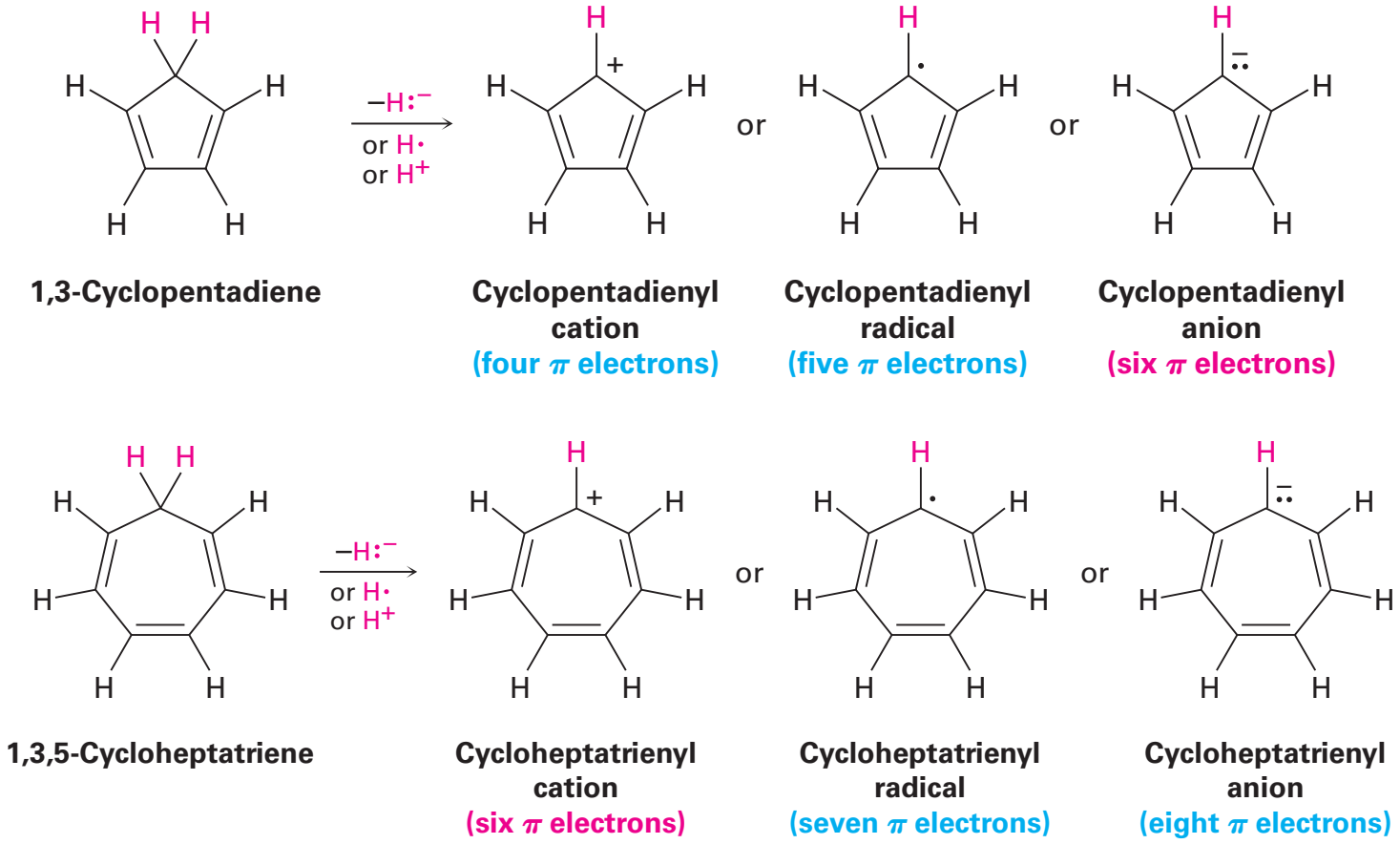
Six π electrons; aromatic ions

In the related neutral hydrocarbons, 1,3-cyclopentadiene and 1,3,5-cycloheptatriene, one hydrogen from the saturated CH_2 carbon is removed.

The carbon then rehybridizes from sp^3 to sp^2, the resultant products would be fully conjugated, with a *p* orbital on every carbon.

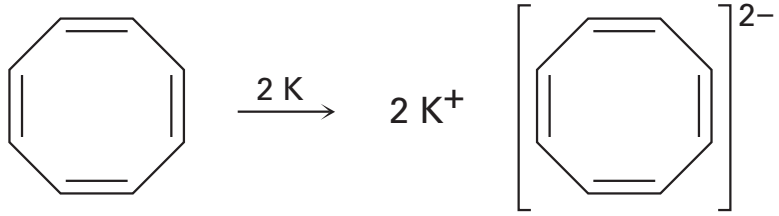
Among the potential products, only the six-π-electron cyclopentadienyl anion and cycloheptatrienyl cation should be aromatic according to the Hückel's rule.

The other products are predicted to be unstable and antiaromatic.

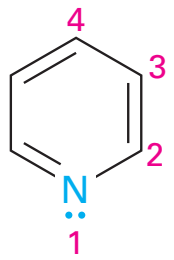


Problem 15-7

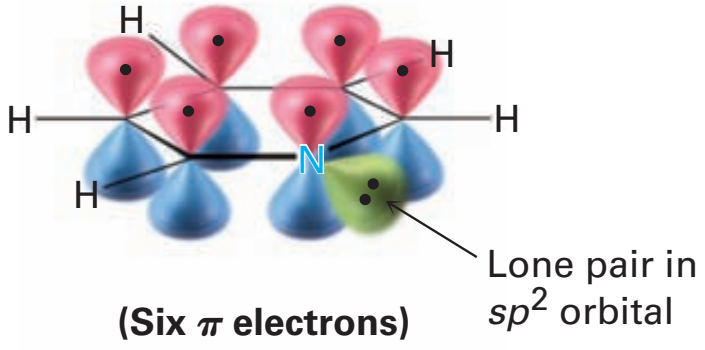
Cyclooctatetraene readily reacts with potassium metal to form the stable cyclooctatetraene dianion, $C_8H_8^{2-}$. Why do you suppose this reaction occurs so easily? What geometry do you expect for the cyclooctatetraene dianion?



Heterocyclic compounds can also be aromatic. A heterocycle is a cyclic compound that contains atoms of two or more elements in its ring, usually carbon along with nitrogen, oxygen, or sulfur. Pyridine and pyrimidine are six-membered heterocycles.

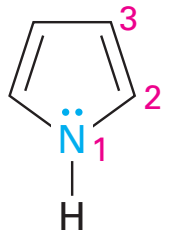


Pyridine

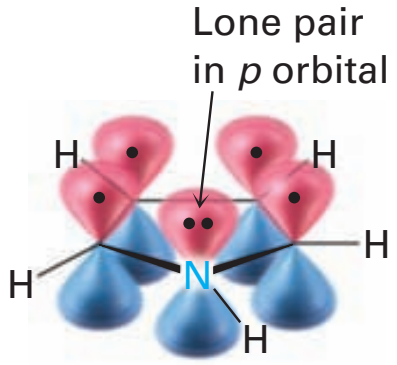


(Six π electrons)

Pyrrole has two nitrogen atoms in a five-membered unsaturated ring. each of the four sp^2-hybridized carbons contributes one π electron and the sp^2-hybridized nitrogen atom contributes the two from its lone pair, which occupies a *p* orbital.

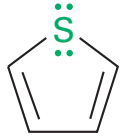


Pyrrole

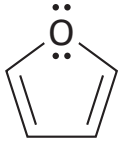


(Six π electrons)

Thiophene, a sulfur-containing heterocycle, undergoes typical aromatic substitution reactions rather than addition reactions.

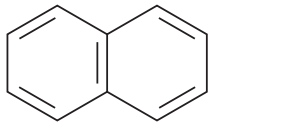


Thiophene

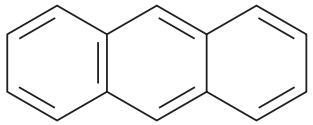


Furan

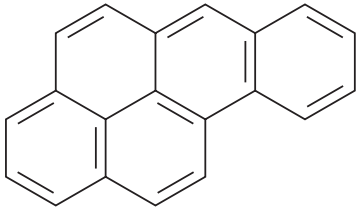
The **Hückel rule** is only **strictly applicable to monocyclic compounds**, but the general concept of **aromaticity** can be **extended to** include ***polycyclic*** aromatic compounds.



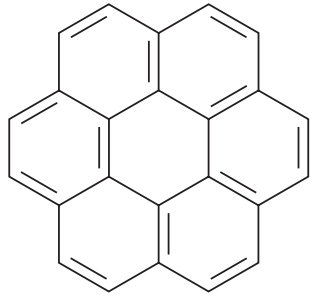
Naphthalene



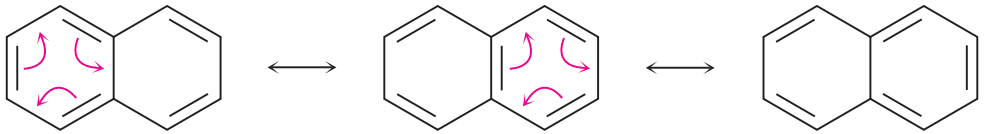
Anthracene



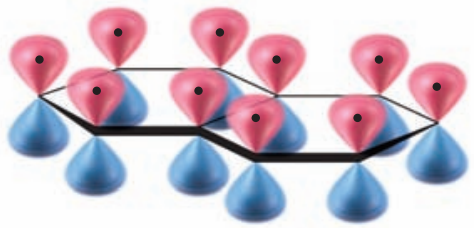
Benzo[a]pyrene

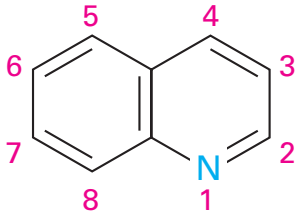


Coronene

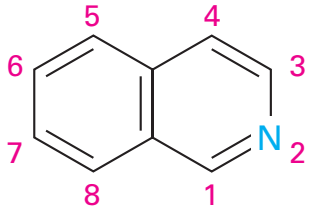


Naphthalene

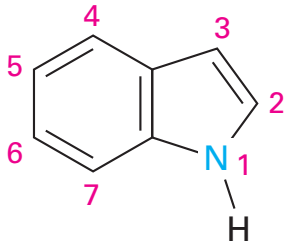




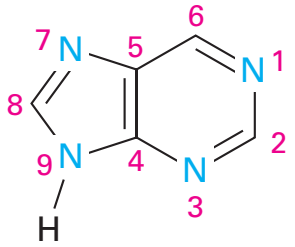
Quinoline



Isoquinoline

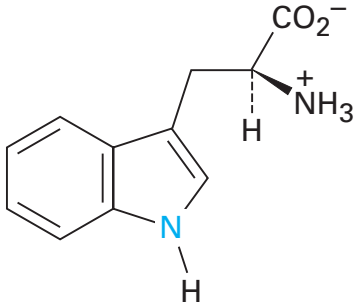


Indole

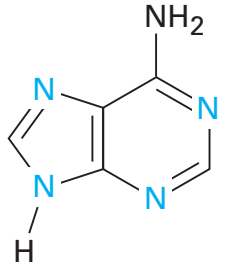


Purine

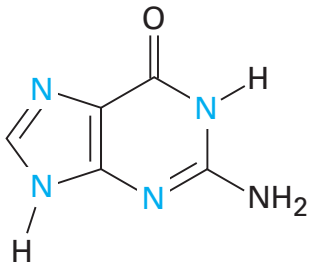
Biological molecules contain polycyclic aromatic rings:



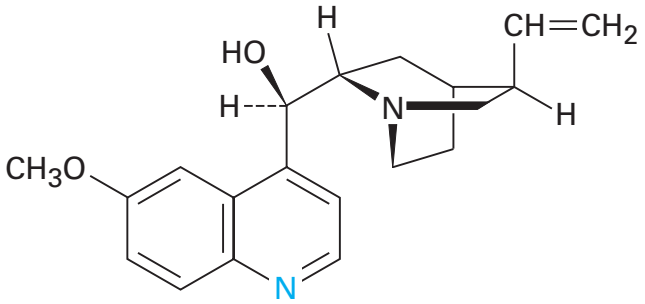
Tryptophan
(an amino acid)



Adenine
(in DNA and RNA)



Guanine
(in DNA and RNA)



Quinine
(an antimalarial agent)