Chapter 16:
Aromatic Compounds
Kekulé structure
- Kekulé was first to propose a cyclic structure for benzene with alternating single/double bonds

Kekule's structure with double bonds shorter than single bonds
We know now that all bonds are equidistant (1.397 Å). This means that benzene is a resonance hybrid of 2 Kekulé structures and that π electrons are delocalized.

Kekule: \((1.34 + 1.48)/2 = 1.41\) Å
This resonance stabilize the aromatic system so much that normal reactions of double bonds do not happen for aromatic compounds.
Aromaticity and Hückel’s rule (16-5) ✓ To be aromatic a molecule must:

- Be cyclic
- Have $4n+2$ π electrons
  where $n= 0, 1, 2, 3, \ldots$ (or have an odd number of pairs of electrons)
- Electron must be in conjugation: alternating single and double bonds

![苯](image)

$$4n + 2 = 6$$
$$n = (6-2)/4$$
$$n = 1$$

aromatic
Polycyclic benzenoids are aromatic:

(Only one Kekulé structure is shown for each compound.)
All these compounds are members of a larger family called: **Annulenes**

Annulenes are compounds with conjugated double bonds and they can either be aromatic or not.
Question:
What is the name of this annulene? Is it aromatic?
Aromatic Ions (16-8)

Other species such as ions can also be aromatic. Aromaticity is not limited to neutral molecule.

\[
\begin{align*}
\text{Cyclopentadienyl anion} & \quad \text{(six pi electrons)} \\
\text{pK}_a = 16 & \quad \text{pK}_a = 18
\end{align*}
\]
Another example is the tropylium ion which is also aromatic.

And the cyclooctatetraene dianion

\[
\text{cyclooctatetraene} + 2\text{K}^+ \rightarrow \text{cyclooctatetraene}^{2-} = 2\text{K}^+ + 10\text{pi electrons}
\]
Practice Question

✓ Are the following ions aromatic or not?

\[
\text{[Chemical structures of ions]}
\]
Heterocyclic Aromatic Compounds (16-9)

Heterocycles (one or more atom in the ring is not a carbon) can also be aromatic.

pyridine

\[
\text{pyridine, } pK_b = 8.8
\]

\[
\begin{align*}
\text{pyridine} & + \text{H}_2\text{O} & \overset{\Leftrightarrow}{\longrightarrow} & \text{pyridinium ion} & + \text{OH} \\
\text{pyridine} & + \text{H}_2\text{O} & \overset{\Leftrightarrow}{\longrightarrow} & \text{pyridinium ion} & + \text{OH}
\end{align*}
\]

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✓ Pyrrole is also aromatic.

orbital structure of pyrrole
(six π electrons, aromatic)

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✓ As well as pyrimidine, imidazole and purine

pyrimidine
imidazole
purine
Oxygen and sulfur can also be part of the aromatic heterocycles as shown in the following examples.
Nomenclature of benzene derivatives (16-13)

Usually the name of compounds containing the benzene ring end with the suffix: benzene

Other common names are often used.

common name: phenol (benzenol)  toluene (methylbenzene)  aniline (benzenamine)  anisole (methoxybenzene)

common name: styrene (vinylbenzene)  acetophenone (methyl phenyl ketone)  benzaldehyde  benzoic acid
A special nomenclature exists for disubstituted benzene derivatives, the terms *ortho*, *meta* and *para* are normally used.

- 1,2 or ortho: X - Y
  - Common name: o-dichlorobenzene
  - IUPAC name: 1,2-dichlorobenzene

- 1,3 or meta: X - Y
  - Common name: m-chloroperoxybenzoic acid
  - IUPAC name: 3-chloroperoxybenzoic acid

- 1,4 or para: Y - X
  - Common name: p-nitrophenol
  - IUPAC name: 4-nitrophenol
Which of the following are aromatic?