2302687 – Heterocyclic Compounds – Part I

Lecture 1-4

Aromaticity

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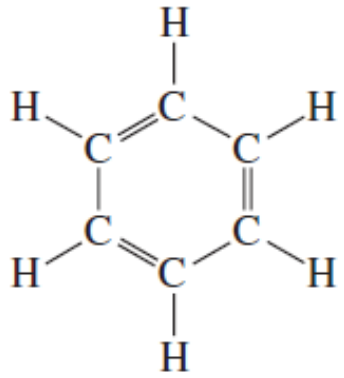
Recommended Textbook:

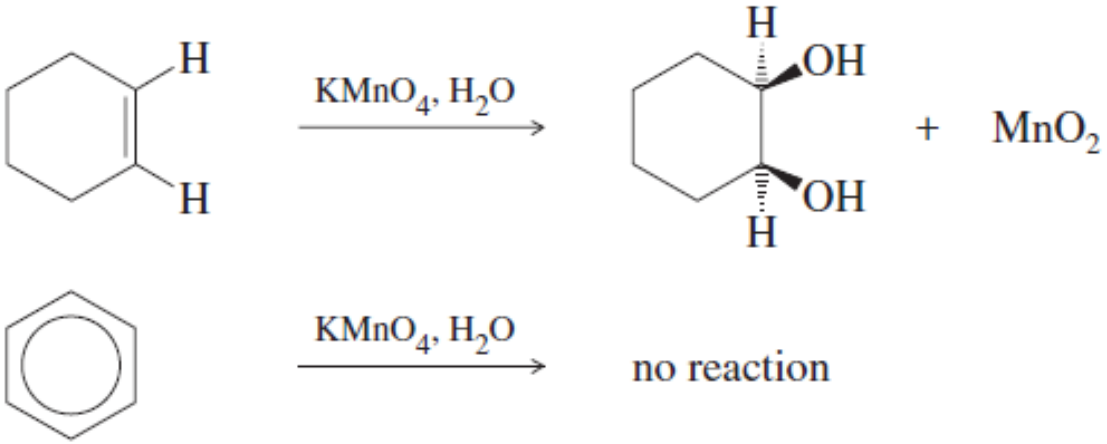
Heterocyclic Chemistry, 5th Edition, J. A. Joule, K. Mills, **2010**, Wiley

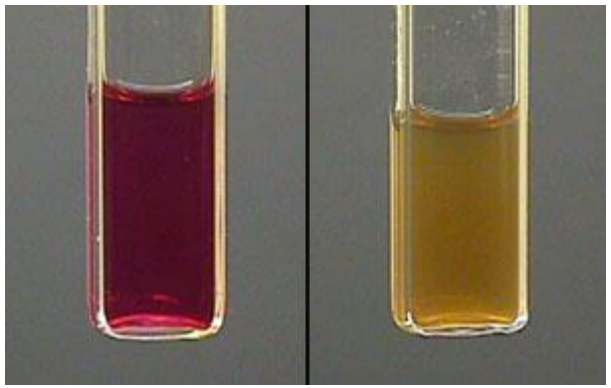
Aromaticity – Benzene



- **The Kekulé Structure** : In 1866, Friedrich Kekulé proposed a cyclic structure for benzene with three double bonds

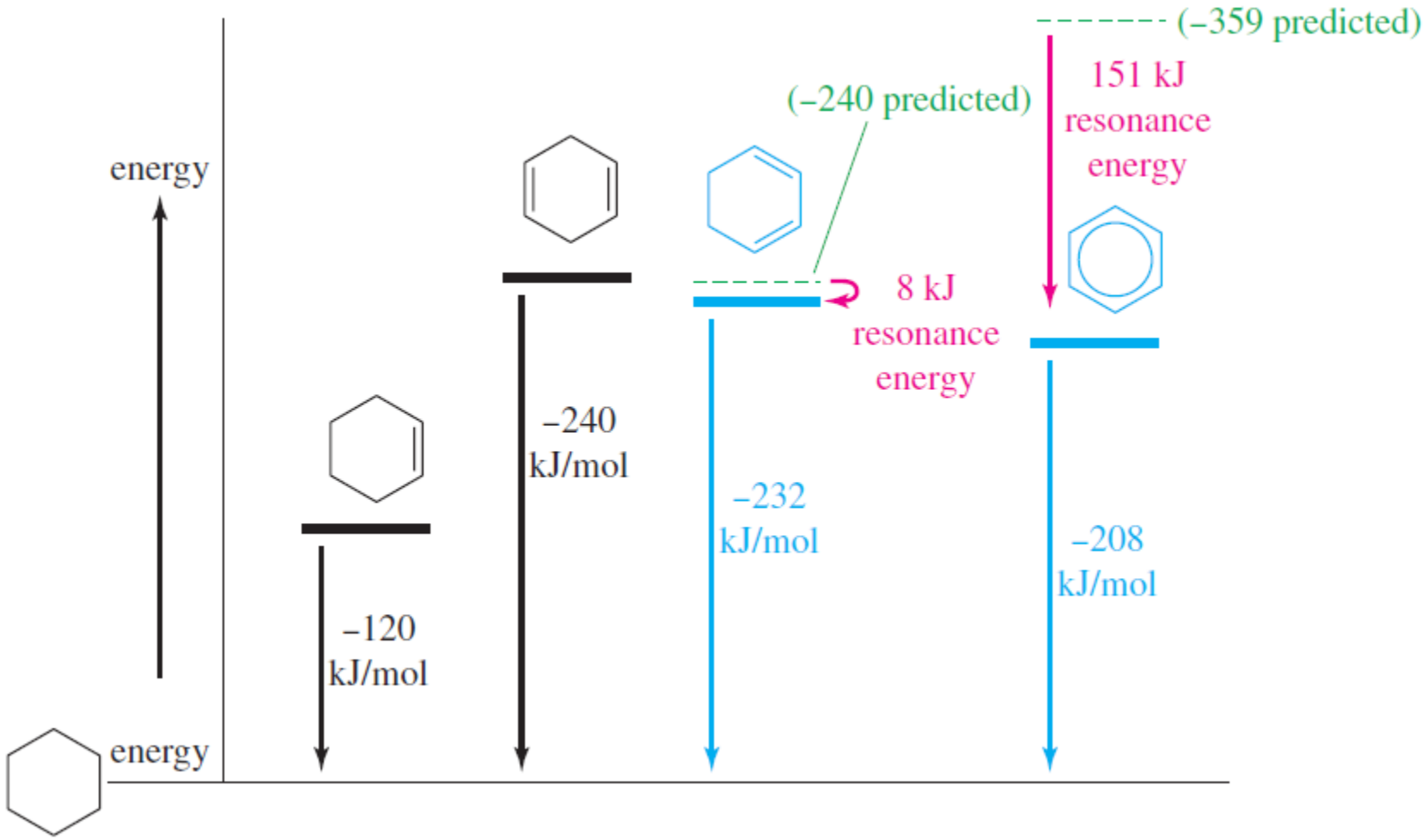
- Benzene is actually much **more stable** than we would expect; For example, an alkene decolorizes potassium **permanganate** by reacting to form a glycol. When permanganate is added to benzene, however, no reaction occurs





Aromaticity – The Unusual Stability

- Comparing **molar heats of hydrogenation**



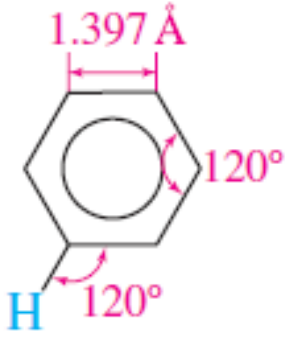
The huge 151 kJ/mol resonance energy of benzene cannot be explained by conjugation effects alone

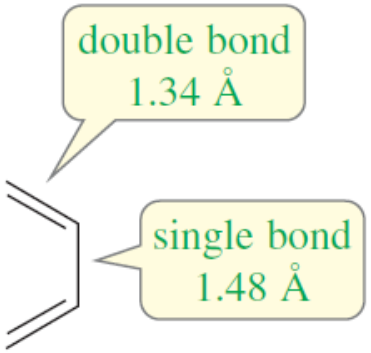
Aromaticity – Benzene

- Benzene is actually a **resonance hybrid** of the two Kekulé structures. This representation implies that the pi electrons are delocalized

resonance representation

- **Benzene** is a planar symmetrical hexagon with six trigonal (sp^2) carbon atoms. All the bond lengths are **1.39 Å** and all the bond angles are exactly **120°**

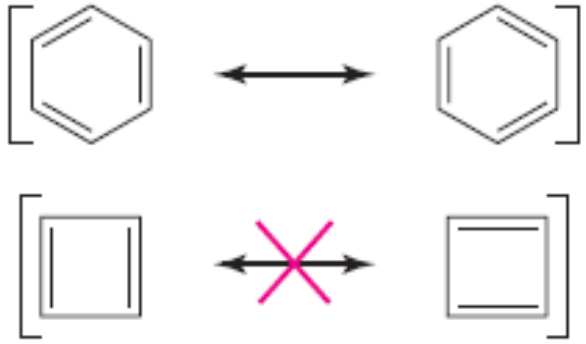




- Define an **aromatic compound** to be a cyclic compound containing some number of conjugated double bonds and having an unusually **large resonance energy**

Aromaticity – Annulenes

- **Annulenes** (cyclic hydrocarbons with alternating single and double bonds) are not always aromatic!



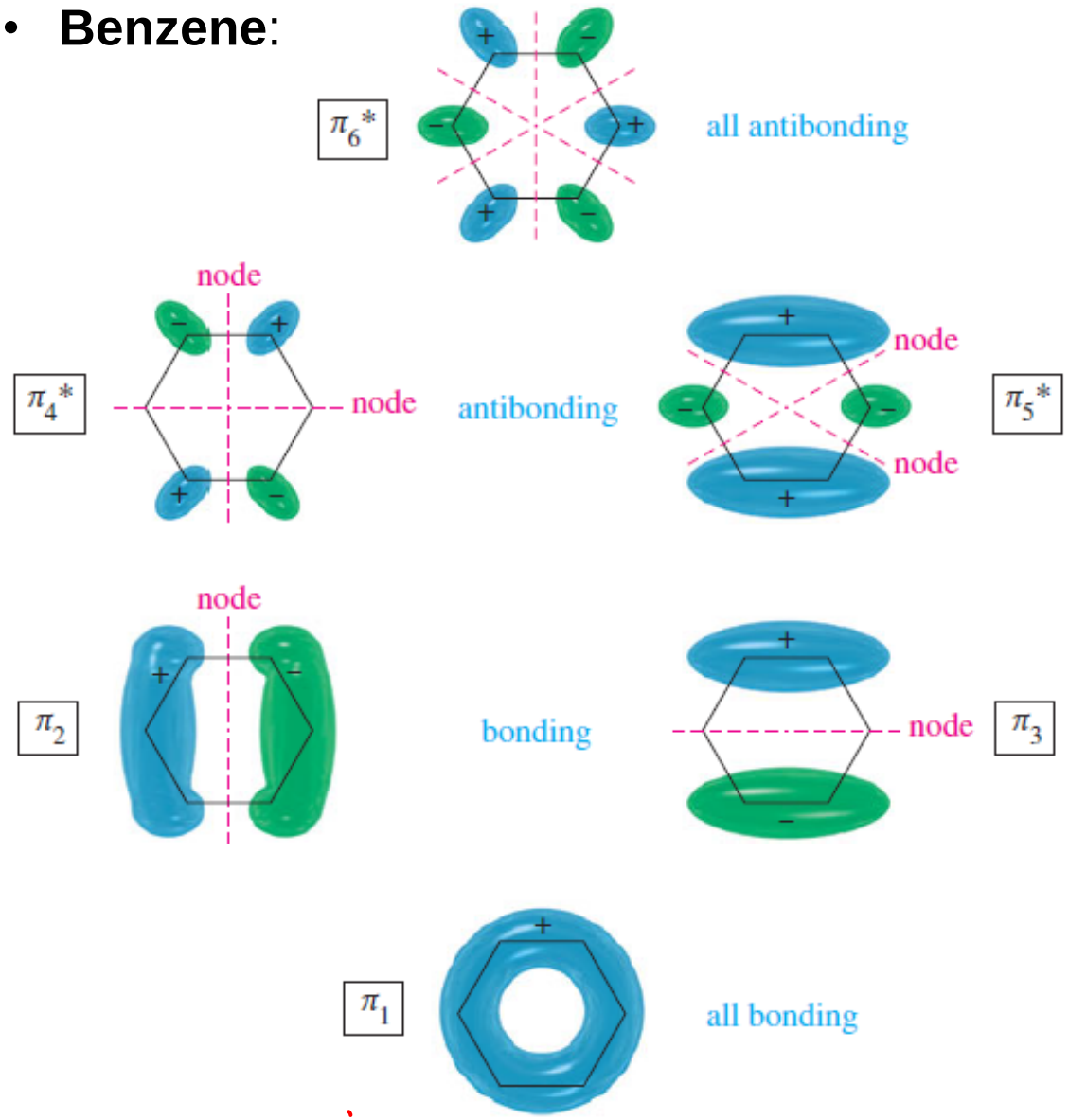
- Cyclobutadiene and cyclooctatetraene were mistakenly expected to be aromatic

- **Cyclobutadiene** has never been isolated and purified. It undergoes an extremely fast Diels–Alder dimerization

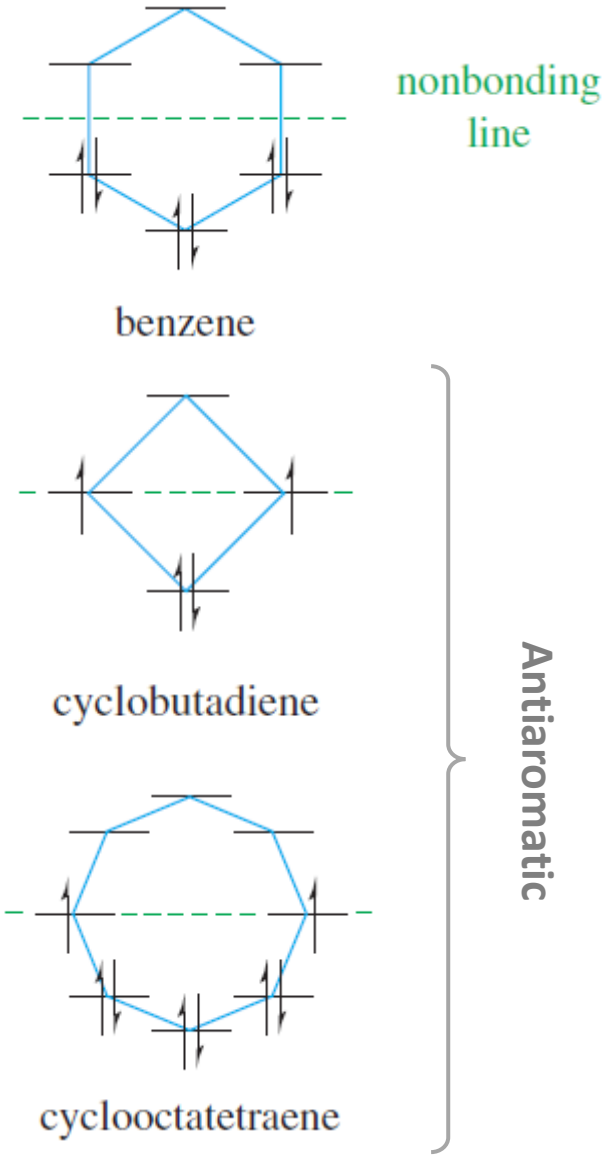
- Structural studies have shown that **cyclooctatetraene** is not planar. It is most stable in a "**tub**" conformation, with poor overlap between adjacent pi bonds

Aromaticity – Molecular orbital

- **Benzene**:

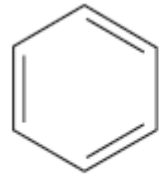


The polygon rule

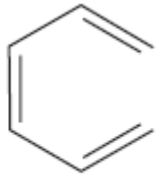


Aromaticity

- **Aromatic** structures are **more stable** than their open-chain counterparts

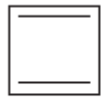


more stable (aromatic)

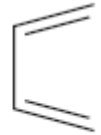


less stable

- **Antiaromatic** structures are **less stable** than their open-chain counterparts (delocalization of pi electrons *increases* the electronic energy!)

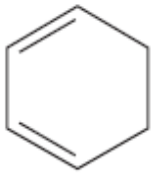


less stable (antiaromatic)

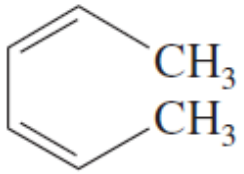


more stable

- A cyclic compound that does not have a continuous, overlapping ring of p orbitals cannot be aromatic or antiaromatic. It is said to be **nonaromatic**, or **aliphatic**. Its electronic energy is **similar** to that of its open-chain counterpart



(nonaromatic)



Aromaticity

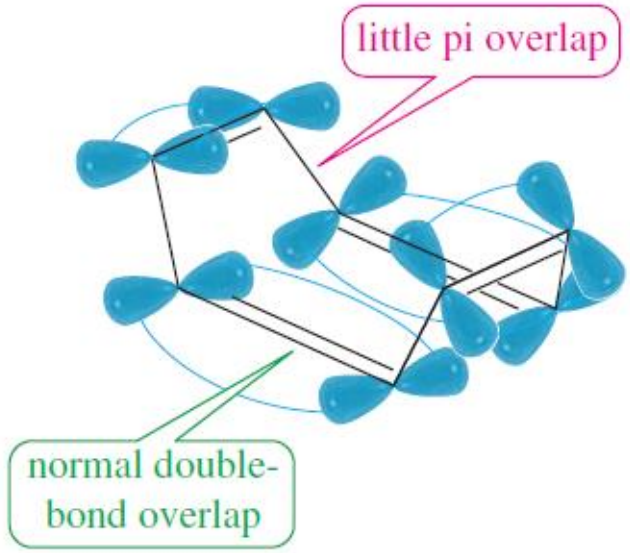
Criteria:

- The molecule must be **cyclic**
- This cycle must be **fully conjugated**
- The cycle must be **planar**
- The electrons must be able to "**circulate**"

Hückel's Rule: If the number of pi electrons in the cyclic system is:

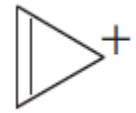
- **(4*N* + 2)** = the system is **aromatic**
- **(4*N*)** = the system is **antiaromatic**

Cyclooctatetraene would be **antiaromatic** if Hückel's rule applied (4*N*; *N* = 2). Cyclooctatetraene adopts a nonplanar "**tub**" conformation that avoids most of the overlap between adjacent pi bonds; becomes **nonaromatic** instead!

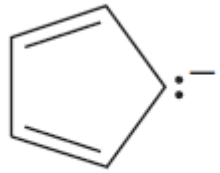


Aromaticity – Examples

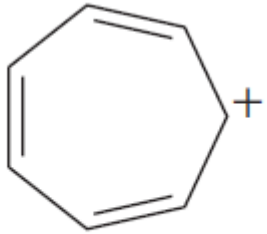
Aromatic Compounds



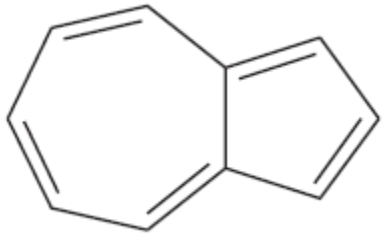
cyclopropenyl cation



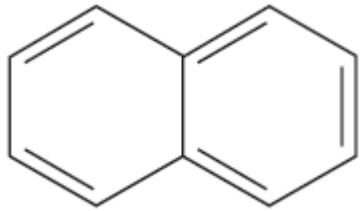
cyclopentadienyl anion



cycloheptatrienyl cation

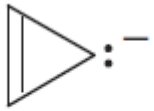


azulene



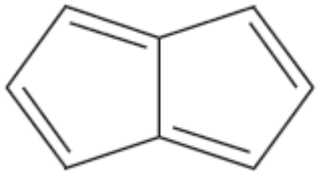
naphthalene

Antiaromatic Compounds

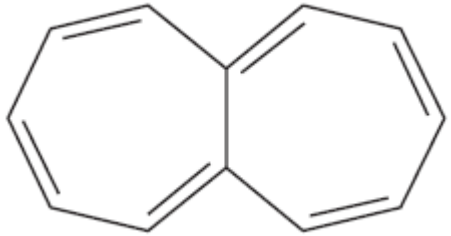


cyclopropenyl anion

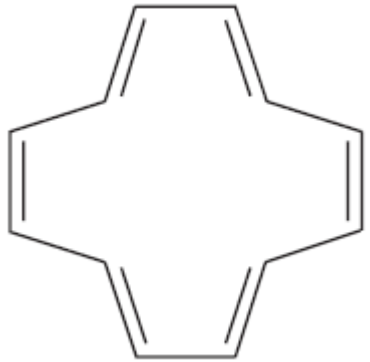
Antiaromatic (if planar)



pentalene



heptalene



[12]annulene