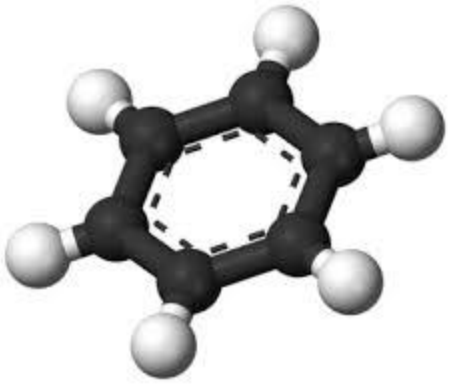
Aromaticity - 1



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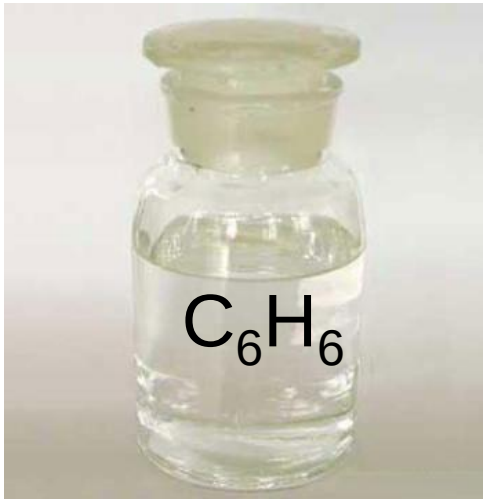
Recommended Textbook:

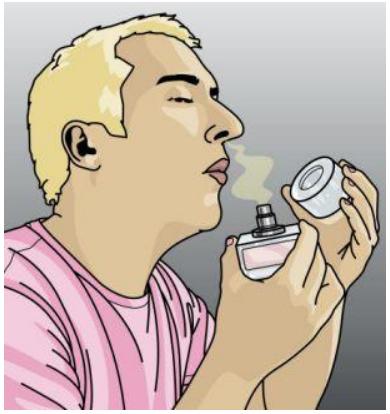
Chapter 16 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Discovery of Benzene

- Isolated in 1825 by Michael Faraday who determined **C:H ratio** to be **1:1**
- Synthesized in 1834 by Eilhard Mitscherlich who determined molecular formula to be **C_6H_6**. He named it *benzin*

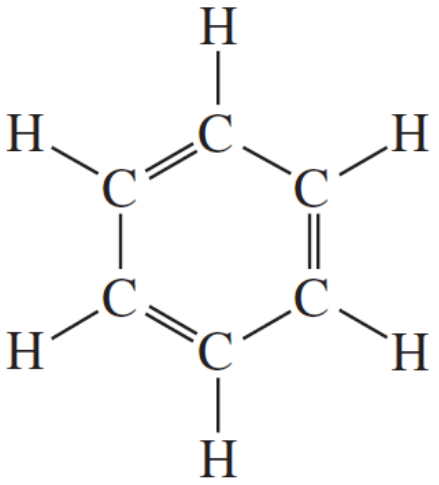


- Other related compounds with low C:H ratios had a pleasant smell, so they were classified as **aromatic**



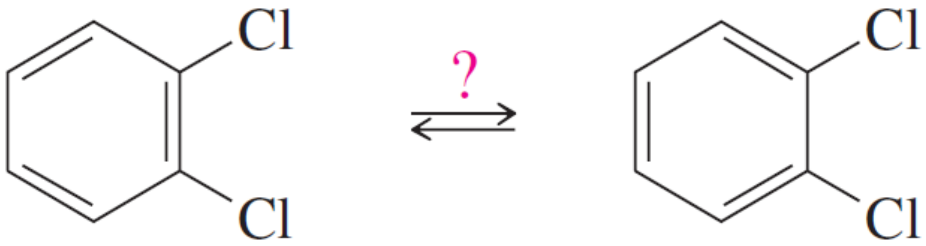
Kekulé Structure

- Proposed in 1866 by Friedrich Kekulé, shortly after multiple bonds were suggested



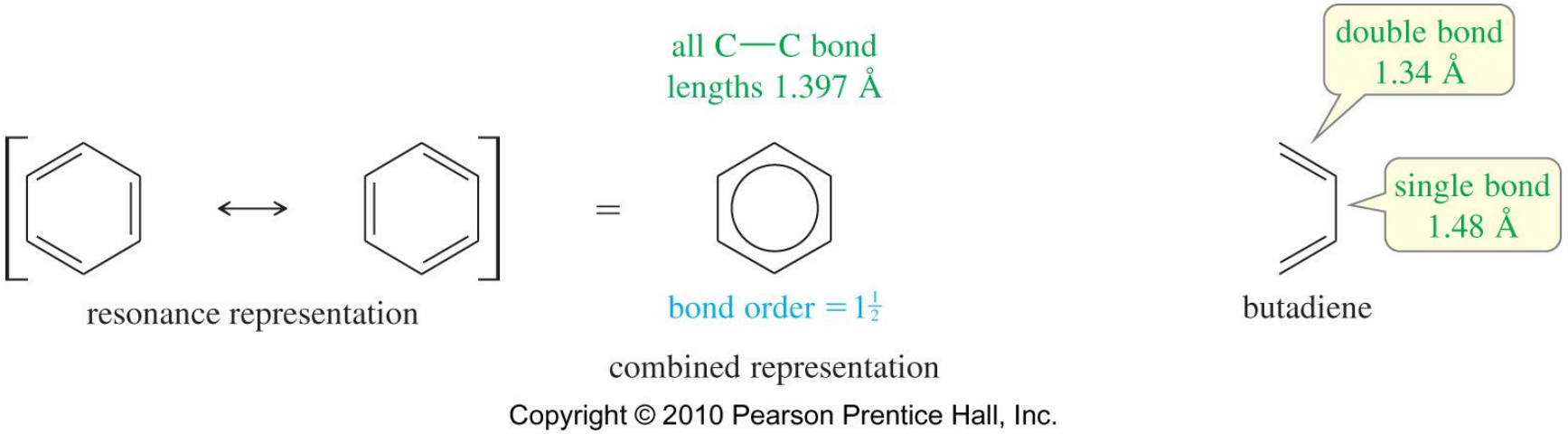
Kekulé structure of benzene

- Failed to explain existence of only **one isomer of 1,2-dichlorobenzene**



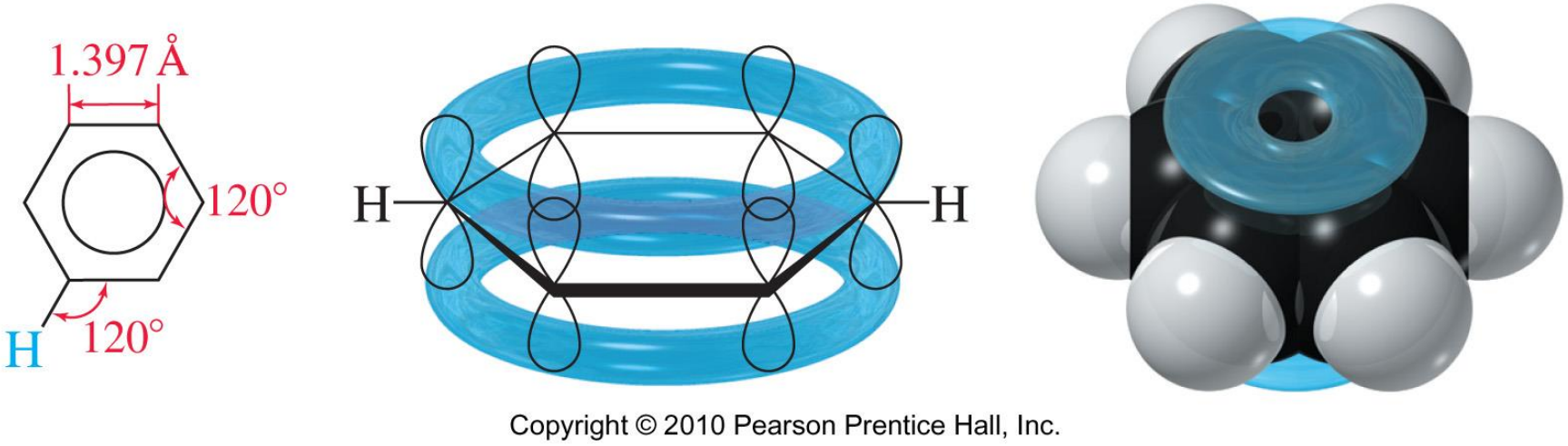
1,2-dichlorobenzene

Resonance Structures of Benzene



- Benzene is actually a **resonance hybrid** between the two Kekulé structures
- The **C—C bond lengths** in benzene are shorter than typical single-bond lengths, yet longer than typical double-bond lengths (bond order 1.5)
- Benzene's resonance can be represented by drawing a circle inside the six-membered ring as a **combined representation**

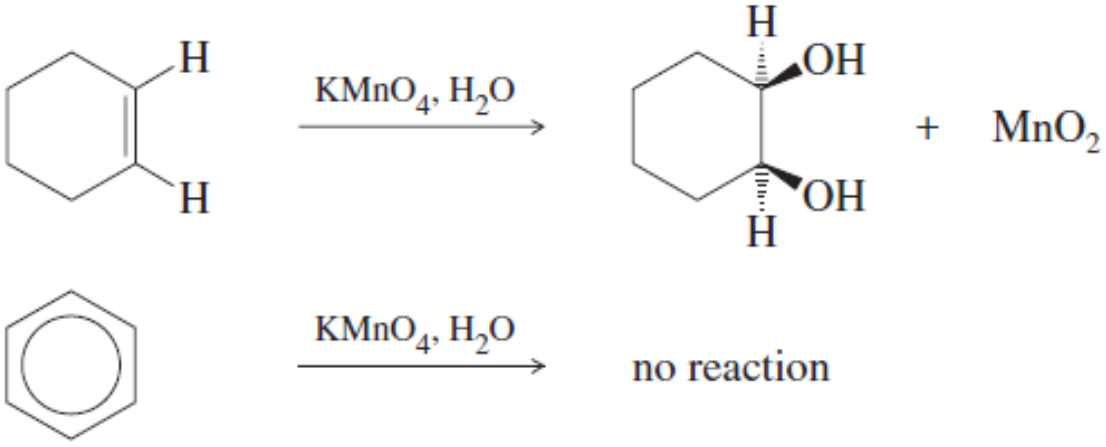
Structure of Benzene

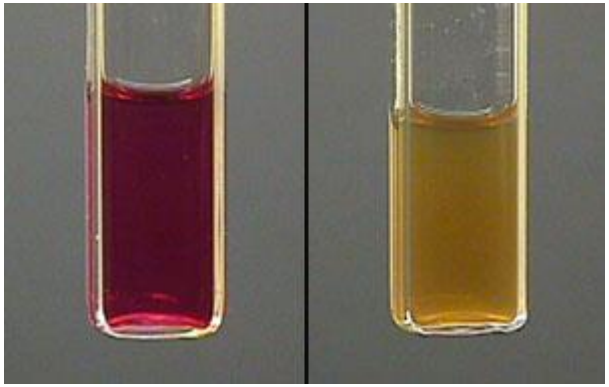


- Each **sp^2** hybridized C in the ring has an unhybridized **p orbital** perpendicular to the ring which **overlaps** around the ring.
- The **six pi electrons are delocalized** over the six carbons.

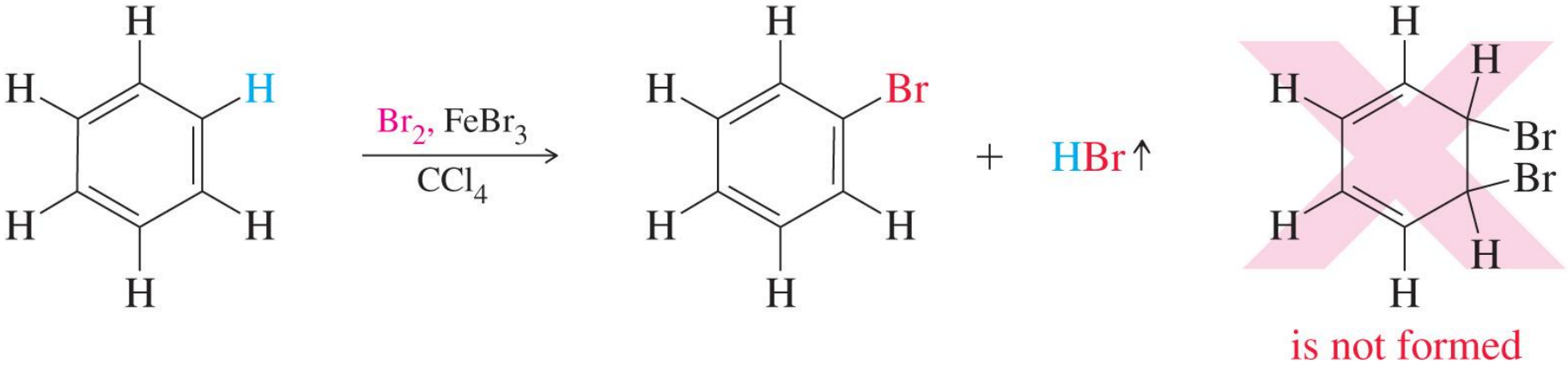
Unusual Reactivity of Benzene

- 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



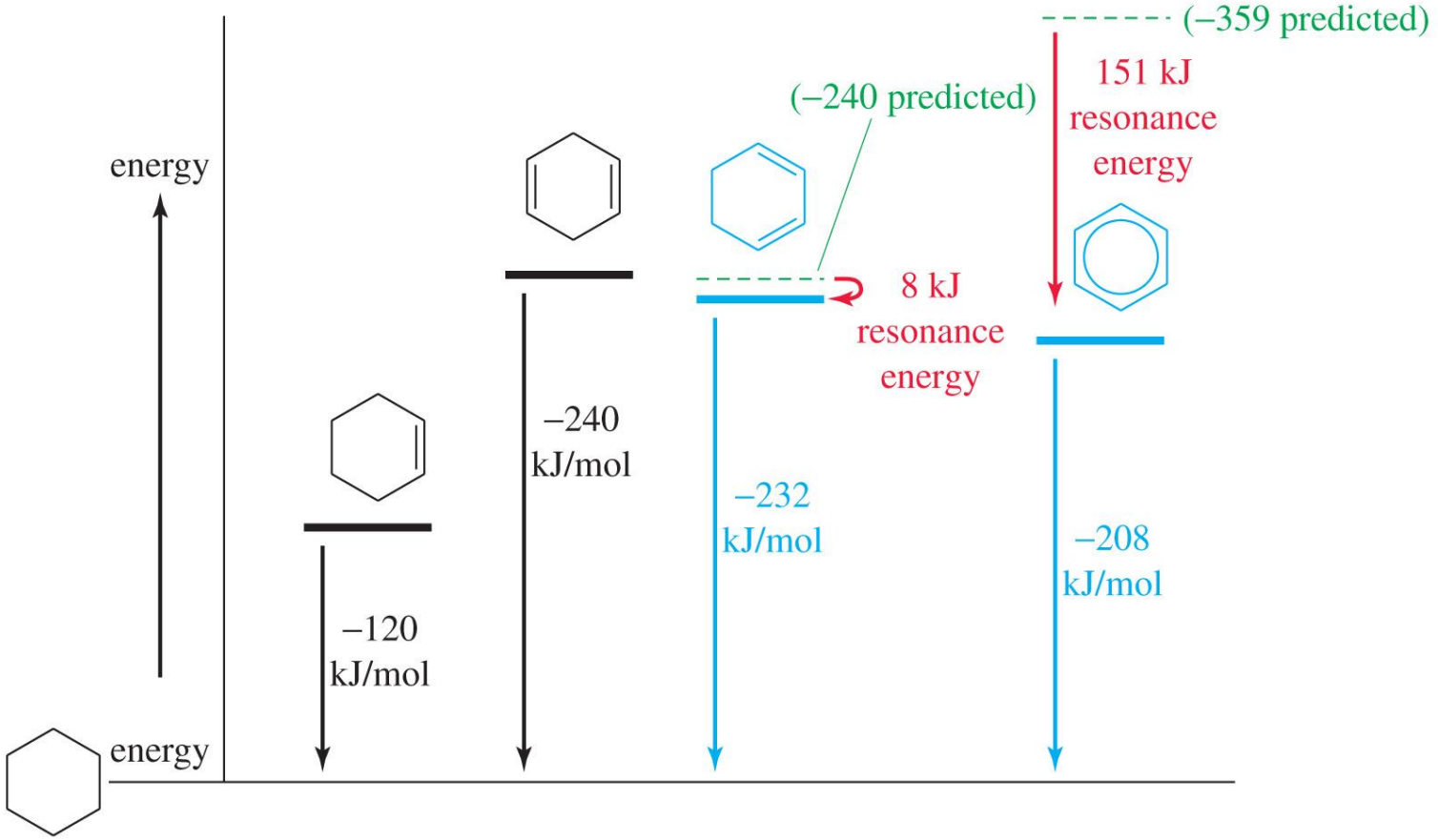


Unusual Reactivity of Benzene



- When bromine adds to benzene, a **catalyst** such as **$FeBr_3$** is needed.
- The reaction that occurs is the **substitution** of a hydrogen by bromine (cf. **addition** of bromine across alkenes)
- **Addition** of Br_2 to the double bond is not observed.

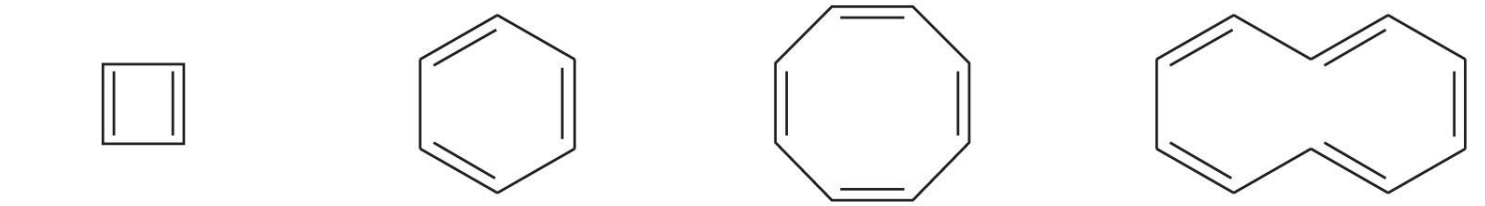
Resonance Energy



- Predicted heat of hydrogenation of -359 kJ/mol; observed value = -208 kJ/mol, a difference of **151 kJ (resonance energy)**

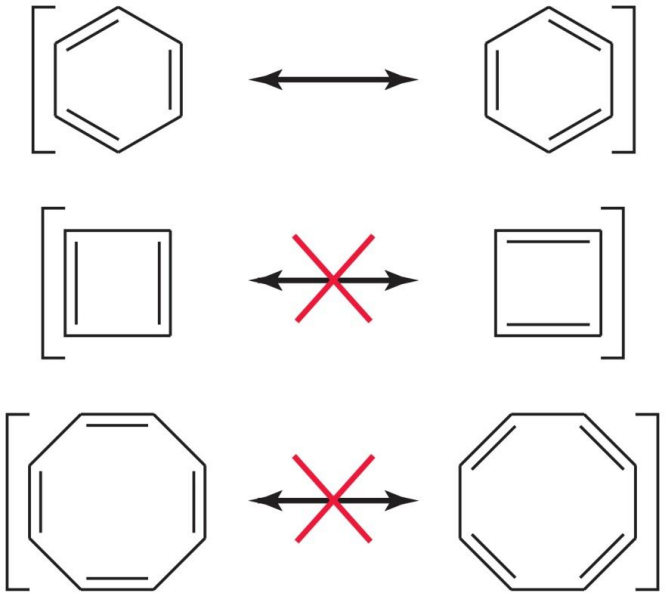
Annulenes

- Hydrocarbons with **alternating single and double bonds**



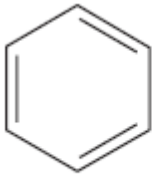
cyclobutadiene [4]annulene | benzene [6]annulene | cyclooctatetraene [8]annulene | cyclodecapentaene [10]annulene

- All annulenes were proposed to be aromatic (?)
- **However!!** *cyclobutadiene is so reactive that it dimerizes before it can be isolated*
- *Cyclooctatetraene adds Br_2 readily to the double bonds*

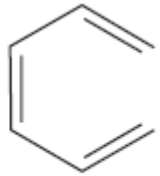


Aromaticity

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

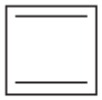


more stable (aromatic)



less stable

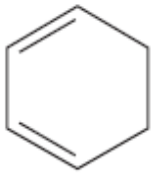
- **Antiaromatic** structures are **less stable** than their open-chain counterparts (delocalization of pi electrons *increases* the electronic energy!)



less stable (antiaromatic)

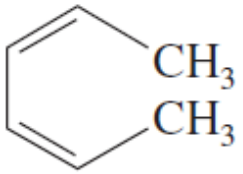
more stable

- 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



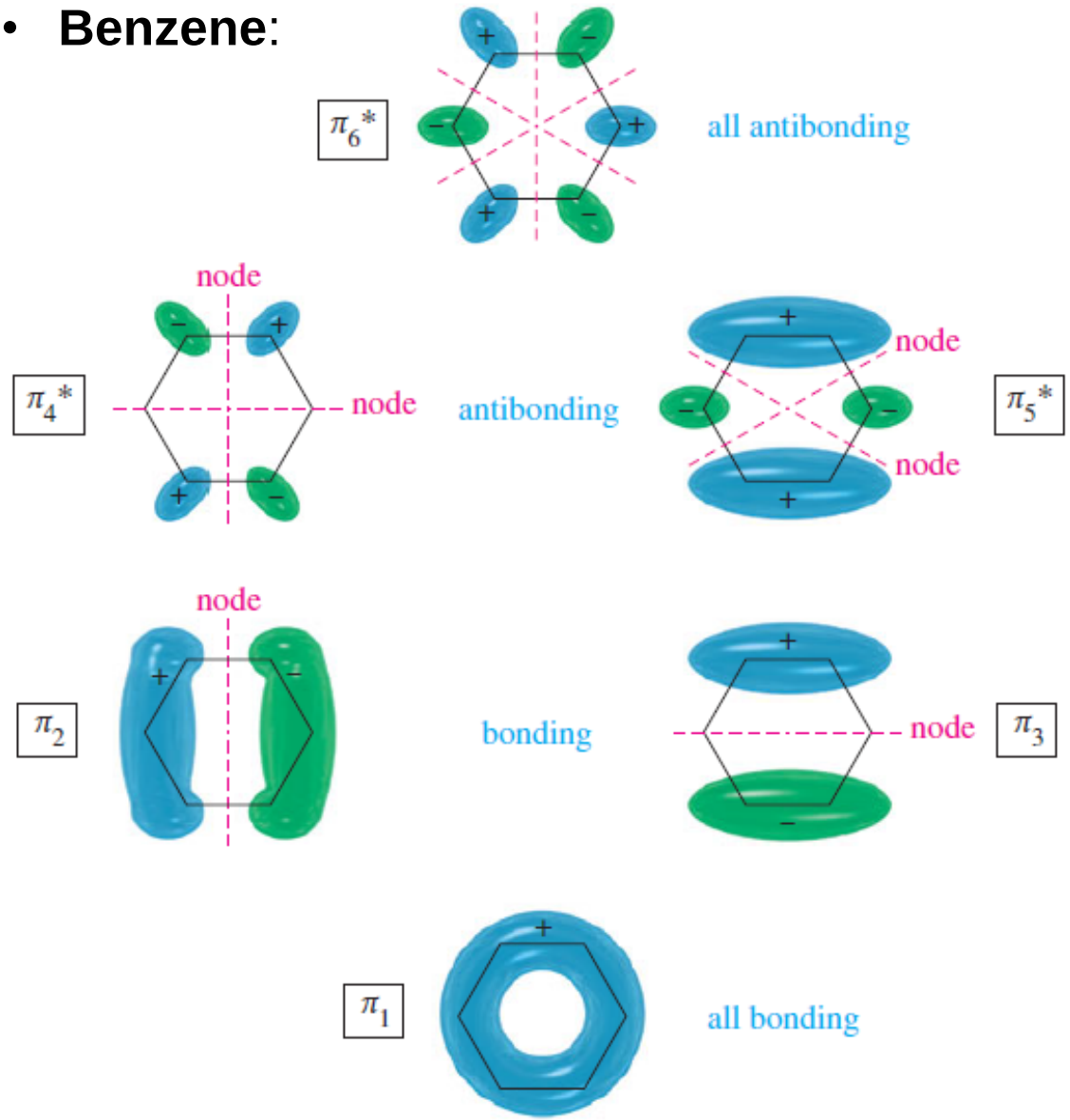
(nonaromatic)

⟵ similar stabilities ⟶

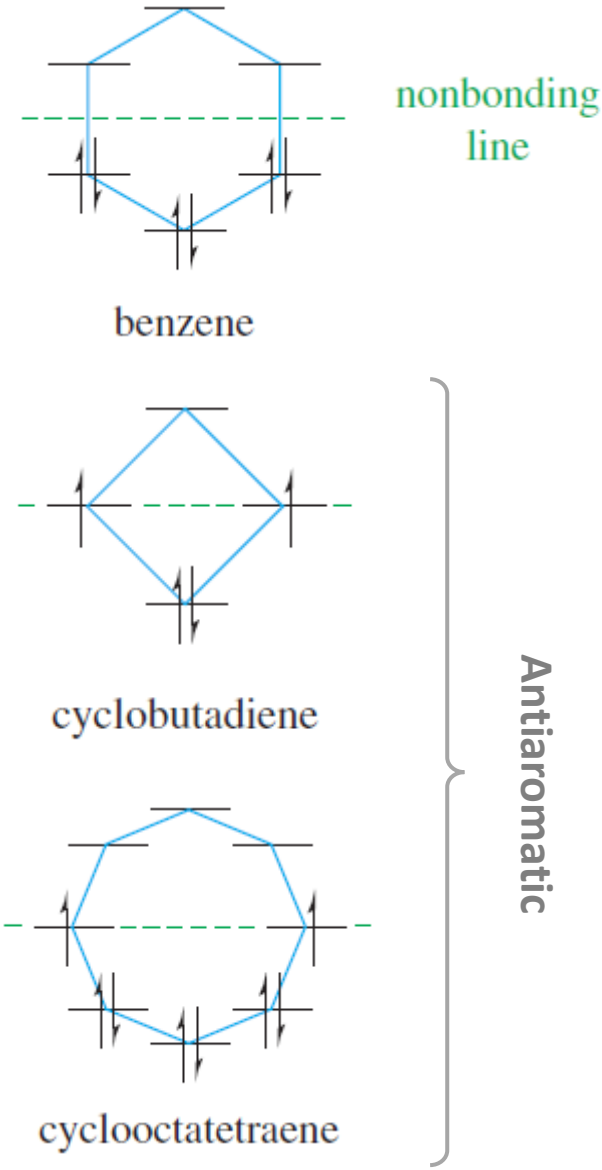


Aromaticity – Molecular orbital

- **Benzene**:



The polygon rule



Aromaticity

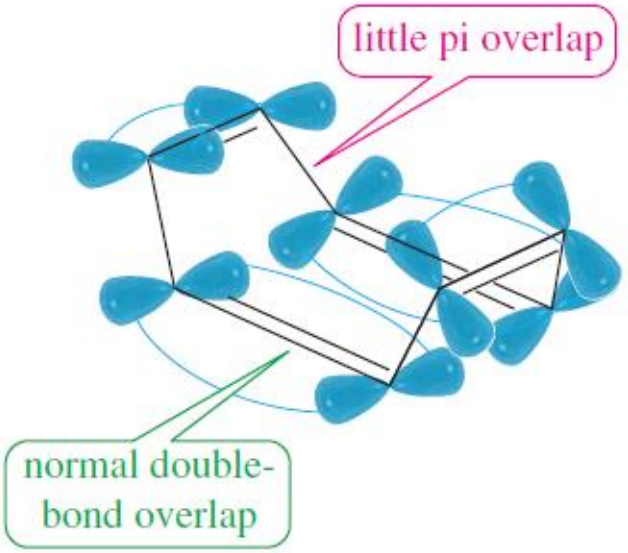
Criteria:

- 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**

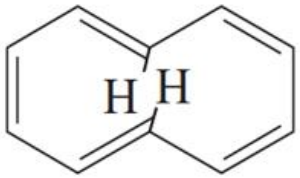
Cyclooctatetraene would be **antiaromatic** if Hückel's rule applied (4*N*; *N* = 2). Cyclooctatetraene adopts a nonplanar "**tub**" conformation that avoids most of the overlap between adjacent pi bonds; becomes **nonaromatic** instead!



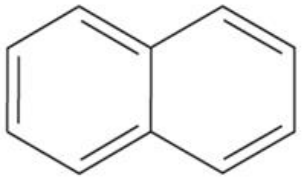
Problem

Classify the following compounds as aromatic, antiaromatic, or nonaromatic.

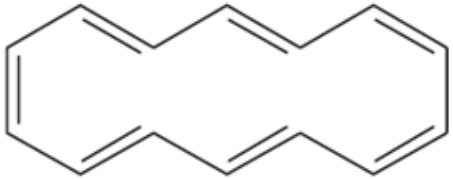
all-cis

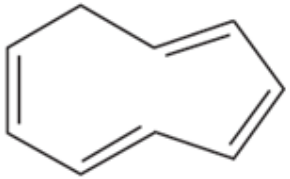


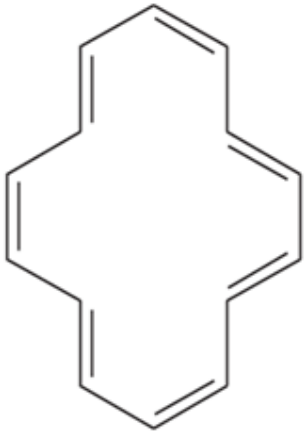
two trans

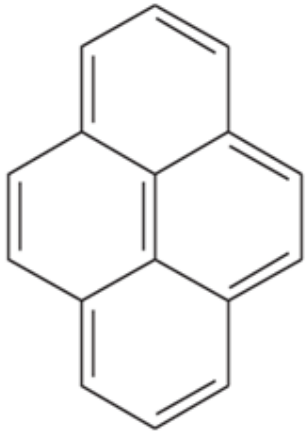


naphthalene

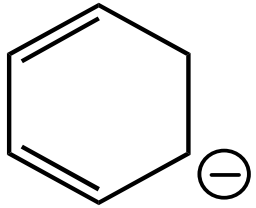


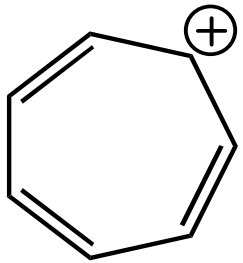






Which of the following is an aromatic compound?





There is an sp^3 carbon in the ring, delocalization will not be complete.

All carbons are sp^2 hybridized and it obeys Huckel's rule.