Benzene and Aromaticity

B. Pharm. Semester-1

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Dr. BALAKUMAR CHANDRASEKARAN

Professor-Faculty of Pharmacy

Philadelphia University-Jordan

Learning Outcomes

- **At the end of this lesson students will be able to**
  - **Define aromatic compounds**
  - **Understand why this chapter is important**
  - **Nomenclature of aromatic compounds**
  - **Explain the structure and stability of benzene**
  - **Aromaticity and Huckel's rule**
  - **Aromatic ions**
  - **Cyclopentadienyl anion and cycloheptatrienyl cation**
  - **Heterocyclic aromatic compounds: Pyridine and pyrrole**
  - **Polycyclic aromatic compounds**

Objective

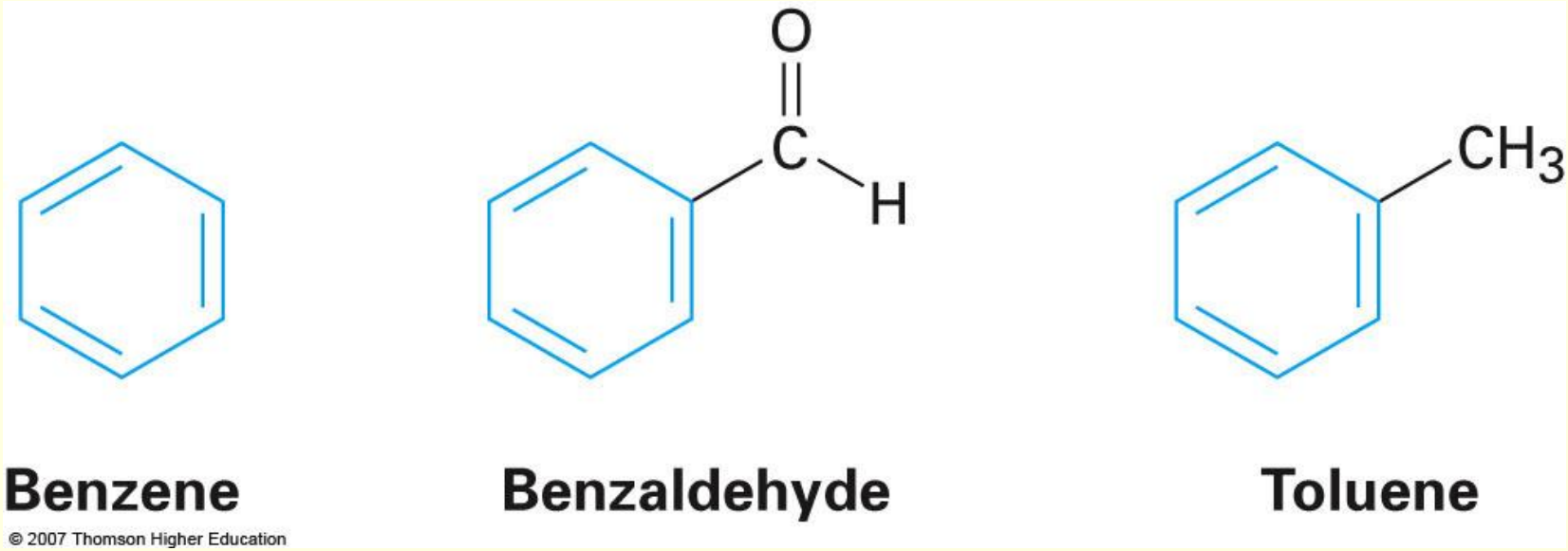
The objective of this course is to give to the students of pharmacy the basic knowledge about the organic chemistry.

Aromatic Compounds

- Earlier days of organic chemistry, the word *Aromatic* was used to describe such fragrant substances [benzene (coal distillate), benzaldehyde (from cherries, peaches and almonds), toluene (from Tolu balsam).
- Later, they are grouped based on their chemical behavior (unsaturated compounds that undergo substitution rather than addition).
- Currently aromatic was distinguished from *aliphatic* compounds by electronic configuration.

Aromatic Compounds

Today, we use the word *Aromatic* refers to the class of compounds that contain six-membered benzene-like rings with three double bonds.



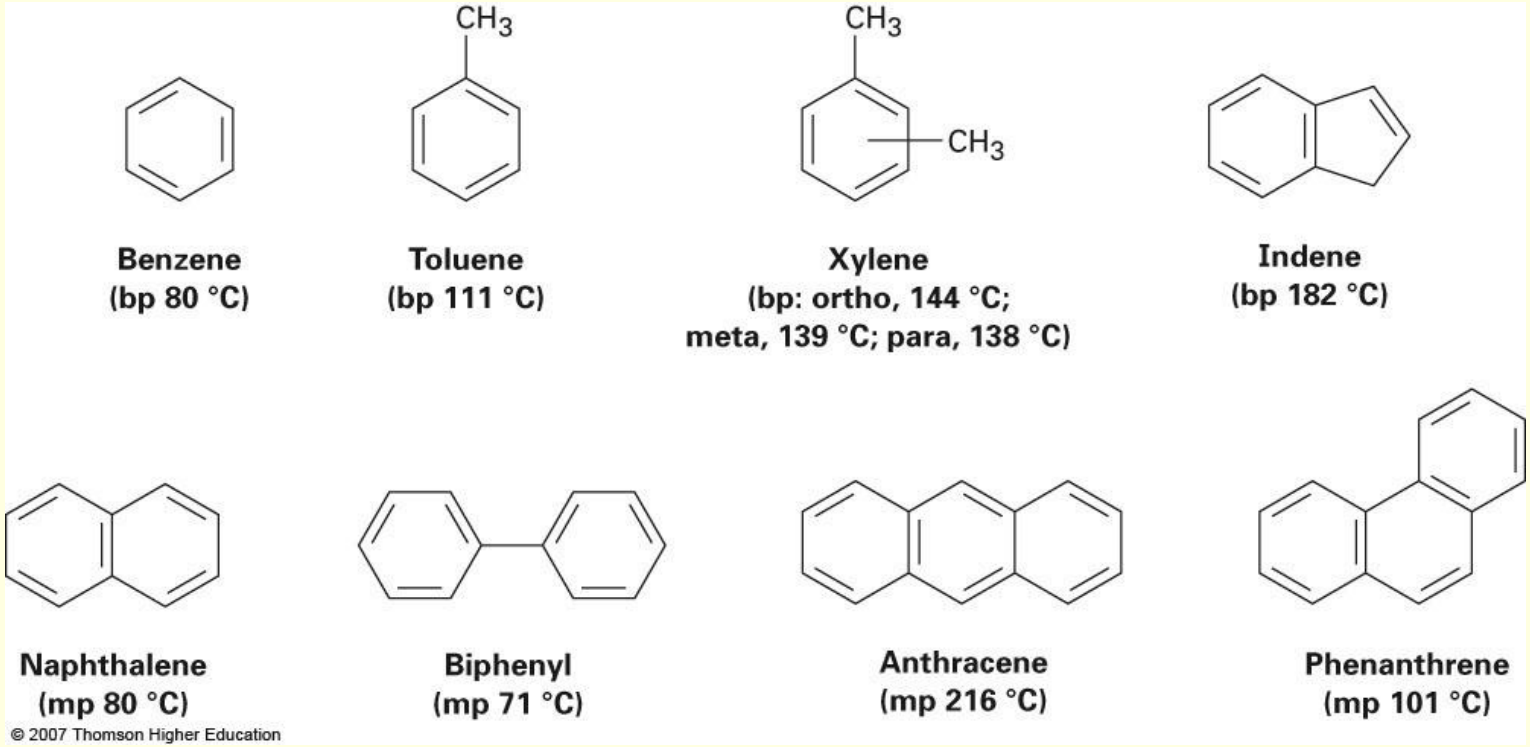
Why this Chapter?

- The reactivity of the substituted aromatic compounds is tied to their exact structure.

- Aromatic compounds provide a sensitive probe for studying relationship between the structure and reactivity.

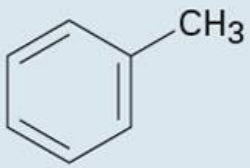
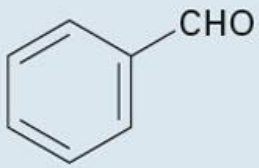
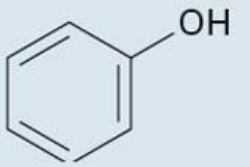
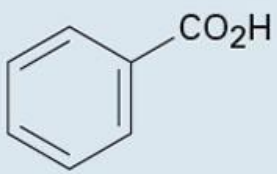
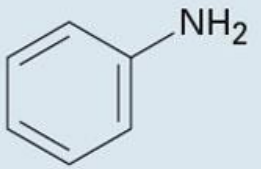
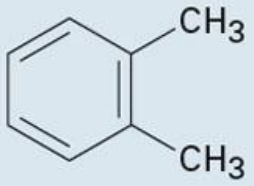
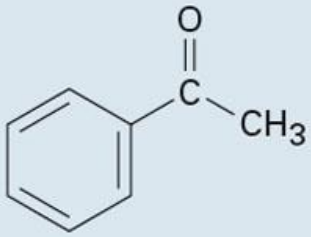
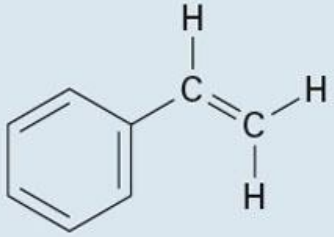
Sources and Names of Aromatic Hydrocarbons

- Two sources: Coal and petroleum
- From high temperature distillation of coal tar
- Heating petroleum at high temperature and pressure over a catalyst



Common names: Aromatic compounds

Table 15.1 Common Names of Some Aromatic Compounds

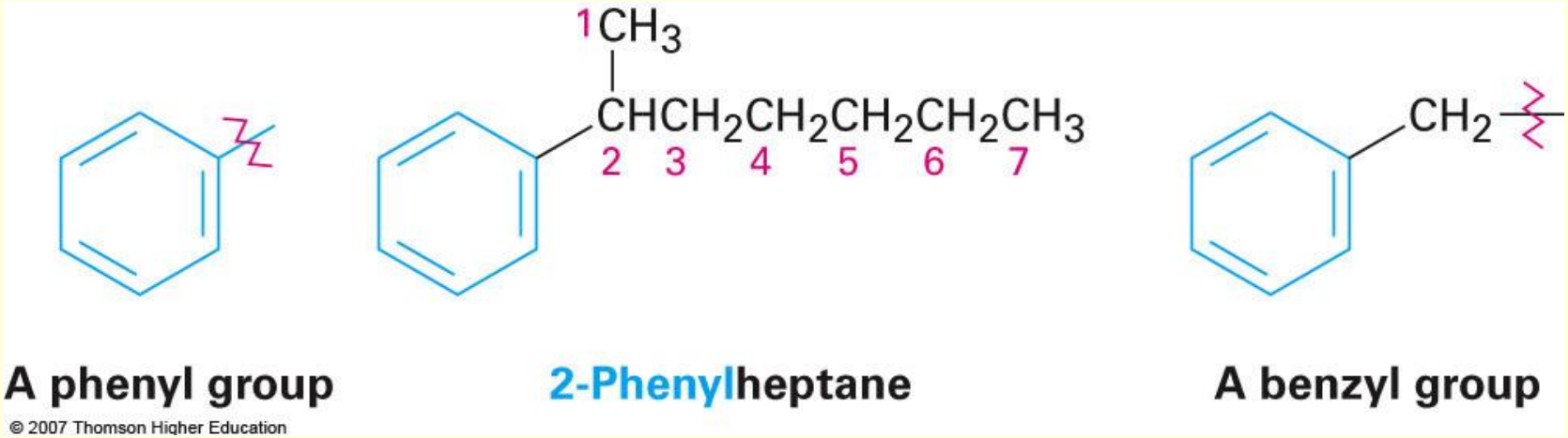
Structure	Name	Structure	Name
	Toluene (bp 111 °C)		Benzaldehyde (bp 178 °C)
	Phenol (mp 43 °C)		Benzoic acid (mp 122 °C)
	Aniline (bp 184 °C)		*ortho*-Xylene (bp 144 °C)
	Acetophenone (mp 21 °C)		Styrene (bp 145 °C)

Naming Aromatic Compounds

- Many common names (toluene = methylbenzene; aniline = aminobenzene)
- Monosubstituted benzenes systematic names as hydrocarbons with *–benzene*
  - C_6H_5Br = bromobenzene
  - $C_6H_5NO_2$ = nitrobenzene, and $C_6H_5CH_2CH_2CH_3$ is propylbenzene

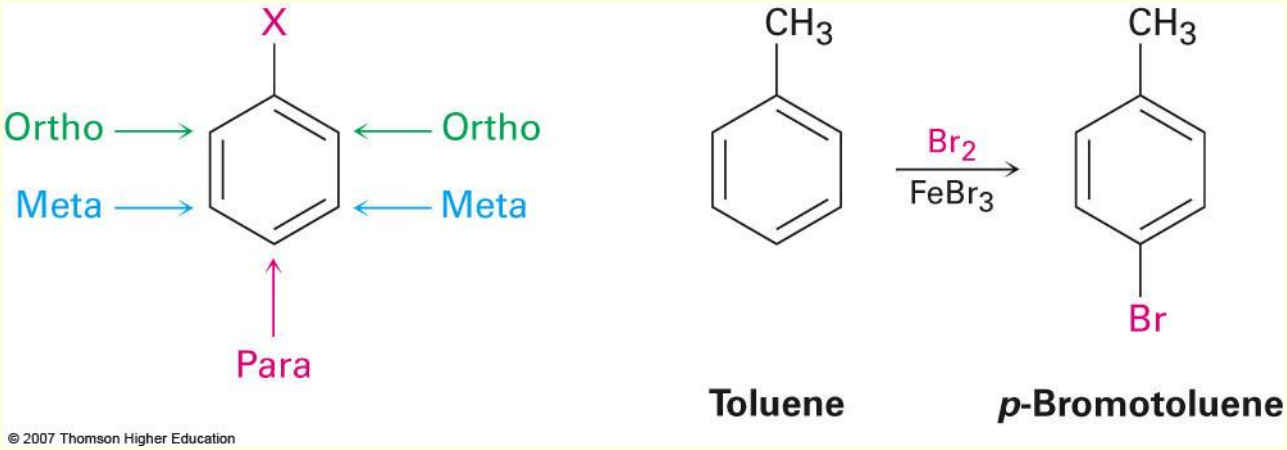
The Phenyl Group

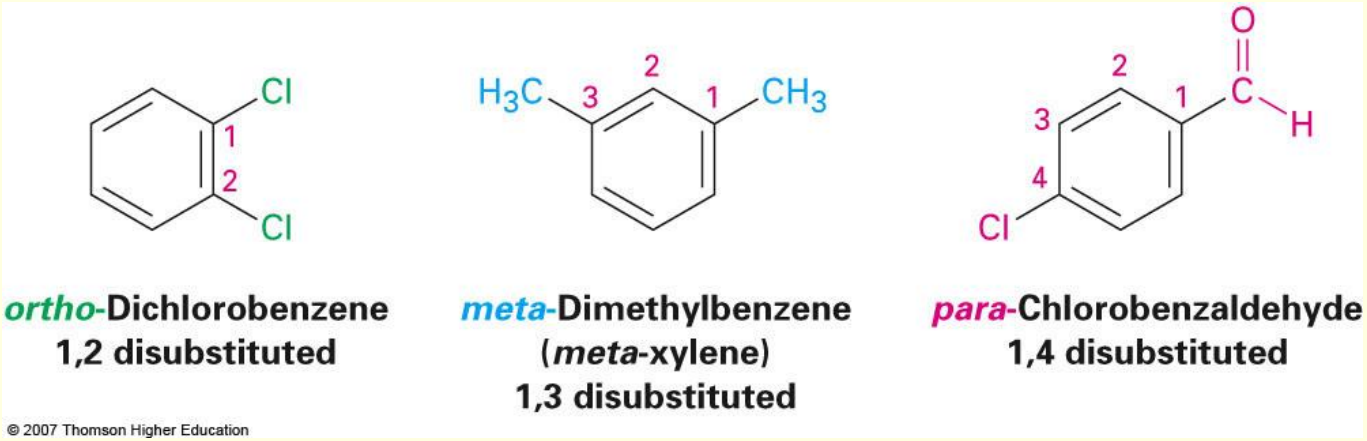
- When a benzene ring is a substituent, the term **phenyl** is used (for C_6H_5□)
  - You may also see "Ph" or "ϕ" in place of "C_6H_5"
- "**Benzyl**" refers to "$C_6H_5CH_2$□"



Disubstituted Benzenes

- Relative positions on a benzene ring
  - ***ortho- (o)*** on adjacent carbons (1,2 relationship on the ring)
  - ***meta- (m)*** separated by one carbon (1,3 relationship)
  - ***para- (p)*** separated by two carbons (1,4 relationship)
- Describes reaction patterns (“occurs at the para position”)





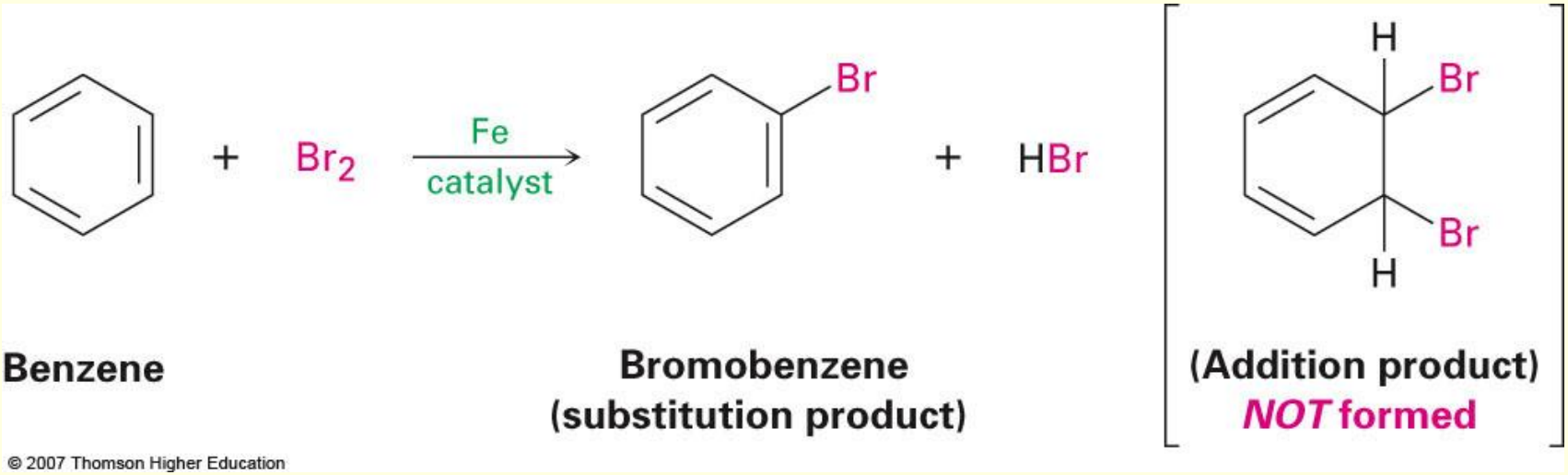
Naming of Benzenes With More Than Two Substituents

- Choose numbers to get lowest possible values for the 2nd substituent.
- List substituents alphabetically with hyphenated numbers.
- Common names, such as “toluene” can serve as root name (as in TNT).

4-Bromo-1,2-dimethylbenzene 2,5-Dimethylphenol 2,4,6-Trinitrotoluene (TNT)

Structure and Stability of Benzene: Molecular Orbital Theory

- Benzene reacts slowly with Br_2 to give bromobenzene (where Br replaces H).
- This is substitution rather than the rapid addition reaction commonly seen for compounds with C=C, suggesting that in benzene there is a higher barrier.



Heats of Hydrogenation as Indicator of the Stability

- Heat of hydrogenation is the quantity of heat evolved when one mole of an unsaturated compound is hydrogenated.
- The addition of H_2 to C=C normally gives the value of about 28-30 K.cal.

Compound	Heat of hydrogenation in K.cal
Cyclohexene	28.6
Cyclohexadiene	55.4
Cyclohexatriene	85.8

But, Benzene = 49.8 K.cal

Heats of Hydrogenation as Indicator of the Stability

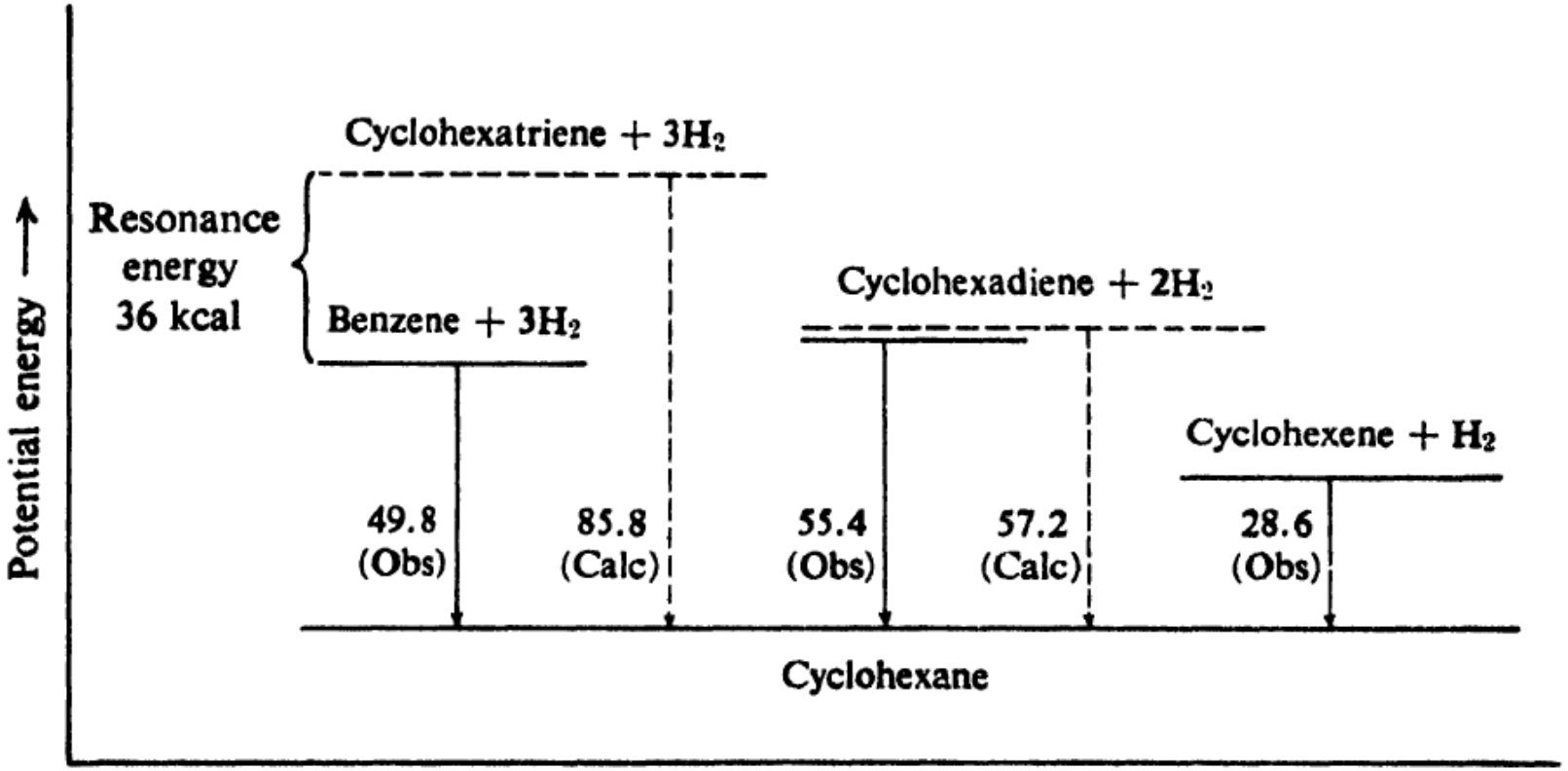
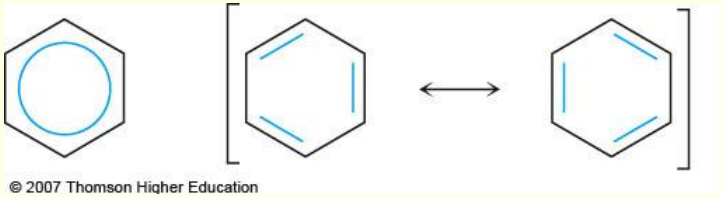


Figure 10.1. Heats of hydrogenation and stability: benzene, cyclohexadiene, and cyclohexene.

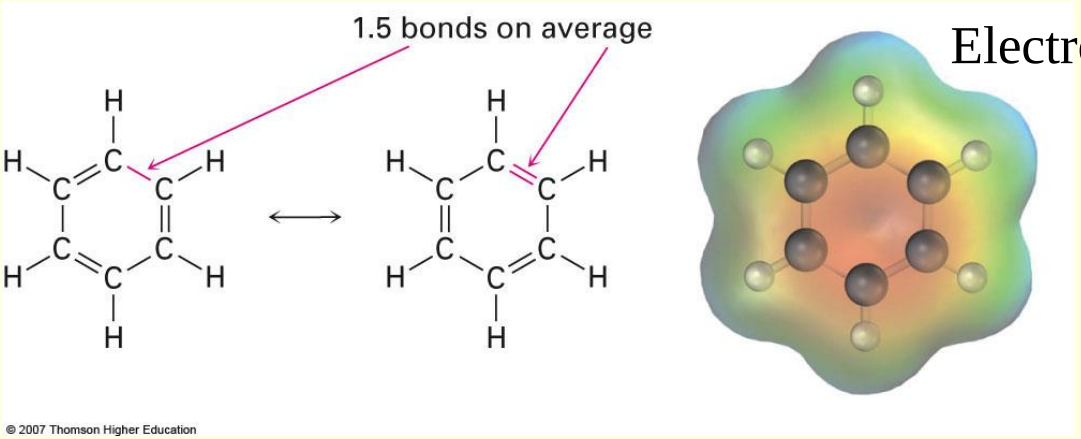
Benzene's Unusual Structure

- All its C-C bonds are the same length: 139 pm (picometer) that is between the lengths of regular single (154 pm) and regular double (134 pm) bonds.
- Electron density in all six C-C bonds is identical
- Structure is planar, hexagonal
- C–C–C bond angles 120°
- Each C is sp^2 and has a *p* orbital perpendicular to the plane of the six-membered ring.



Hybrid **Resonance structures**

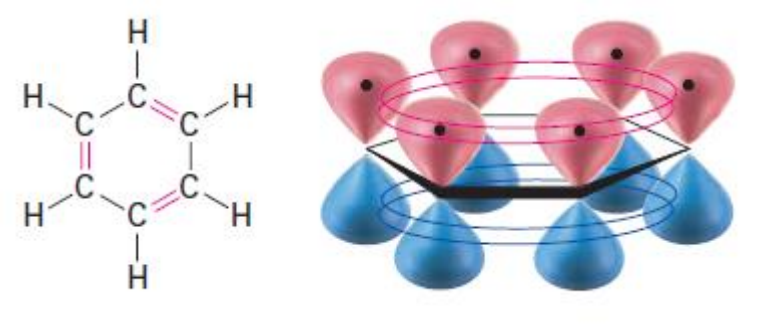
Benzene's Unusual Structure



Electrostatic potential map

- All six carbon atoms and all six 'p' orbital are equivalent.
- Each *p* orbital overlaps and give 6π electrons are completely delocalized around the ring.

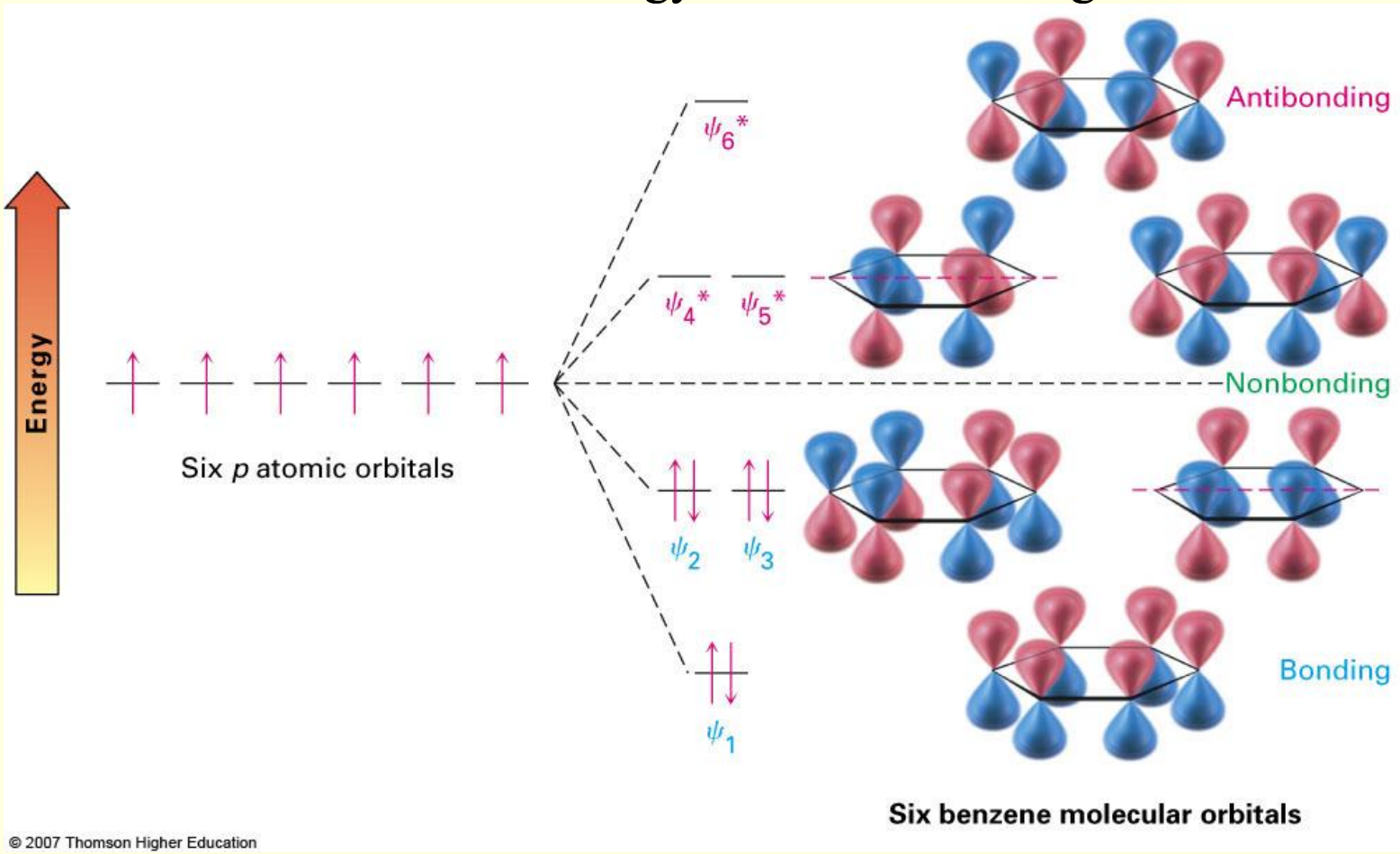
Benzene's Orbital Picture



- Each of the six carbon atoms has a 'p' orbital that can overlap equally well with the neighbouring 'p' orbitals on both sides.
- As a result all C-C bonds are equivalent and benzene must be represented as hybrid of two resonance structures.

Molecular Orbital Description of Benzene

- The 6 p-orbitals combine to give
  - Three bonding orbitals with 6π electrons,
  - Three antibonding with no electrons
- Orbitals with the same energy are said to be 'degenerate'



Aromaticity

Benzene:-

- Planar hexagon: bond angles are 120°, carbon–carbon bond lengths 139 pm
- Cyclic, and conjugated
- Unusually stable and heat of hydrogenation 36 K.cal. less than the expected cyclohexatriene.
- Undergoes substitution rather than electrophilic addition
- Resonance hybrid as the structure of benzene is intermediate between two line-bond structures.

- But, to describe the aromaticity, **Hückel 4n+2 Rule** is required.

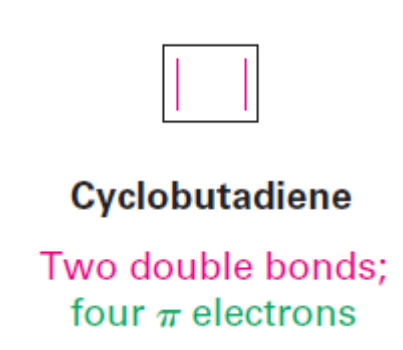
Hückel 4n+2 Rule

- 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 = 0,1,2,3,4….)*
- *In other words, only molecules with 2, 6, 10, 14, 18, . . . π electrons can be aromatic.*
- Huckel's rule, based on calculations – a planar cyclic molecule with alternating double and single bonds has aromatic stability if it has ***4n+ 2*** *π electrons (n is 0,1,2,3,4*).
- For n=1: 4n+2 = 6; **benzene** is stable and the electrons are delocalized.

Hückel 4n+2 Rule

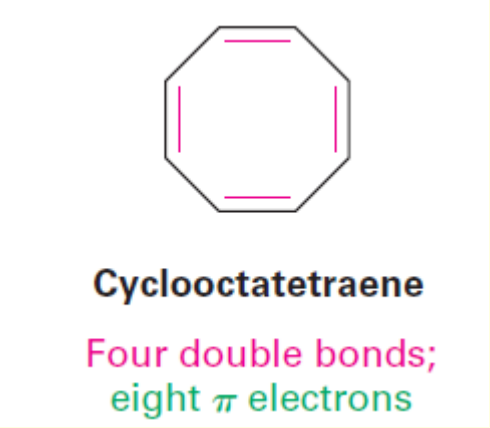
- Molecules with 4n π electrons (4, 8, 12, 16, . . .) can't be aromatic, even though they may be cyclic, planar, and apparently conjugated.
- In fact, planar, conjugated molecules with 4n π electrons are said to be antiaromatic because delocalization of their π electrons would lead to their destabilization.

Examples:-



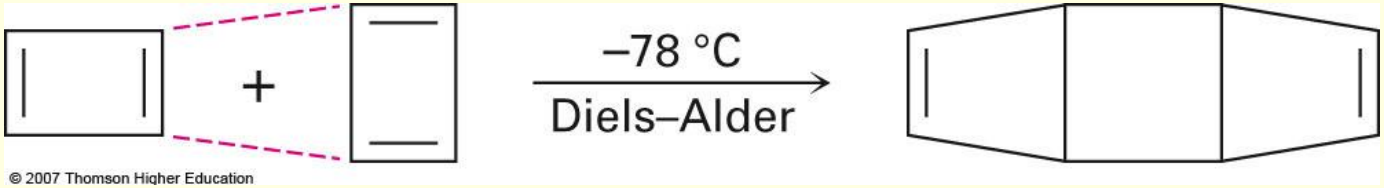
π electrons are localized instead of delocalization, so cyclobutadiene is said to be anti-aromatic.

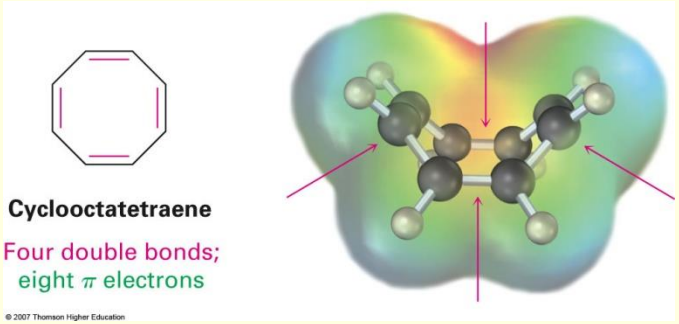
π electrons are localized instead of delocalization, and the molecule is tub-shaped, so cyclooctatetraene is not aromatic.



Compounds With 4n π Electrons Are Not Aromatic (May be Antiaromatic)

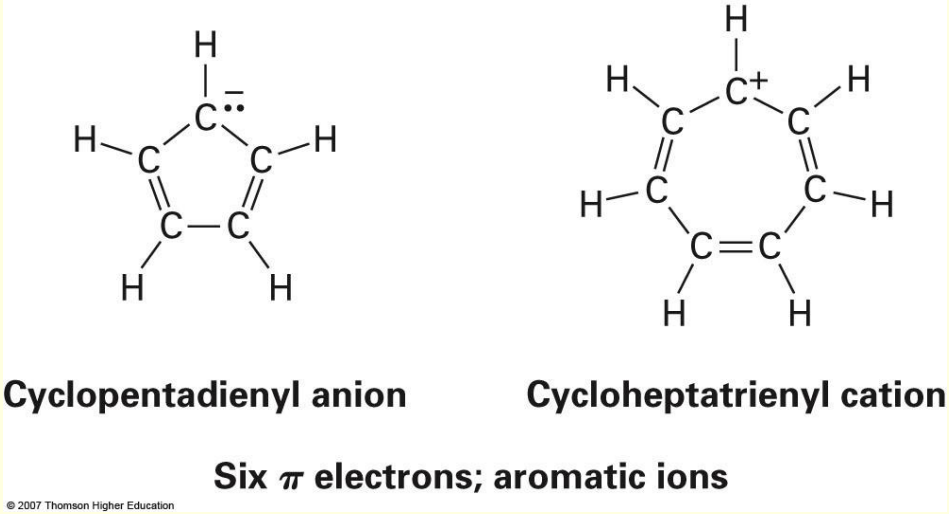
- Planar, cyclic molecules with ***4 n*** π electrons are much *less* stable than expected (antiaromatic)
- They will distort out of plane and behave like ordinary alkenes
- 4- and 8-electron compounds are not delocalized (single and double bonds)
- Cyclobutadiene is so unstable that it dimerizes by a self-Diels-Alder reaction at low temperature
- Cyclooctatetraene has four double bonds, reacting with Br_2, $KMnO_4$, and HCl as if it were four alkenes





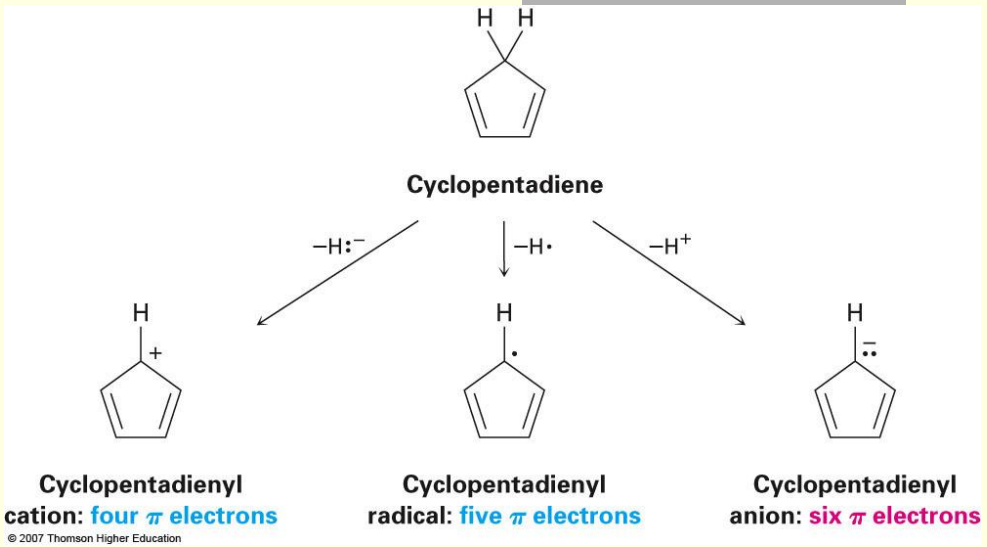
Aromatic Ions

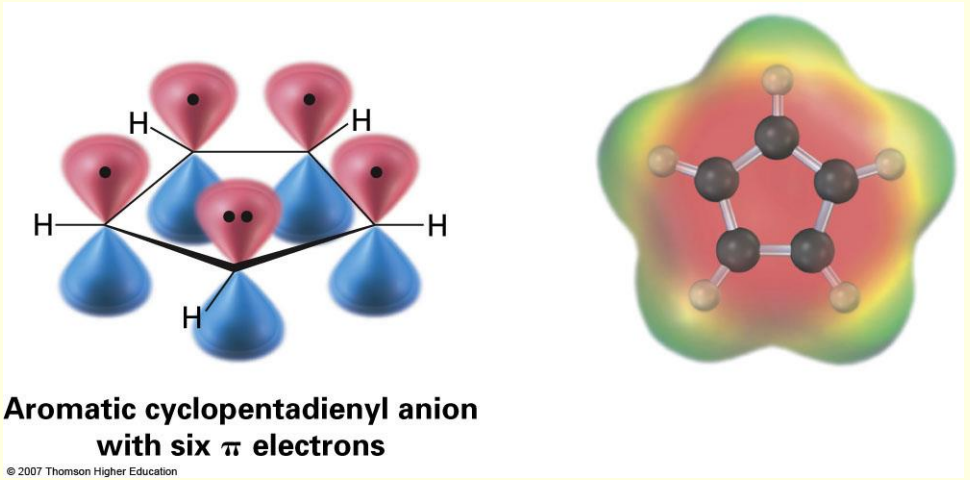
- The $4n + 2$ rule applies to ions as well as neutral species
- Both the cyclopentadienyl *anion* and the cycloheptatrienyl *cation* are aromatic though they are not 6-membered rings.
- The key feature of both is that they contain 6π electrons in a ring of continuous p orbitals



Cyclopentadienyl Anion

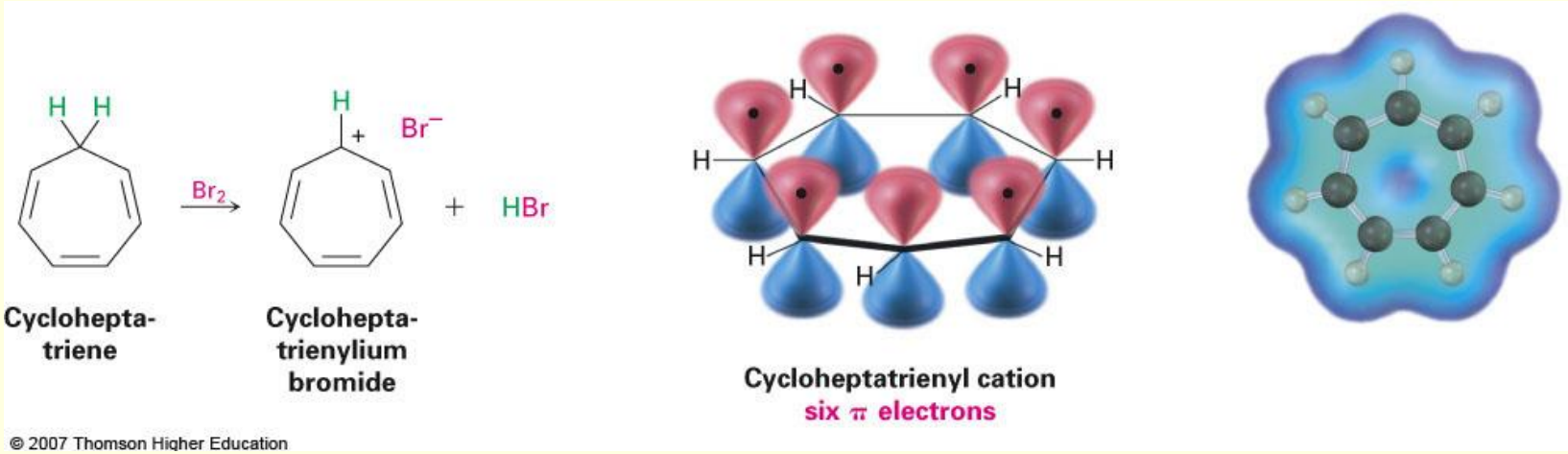
- 1,3-Cyclopentadiene contains conjugated double bonds joined by a CH_2 that blocks delocalization
- Removal of H^+ at the CH_2 produces a cyclic 6 π-electron system, which is stable
- Removal of H^- or H• generates nonaromatic 4π and 5π electron systems
- Relatively acidic (p*K*a = 16) because the anion is stable





Cycloheptatrienyl cation

- Cycloheptatriene has 3 conjugated double bonds joined by a CH_2
- Removal of "H^-" leaves the cation
- The cation has 6π electrons and is aromatic.

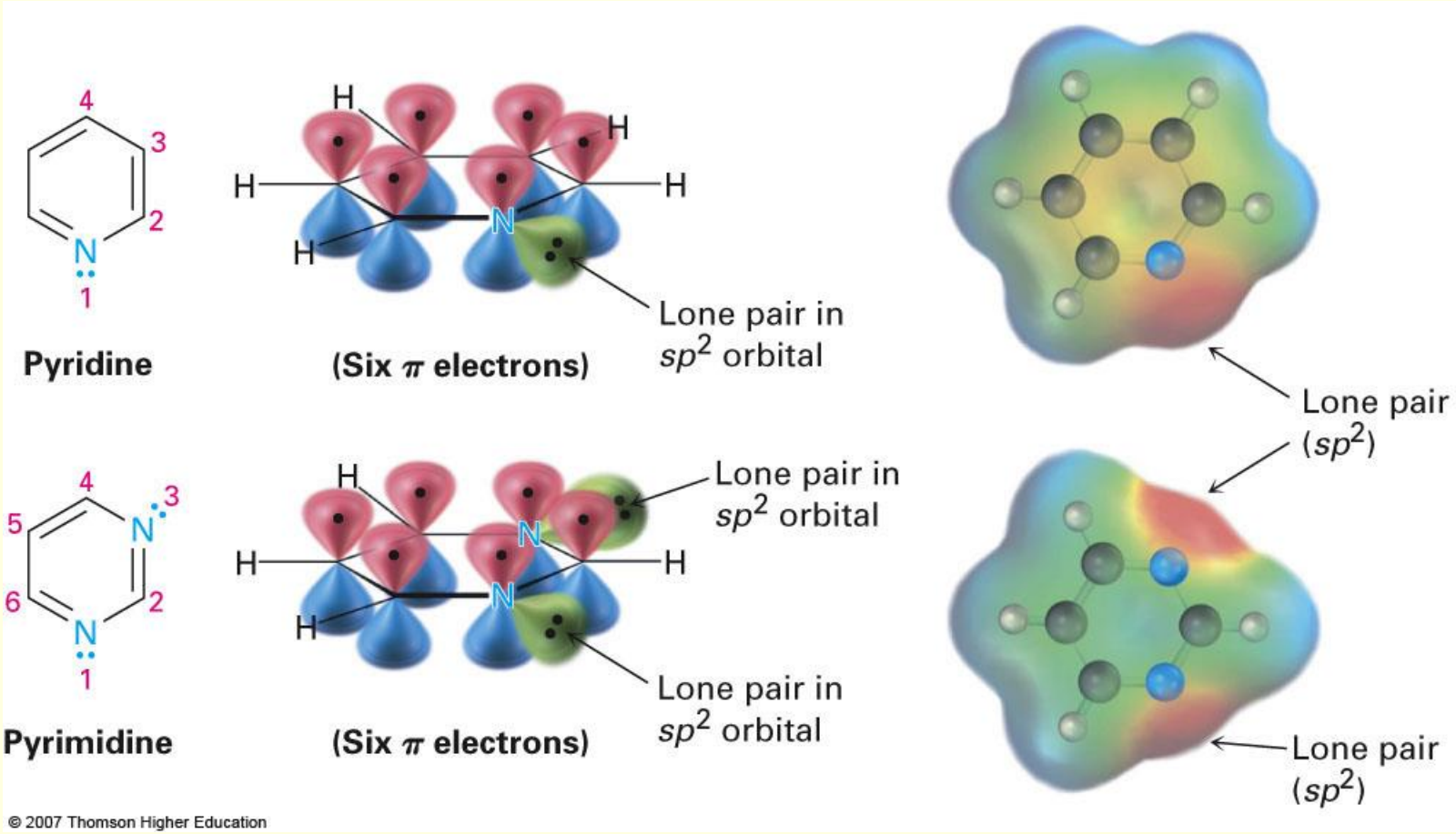


Aromatic Heterocycles: Pyridine and Pyrrole

- Heterocyclic compounds contain elements other than carbon in a ring, such as N,S,O,P
- Aromatic compounds can have elements other than carbon in the ring are heterocyclic. Examples: Pyridine, Pyrimidine, Pyrrole.
- Cyclic compounds that contain only carbon are called carbocyclic.

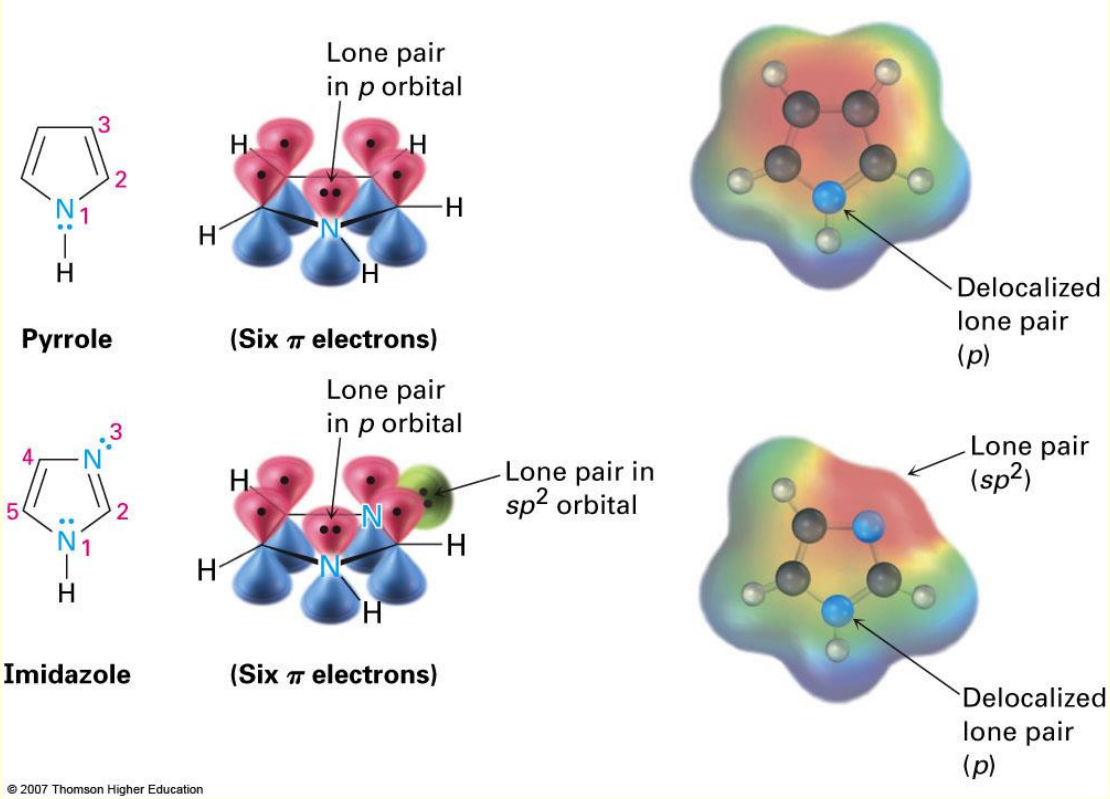
Pyridine

- A 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)
- Pyridine is a relatively weak base compared to normal amines but protonation does not affect aromaticity



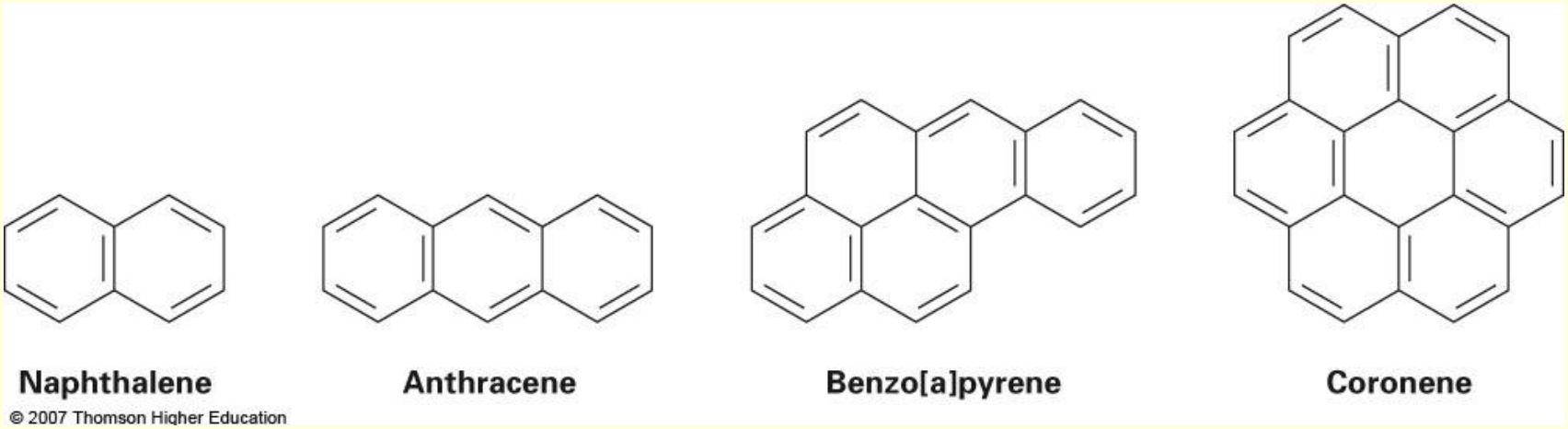
Pyrrole

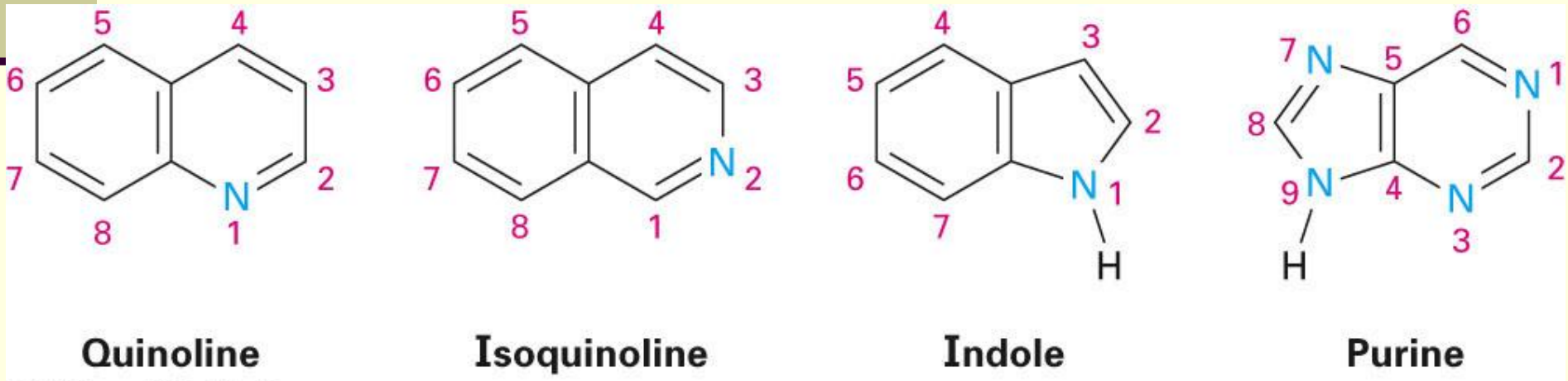
- A five-membered heterocycle with one nitrogen-Pyrrole
- π electron system similar to that of cyclopentadienyl anion
- Four sp^2-hybridized carbons with 4 *p* orbitals perpendicular to the ring and 4 π electrons
- Nitrogen atom is sp^2-hybridized, and lone pair of electrons occupies a *p* orbital (6 π electrons)
- Since lone pair electrons are in the aromatic ring, protonation destroys aromaticity, making pyrrole a very weak base



Polycyclic Aromatic Compounds

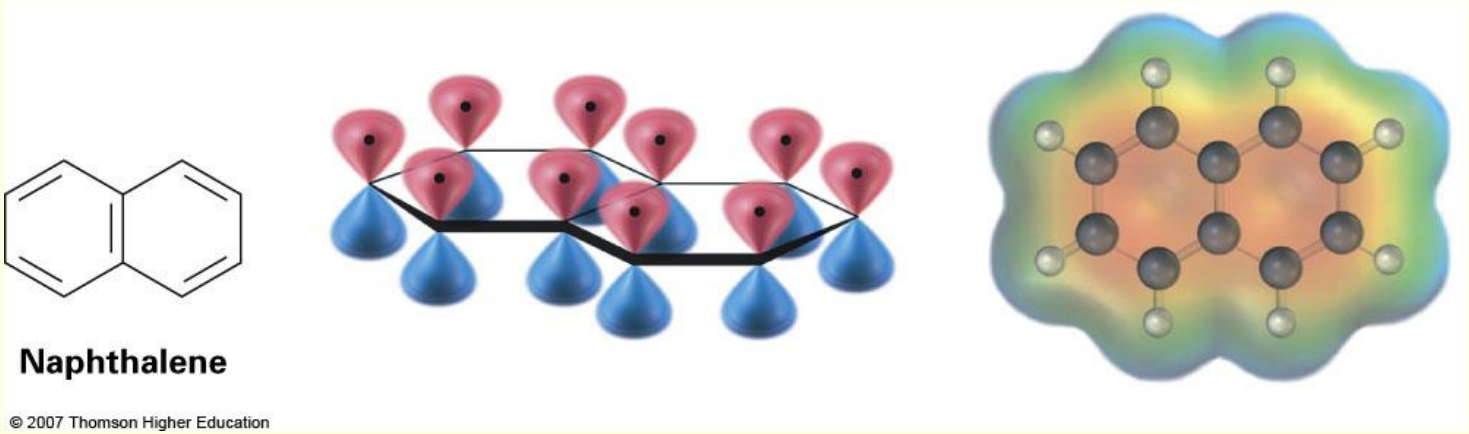
- Aromatic compounds can have rings that share a set of carbon atoms (fused rings)
- Compounds from fused benzene or aromatic heterocycle rings are themselves aromatic





Naphthalene

- Three resonance forms and delocalized electrons



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