

15. Benzene and Aromaticity

Aromatic Compounds

Aromatic was used to describe some fragrant compounds in early 19th century (aroma, benzaldehyde & cinnamaldehyde).

Not correct: later they are grouped by chemical behavior (unsaturated compounds that undergo substitution rather than addition)

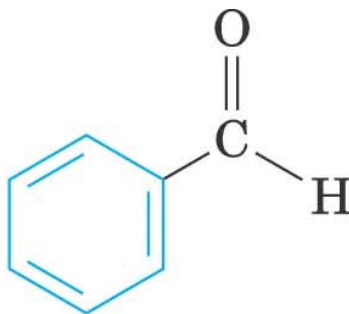
Current: distinguished from *aliphatic* compounds by electronic configuration

(Alkenes react by addition, aromatic compounds by substitution)

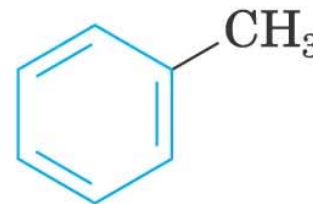


Benzene

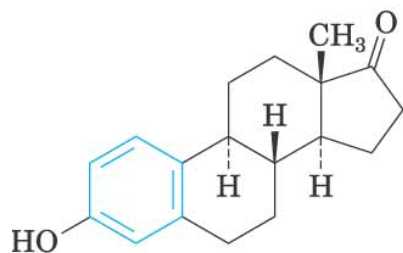
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Benzaldehyde

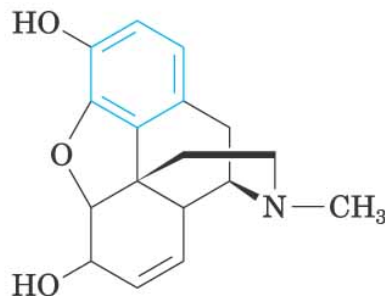


Toluene

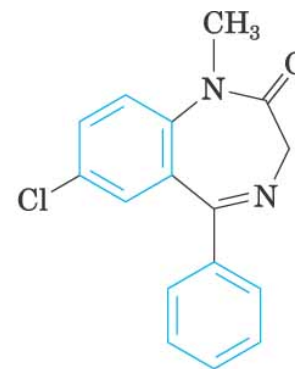


Estrone

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Morphine



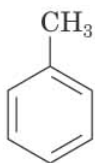
Diazepam (Valium)

15.1 Sources of Aromatic Hydrocarbons

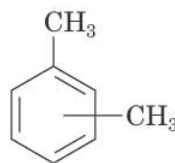
- From high temperature distillation of coal tar
- Heating petroleum at high temperature and pressure over a catalyst



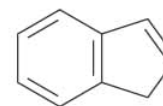
Benzene
(bp 80°C)



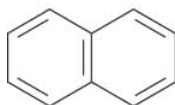
Toluene
(bp 111°C)



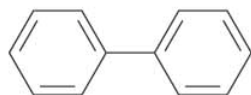
Xylene
(bp: ortho, 144°C;
meta, 139°C; para, 138°C)



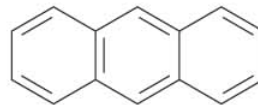
Indene
(bp 182°C)



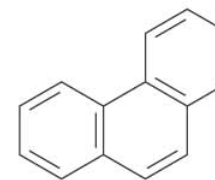
Naphthalene
(mp 80°C)



Biphenyl
(mp 71°C)



Anthracene
(mp 216°C)

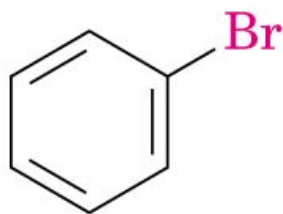


Phenanthrene
(mp 101°C)

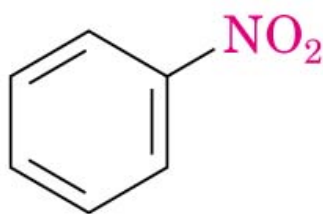
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15.2 Naming Aromatic Compounds

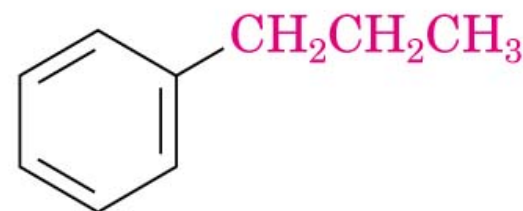
- Many common names are used which have been adopted by IUPAC (toluene = methylbenzene; aniline = aminobenzene)
- Monosubstituted benzenes systematic names as hydrocarbons with *-benzene*
 - $\text{C}_6\text{H}_5\text{Br}$ = bromobenzene
 - $\text{C}_6\text{H}_5\text{NO}_2$ = nitrobenzene, and $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3$ is propylbenzene



Bromobenzene
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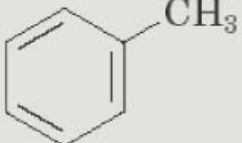
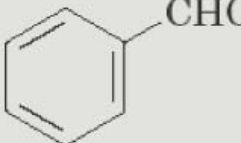
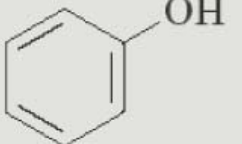
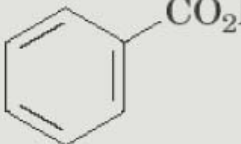
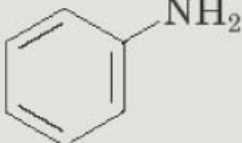
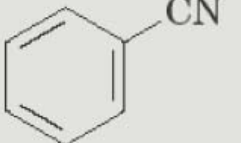
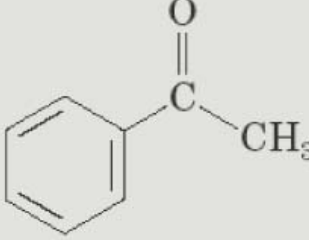
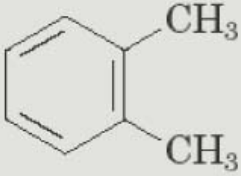
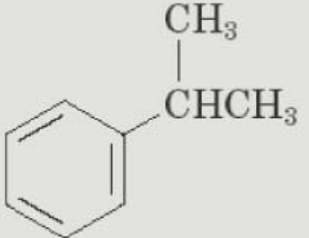
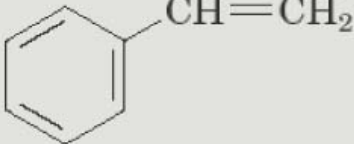


Nitrobenzene



Propylbenzene

TABLE 15.1 Common Names of Some Aromatic Compounds

Formula	Name	Formula	Name
	Toluene (bp 111°C)		Benzaldehyde (bp 178°C)
	Phenol (mp 43°C)		Benzoic acid (mp 122°C)
	Aniline (bp 184°C)		Benzonitrile (bp 191°C)
	Acetophenone (mp 21°C)		<i>ortho</i> -Xylene (bp 144°C)
	Cumene (bp 152°C)		Styrene (bp 145°C)

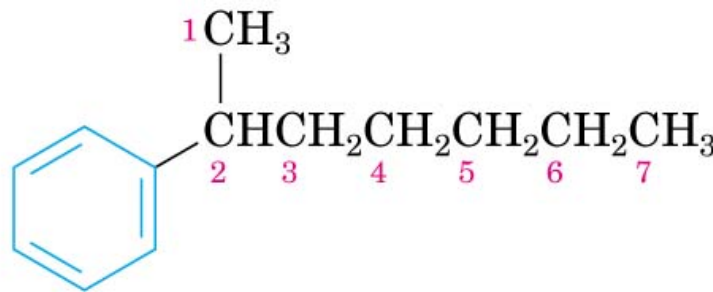
The Phenyl Group

- When a benzene ring is a substituent, the term **phenyl** is used (for C₆H₅—)
 - You may also see “Ph” or “ ϕ ” in place of “C₆H₅”
- “**Benzyl**” refers to “C₆H₅CH₂—”

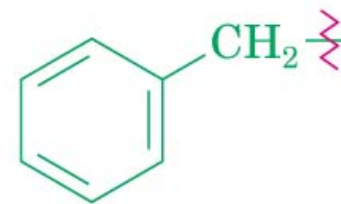


A phenyl group

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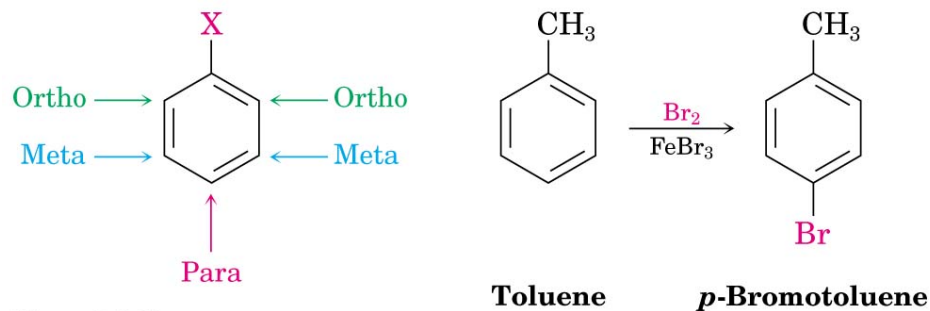
2-Phenylheptane



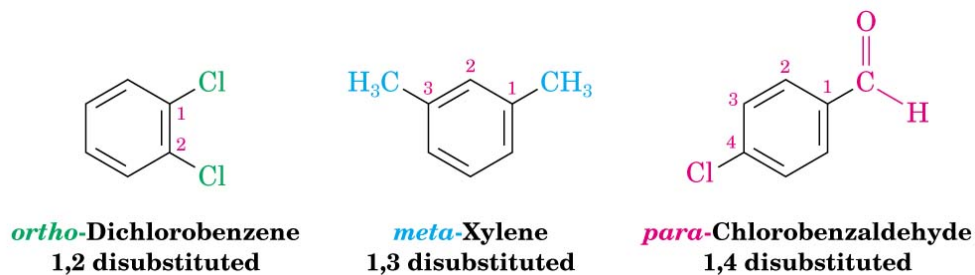
A benzyl group

Disubstituted Benzenes

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



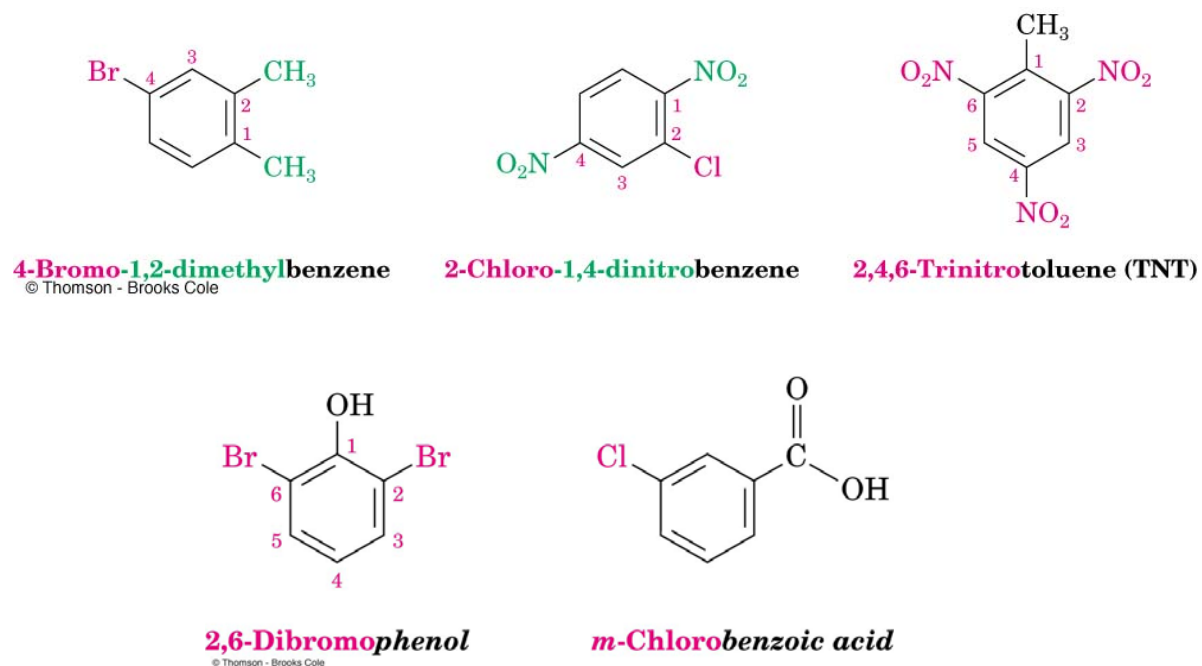
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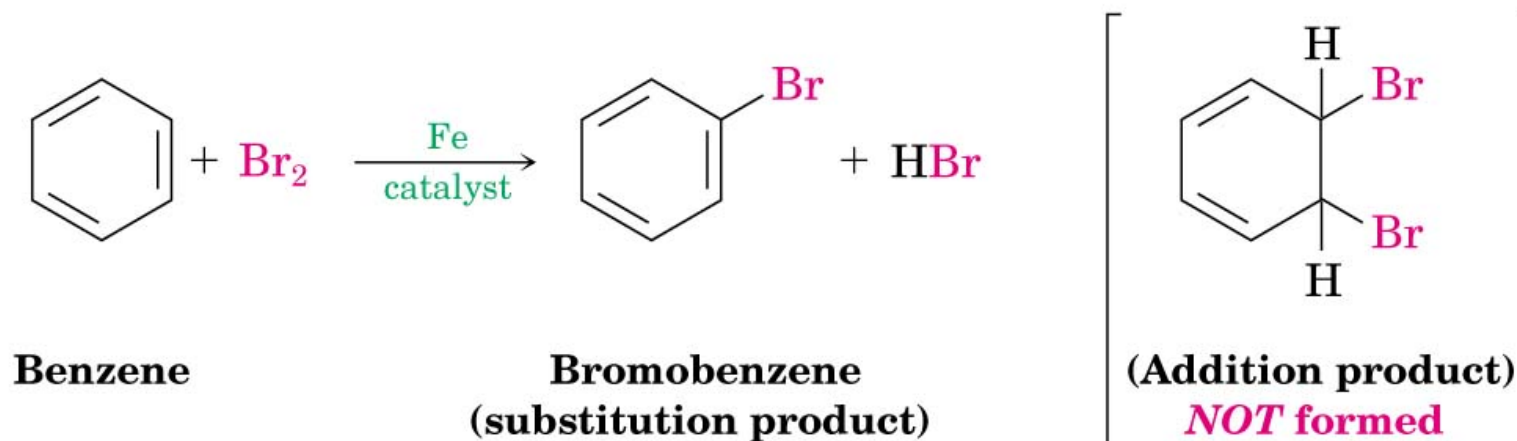
Naming Benzenes With More Than Two Substituents

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



15.3 Structure and Stability of Benzene

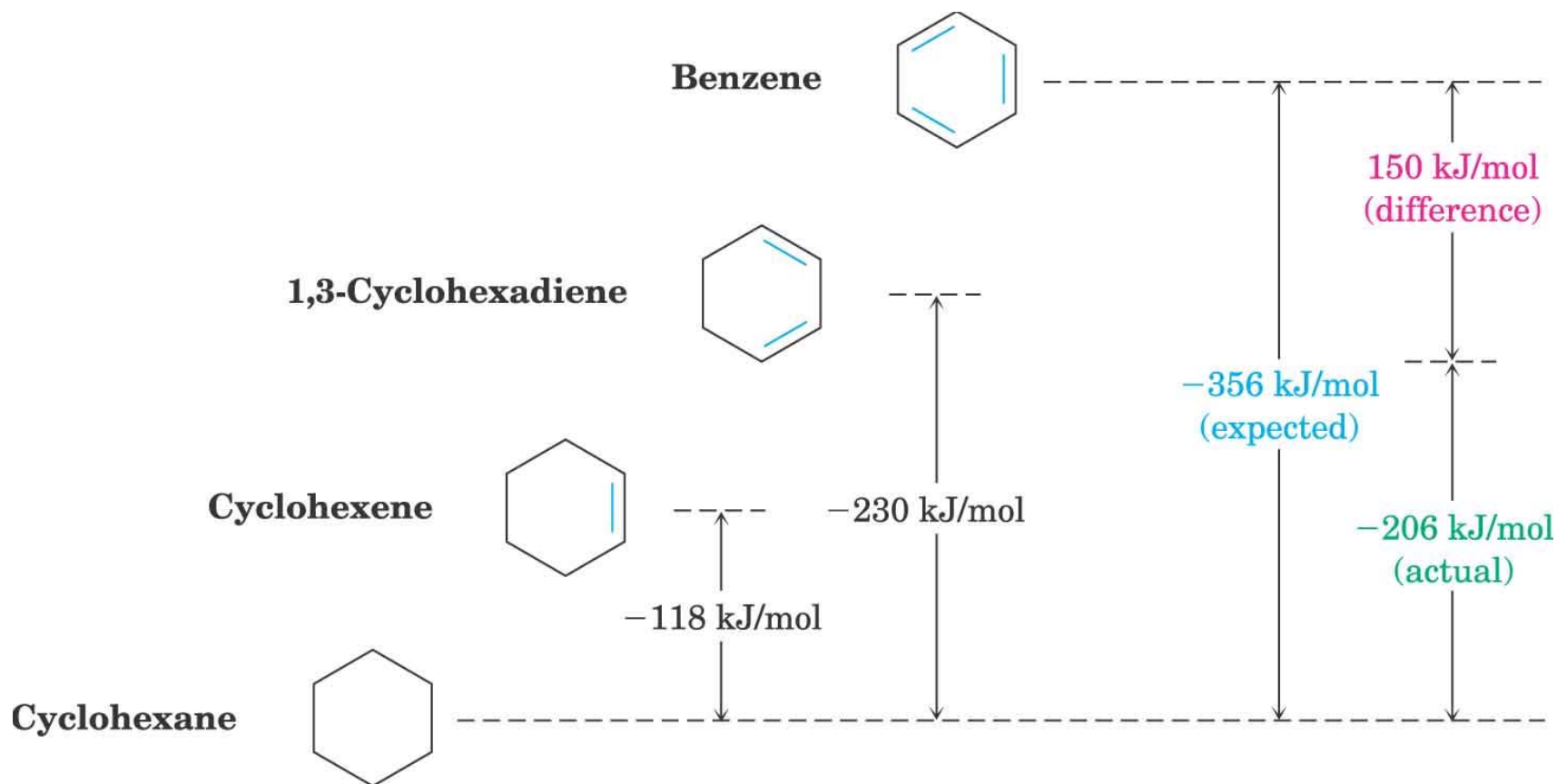
- Benzene reacts slowly with Br₂ in the presence of a catalyst to give bromobenzene (where Br replaces H)
- This is substitution rather than the rapid addition reaction common to compounds with C=C, suggesting that in benzene there is a higher barrier to addition



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Heats of Hydrogenation as Indicators of Stability

- The addition of H_2 to $\text{C}=\text{C}$ normally gives off about 118 kJ/mol – 3 double bonds would give off 356 kJ/mol
 - Two conjugated double bonds in cyclohexadiene add 2 H_2 to liberate 230 kJ/mol of energy
- Benzene has 3 unsaturations but gives off only 206 kJ/mol on reacting with 3 H_2 molecules
- Therefore it has about 150 kJ more “stability” than an isolated set of three double bonds (See Figure 15-2)

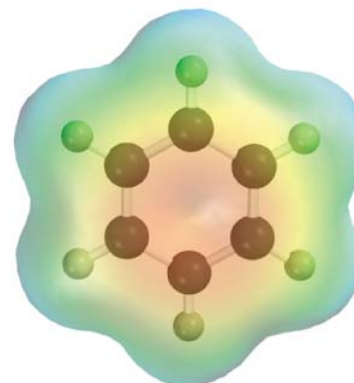
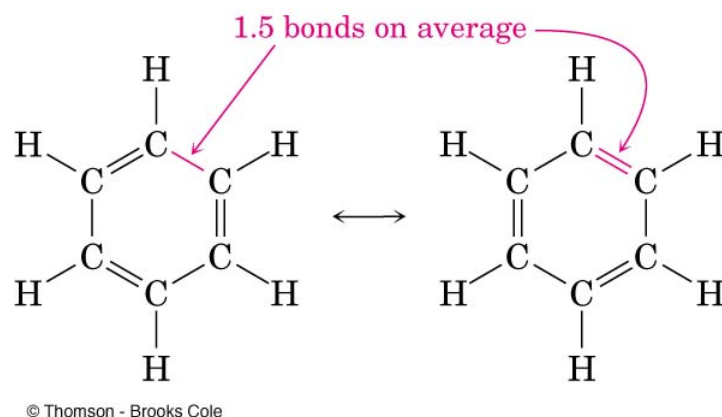


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Benzene's Unusual Structure

- All its C-C bonds are the same length: 139 pm — between single (154 pm) and double (134 pm) bonds
- Electron density in all six C-C bonds is identical

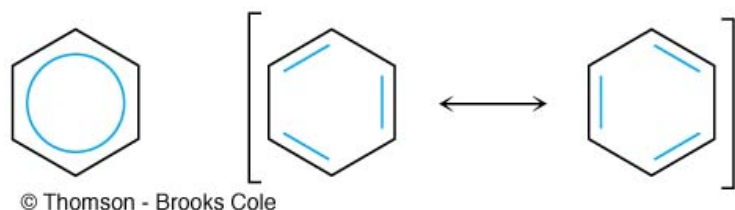
- Structure is planar, hexagonal
- C–C–C bond angles 120°
- Each C is sp^2 and has a p orbital perpendicular to the plane of the six-membered ring



Drawing Benzene and Its Derivatives

- The two benzene resonance forms can be represented by a single structure with a circle in the center to indicate the equivalence of the carbon–carbon bonds
- This does indicate the number of π electrons in the ring but reminds us of the delocalized structure

- We shall use one of the resonance structures to represent benzene for ease in keeping track of bonding changes in reactions



Alternative representations of benzene. The “circle” representation must be used carefully since it doesn’t indicate the number of π electrons in the ring.

15.5 Aromaticity and the $4n + 2$ Rule

- Huckel’s rule, based on calculations – a molecule has to be 1) cyclic, 2) planar with alternating double and single bonds (continuous loop of P orbitals) 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



Benzene

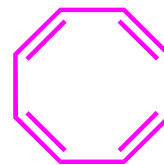
Three double bonds;
six π electrons

Compounds With $4n \pi$ Electrons Are Not Aromatic (May be Antiaromatic)

- Planar, cyclic molecules with $4n \pi$ electrons are much *less* stable than expected (anti-aromatic)
- 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



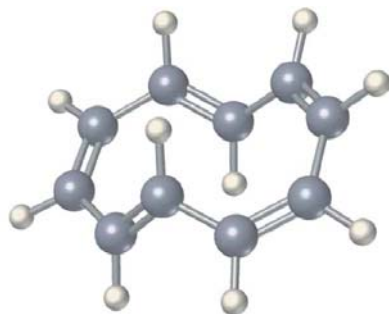
cyclobutadiene



cyclooctatetraene

Is Cyclodecapentaene aromatic?

Cyclodecapentaene

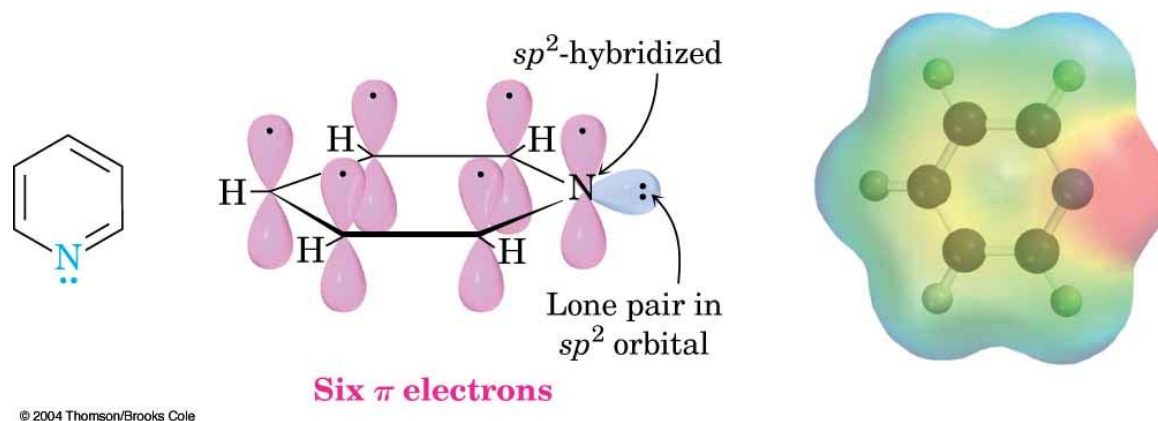


15.7 Aromatic Heterocycles: Pyridine and Pyrrole

- 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
- There are many heterocyclic aromatic compounds and many are very common
- Cyclic compounds that contain only carbon are called carbocycles (not homocycles)
- Nomenclature is specialized

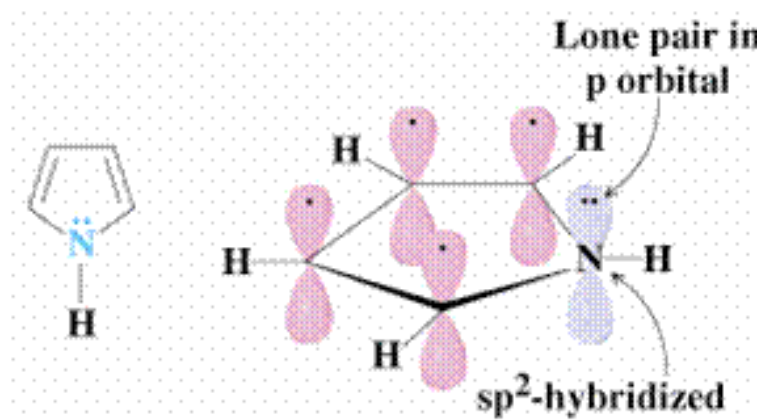
Pyridine

- 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
- π electron system similar to that of cyclopentadienyl anion
- Four sp^2 -hybridized carbons with 4 p orbitals perpendicular to the ring and 4 p 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



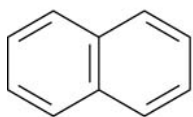
Thiophene



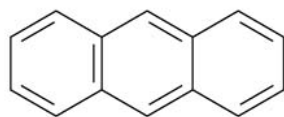
Furan

15.9 Polycyclic Aromatic Compounds: Naphthalene

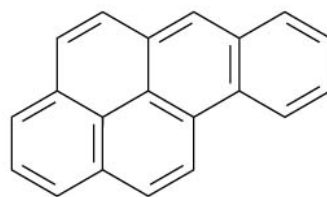
- Aromatic compounds can have rings that share a set of carbon atoms (fused rings)
- Compounds from fused benzene or aromatic heterocycle rings are themselves aromatic



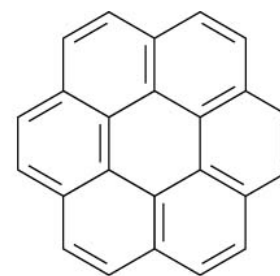
Naphthalene
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Anthracene



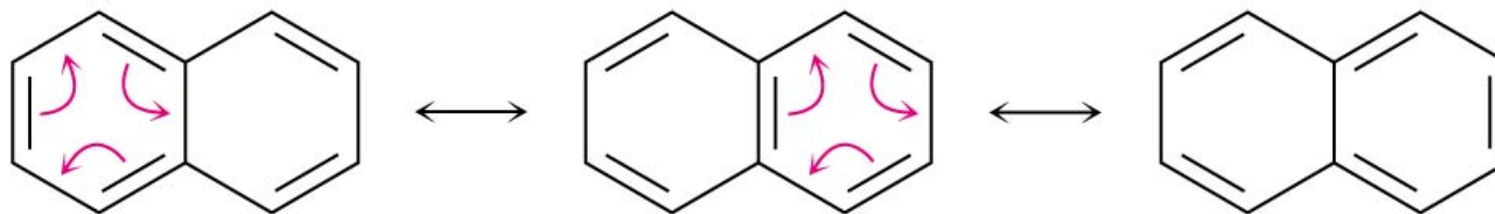
Benzo[a]pyrene

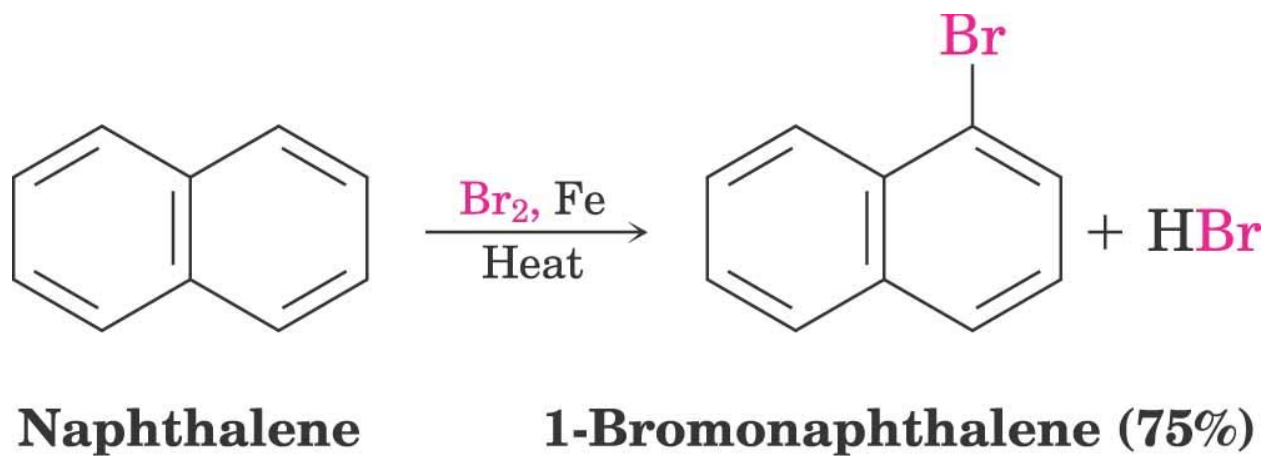
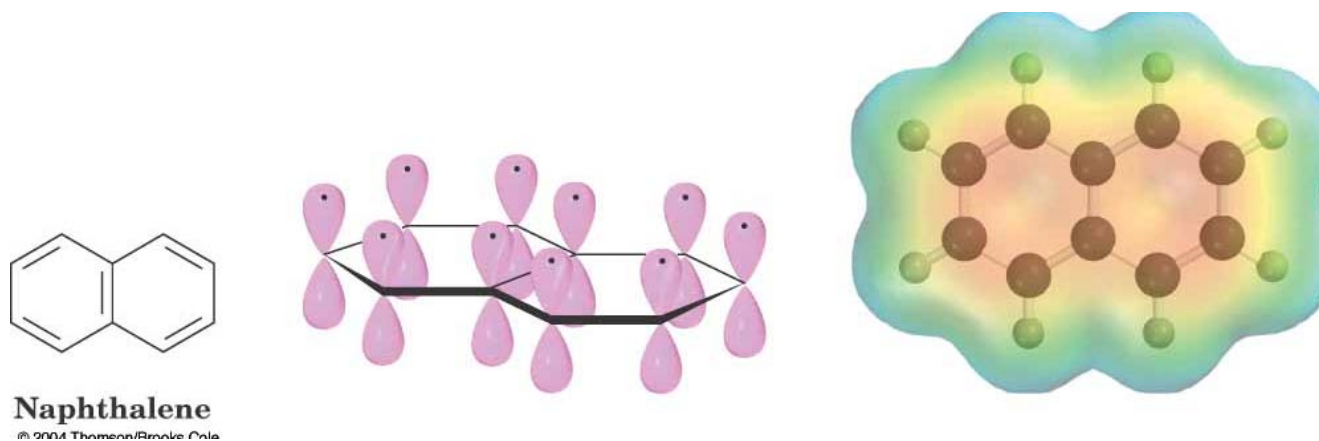


Coronene

Naphthalene Orbitals

Three resonance forms and delocalized electrons





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Naphthalene reacts by substitution not addition.

