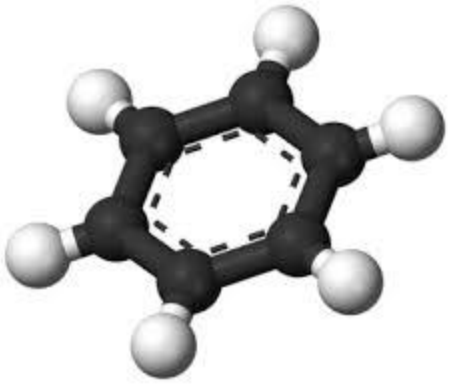
Aromaticity - 2

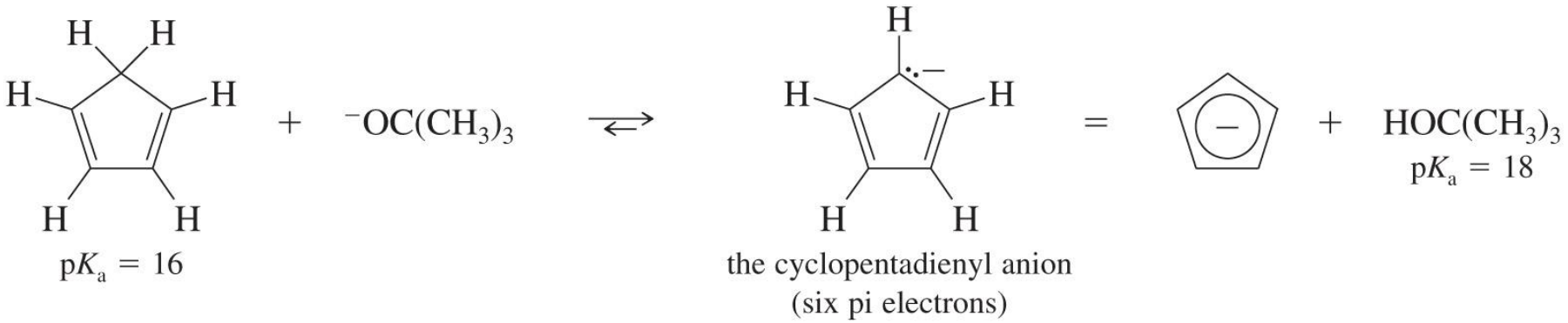


Instructor: Asst. Prof. Dr. Tanatorn Khotavivattana
E-mail: tanatorn.k@chula.ac.th

Recommended Textbook:

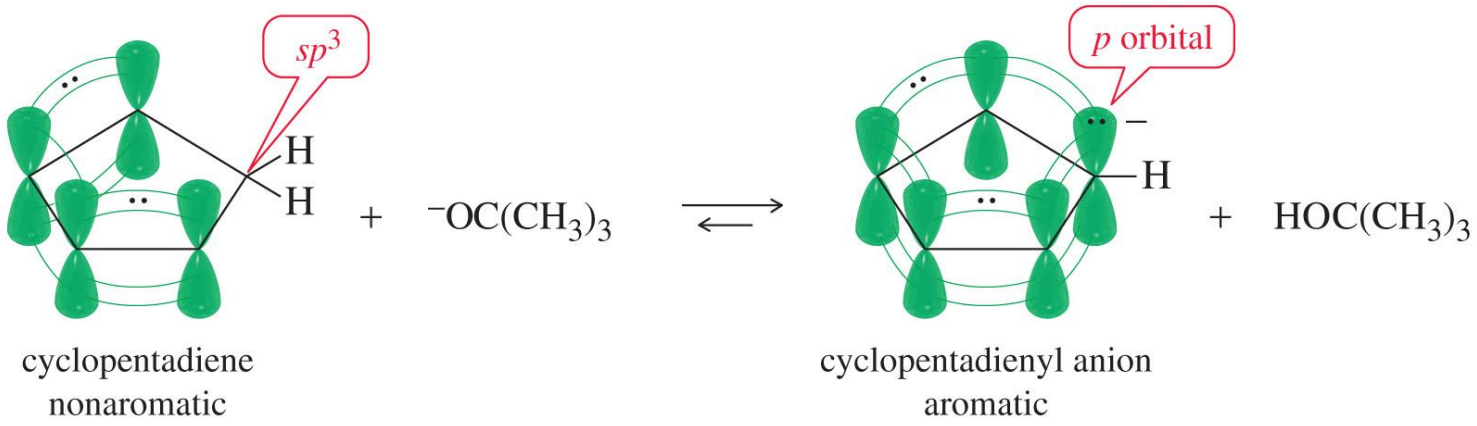
Chapter 16 in *Organic Chemistry*, 8th Edition, L. G. Wade, Jr., **2010**, Prentice Hall (Pearson Education)

Deprotonation of Cyclopentadiene

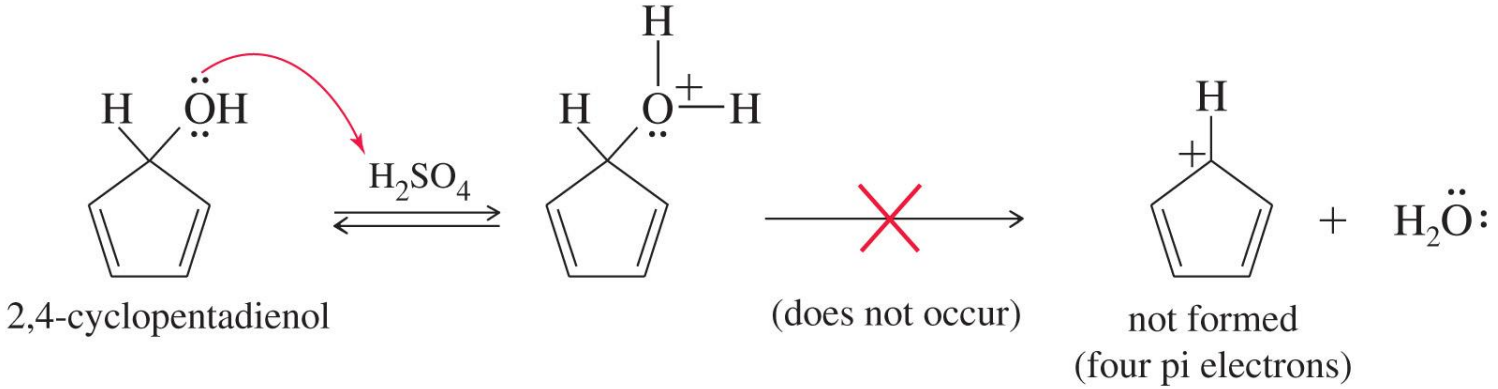


- Cyclopentadiene is **acidic** because **deprotonation will convert it to an aromatic ion**

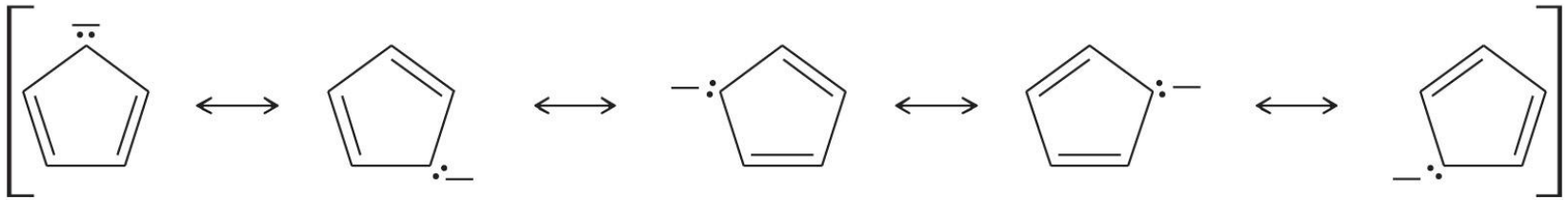
- By deprotonating the sp^3 carbon of cyclopentadiene, the electrons in the p orbitals can be delocalized over all five carbon atoms and the compound would be **aromatic**



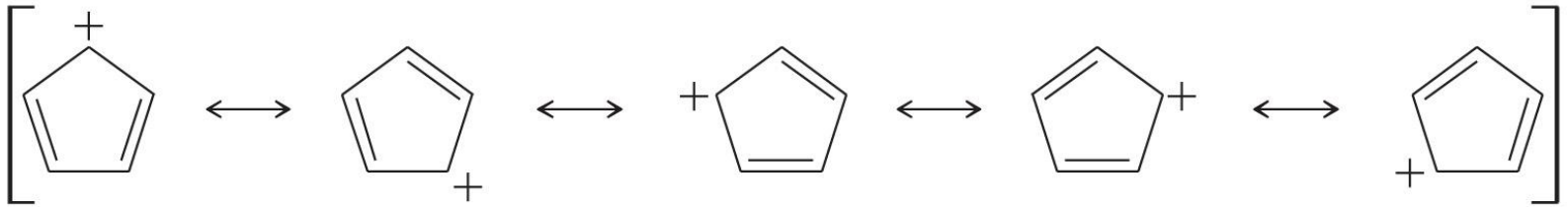
Cyclopentadienyl Cation



- Huckel's rule predicts that the cyclopentadienyl cation, with **four pi electrons**, is **antiaromatic;** therefore, the cyclopentadienyl cation is **not easily formed**



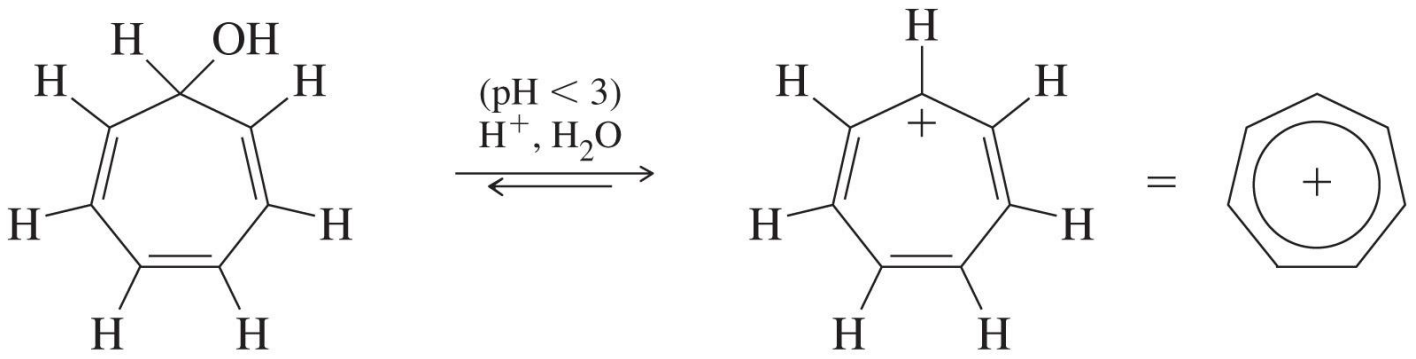
cyclopentadienyl anion: six pi electrons, aromatic



cyclopentadienyl cation: four pi electrons, antiaromatic

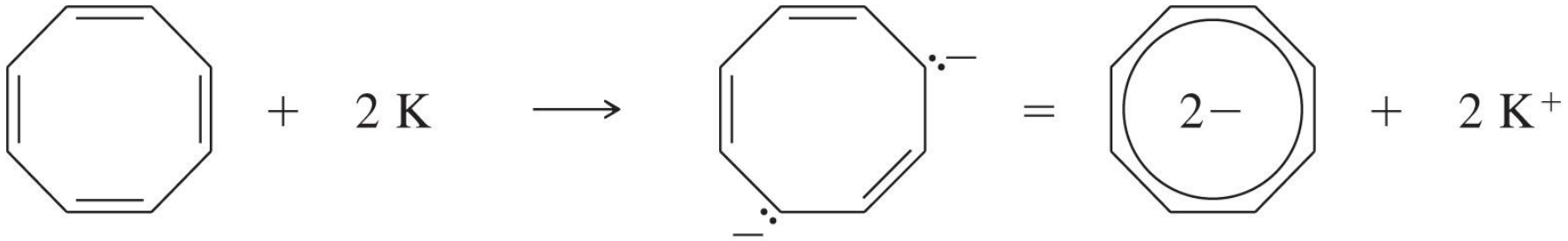
The resonance picture gives a misleading suggestion of stability.

Tropylium Ion



tropylium ion, six pi electrons

Cyclooctatetraene Dianion

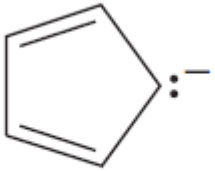


ten pi electrons

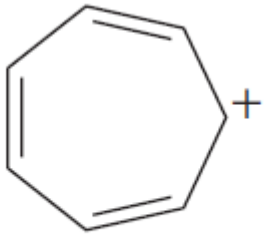
Aromaticity – Examples

Aromatic Compounds

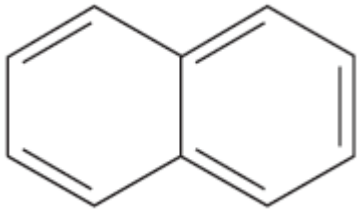
cyclopropenyl cation



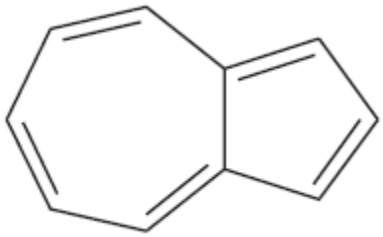
cyclopentadienyl anion



cycloheptatrienyl cation

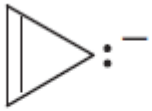


naphthalene



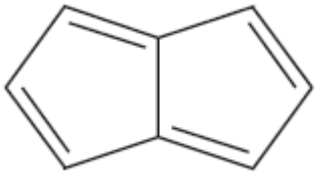
azulene

Antiaromatic Compounds

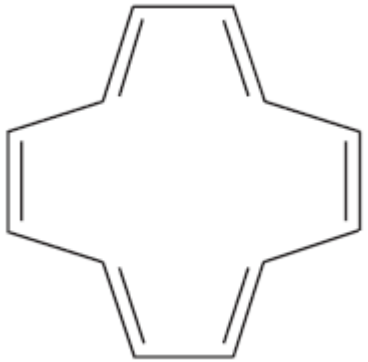


cyclopropenyl anion

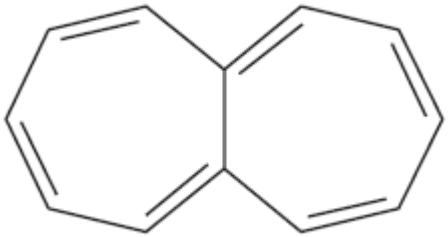
Antiaromatic (if planar)



pentalene



[12]annulene

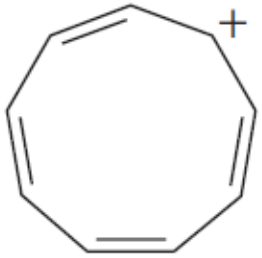


heptalene

Problem #1

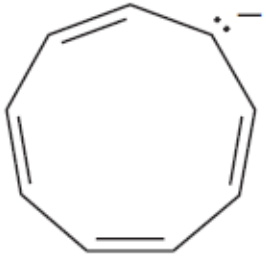
Explain why each compound or ion should be aromatic, antiaromatic, or nonaromatic.

(a)



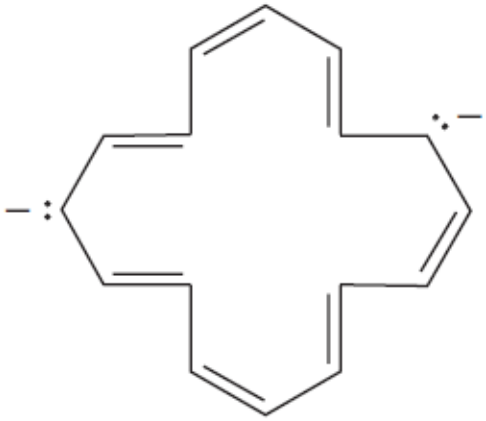
the cyclonona-
tetraene cation

(b)



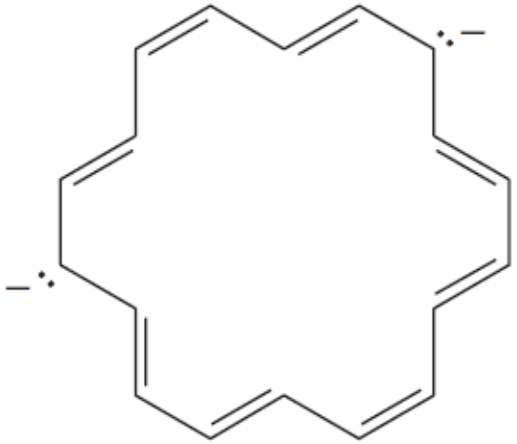
the cyclonona-
tetraene anion

(c)



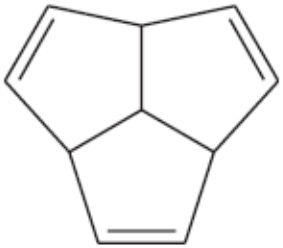
the [16]annulene dianion

(d)



the [18]annulene dianion

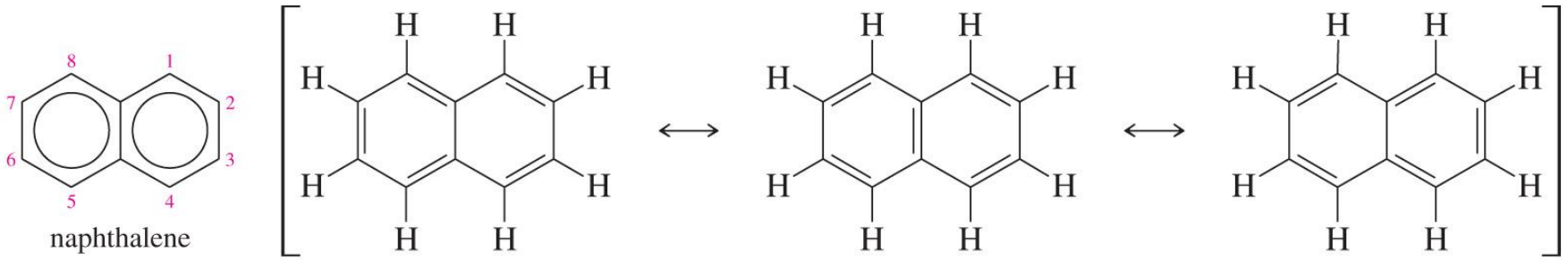
(e)



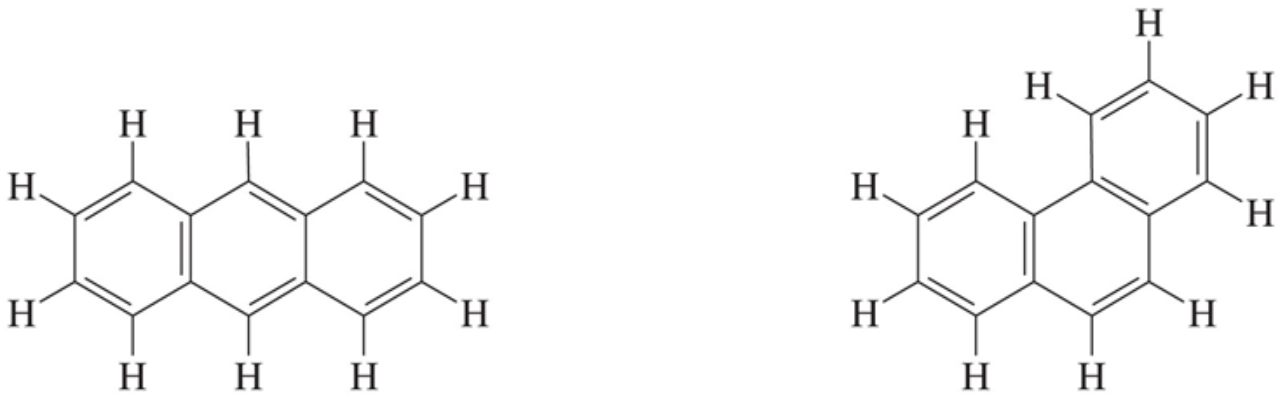
(f) the [20]annulene dication

Polynuclear Aromatic Hydrocarbons (PAHs)

- Composed of two or more fused benzene rings. **Fused rings** share two carbon atoms and the bond between them.
- **Naphthalene** is the simplest fused aromatic hydrocarbon.



naphthalene



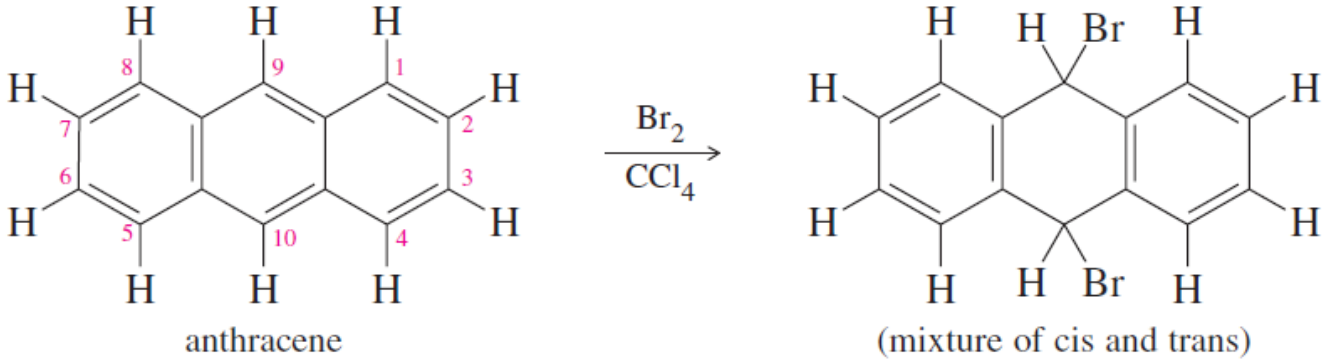
anthracene

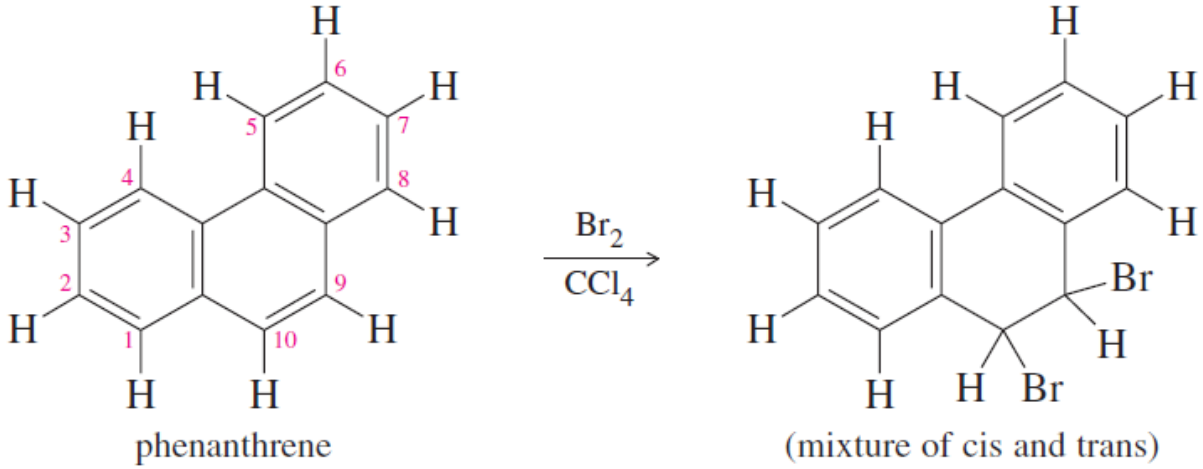
phenanthrene

(Only one Kekulé structure is shown for each compound.)

Polynuclear Aromatic Hydrocarbons (PAHs)

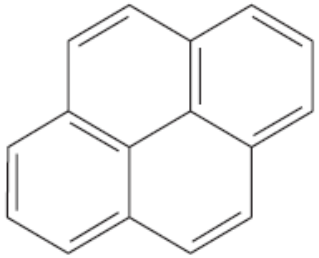
- As the number of fused aromatic rings increases, the **resonance energy per ring continues to decrease** and the compounds become **more reactive**.



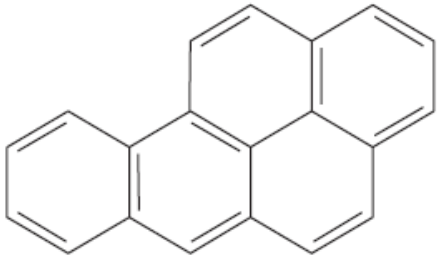


Larger Polynuclear Aromatic Hydrocarbons

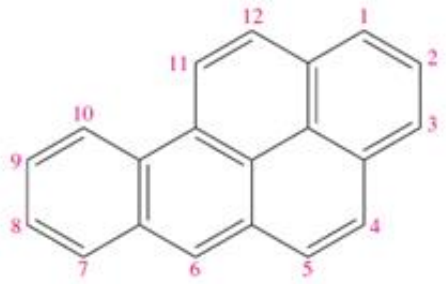
- Formed in combustion (tobacco smoke).
- Many are carcinogenic.



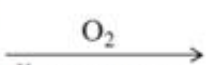
pyrene

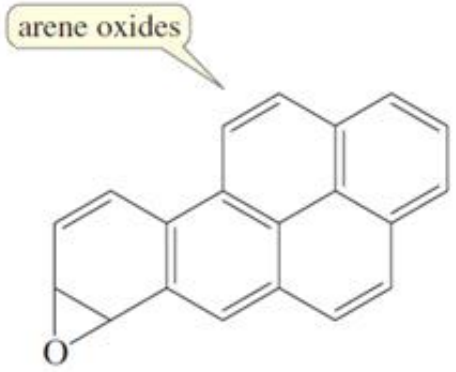


benzo[*a*]pyrene

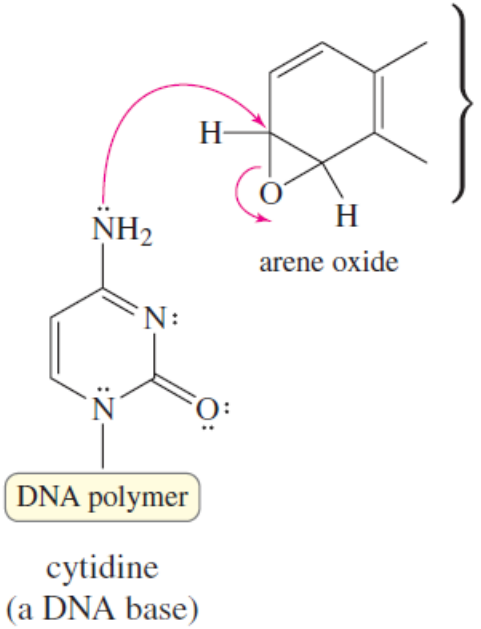


benzo[*a*]pyrene





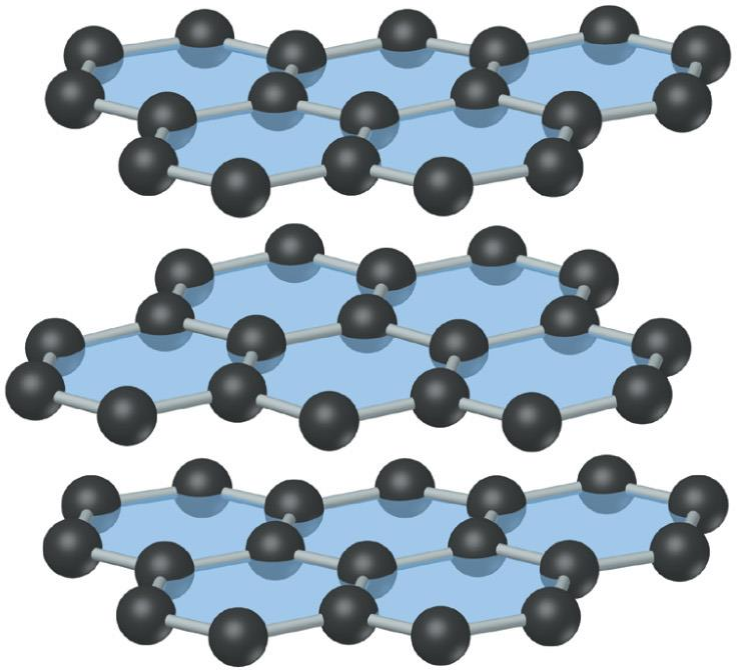
7,8-benzo[*a*]pyrene oxide



cytidine
(a DNA base)

Graphite

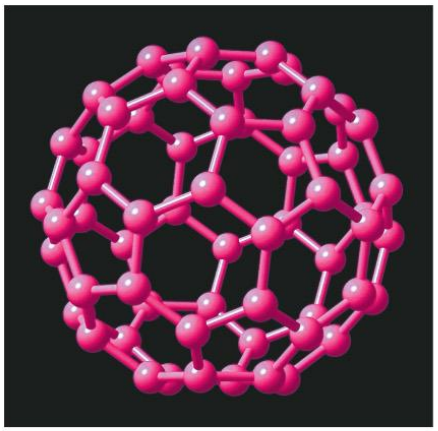
- Planar layered structure.
- Layer of fused benzene rings, bonds: 1.415 Å.
- Only van der Waals forces between layers.
- Conducts electrical current parallel to layers.



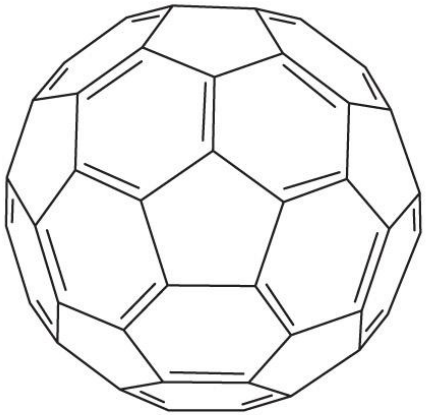
graphite

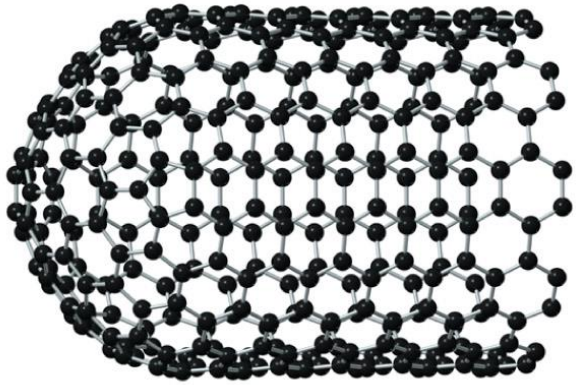
Some New Allotropes

- Fullerenes: 5- and 6-membered rings arranged to form a "soccer ball" structure.
- Nanotubes: half of a C_{60} sphere fused to a cylinder of fused aromatic rings.



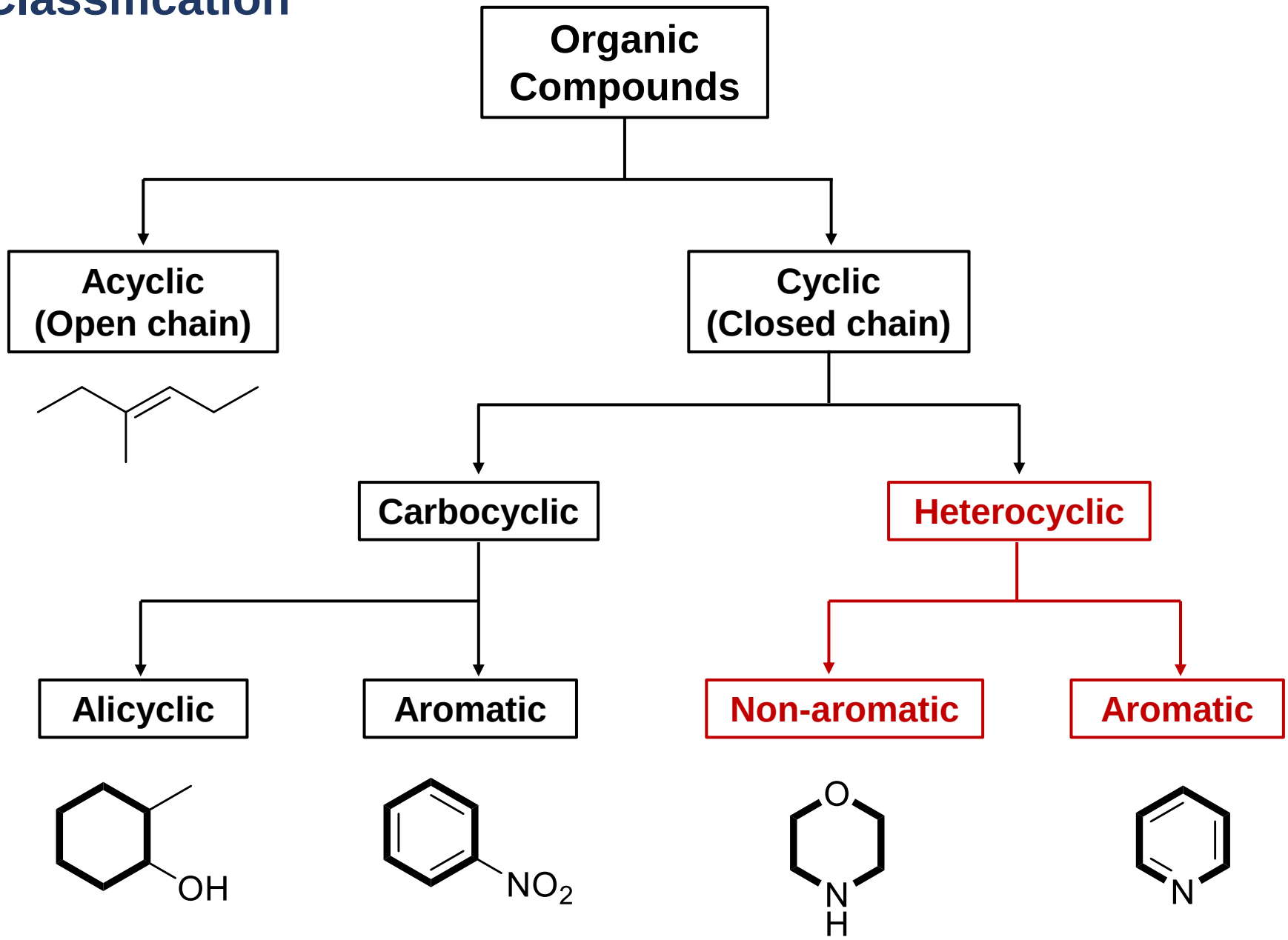
buckyball (C_{60})





carbon nanotube

Classification

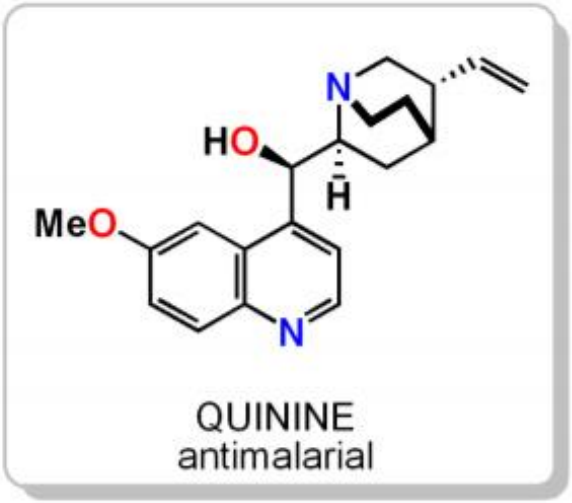


Applications of Heterocyclic Compounds

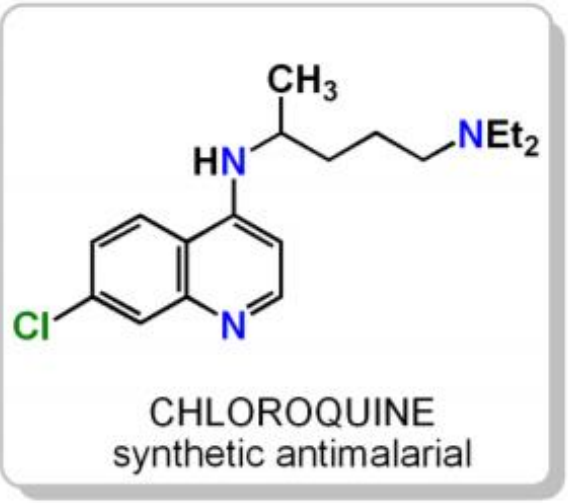
- Heterocyclic compounds can be synthesized in many ways
- Many synthetic (as well as natural) heterocyclic compounds are of extreme value as **medicinals**, **agrochemicals**, **plastics precursors**, **dyes**, **photographic chemicals**, and so on, and new structures are constantly being sought in research in these areas

Applications of Heterocyclic Compounds

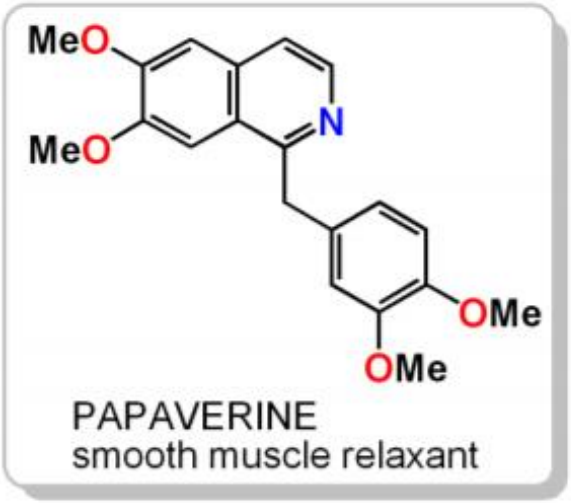
Medicinal chemistry especially is associated intimately with heterocyclic compounds; most of all chemicals used in medicine are based on heterocyclic frameworks



QUININE
antimalarial

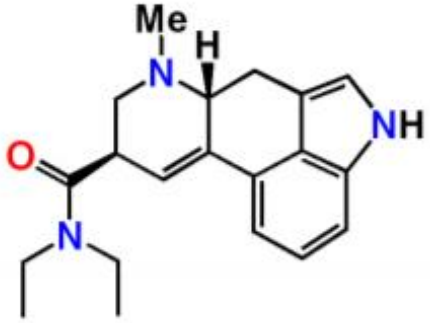


CHLOROQUINE
synthetic antimalarial

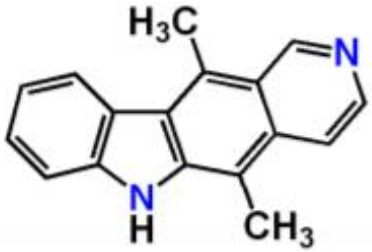


PAPAVERINE
smooth muscle relaxant

FUMITREMORGIN-C



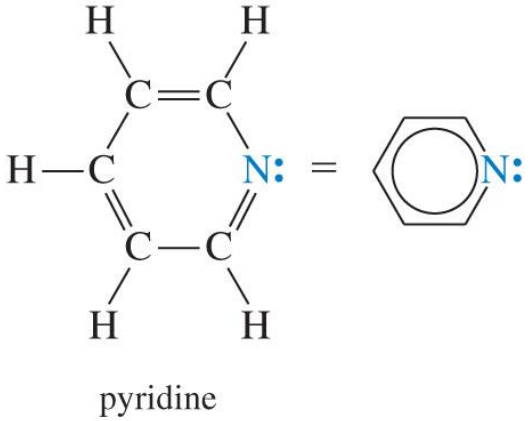
LYSERGIC ACID
DIETHYLAMIDE



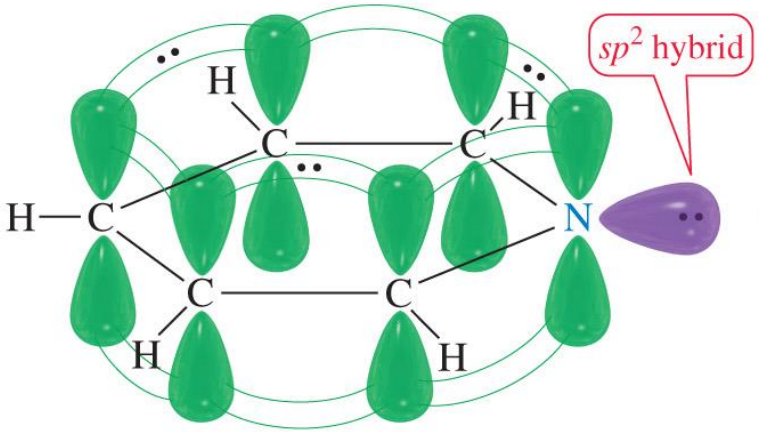
ELLIPTICINE
anti-tumour agent

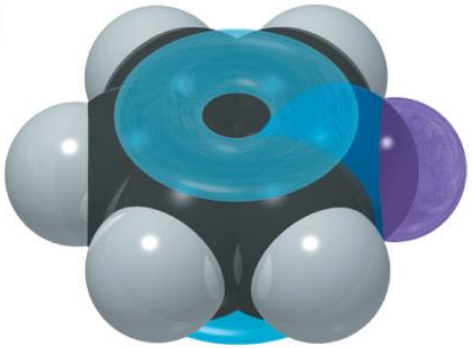
Heterocyclic Aromatic Compounds

Pyridine



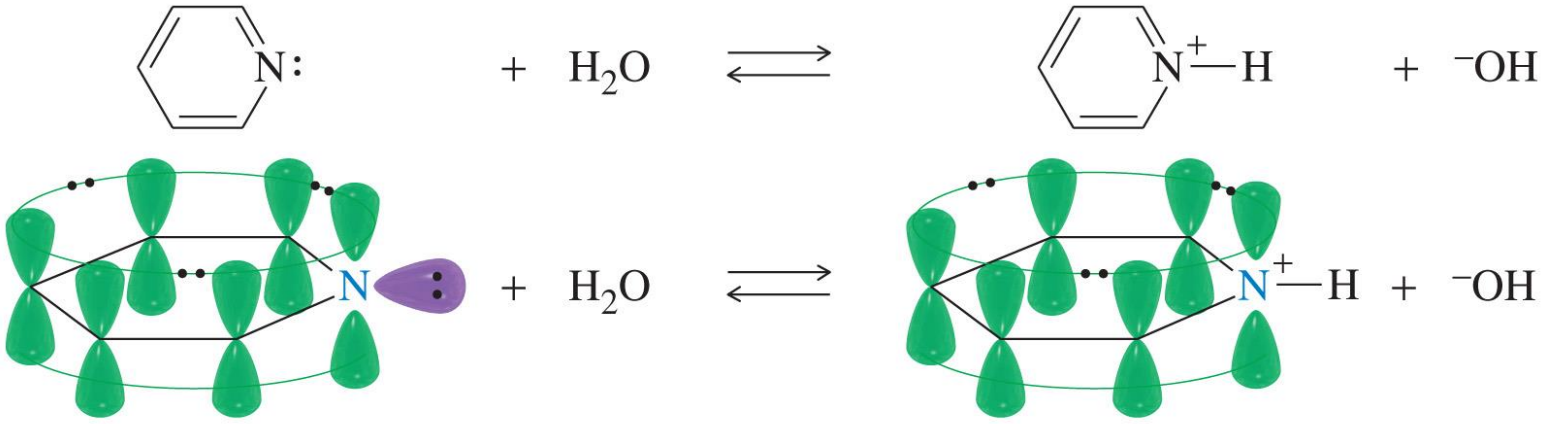
pyridine





- Pyridine has **six** delocalized electrons in its pi system.
- The **two non-bonding electrons on nitrogen** are in an ***sp*²** orbital, and they do not interact with the pi electrons of the ring.

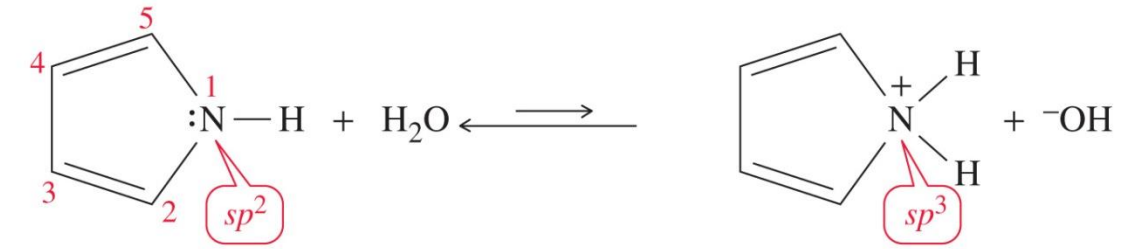
Pyridine



- Pyridine is **basic**, with a pair non-bonding electrons available to abstract a proton.
- The protonated pyridine (the pyridinium ion) is still **aromatic**.

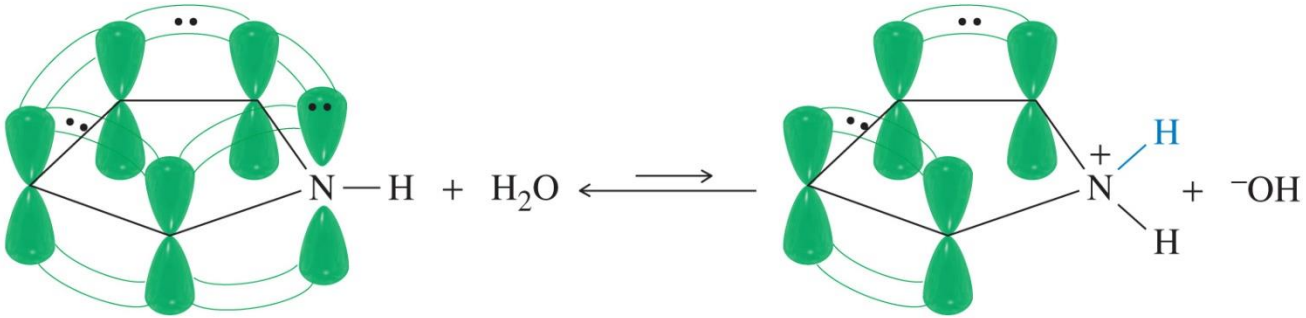
Pyrrole

- Pyrrole is a **much weaker base** than pyridine
- This difference is due to the structure of the protonated pyrrole



pyrrole, pK_b = 13.6
(weak base)

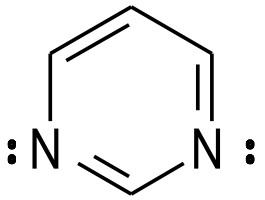
N-protonated pyrrole, pK_a = 0.4
(strong acid)



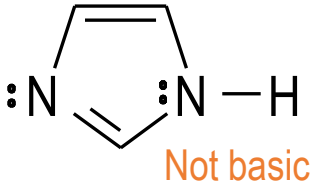
pyrrole
(aromatic)

N-protonated pyrrole
(nonaromatic)

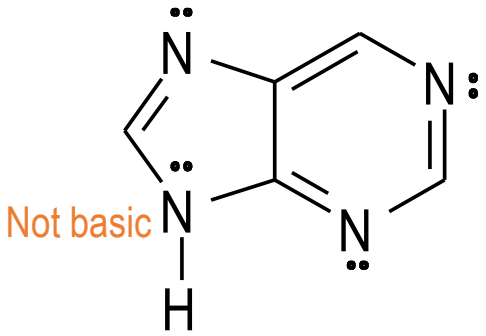
Basic or Nonbasic?



Pyrimidine has two basic nitrogens.

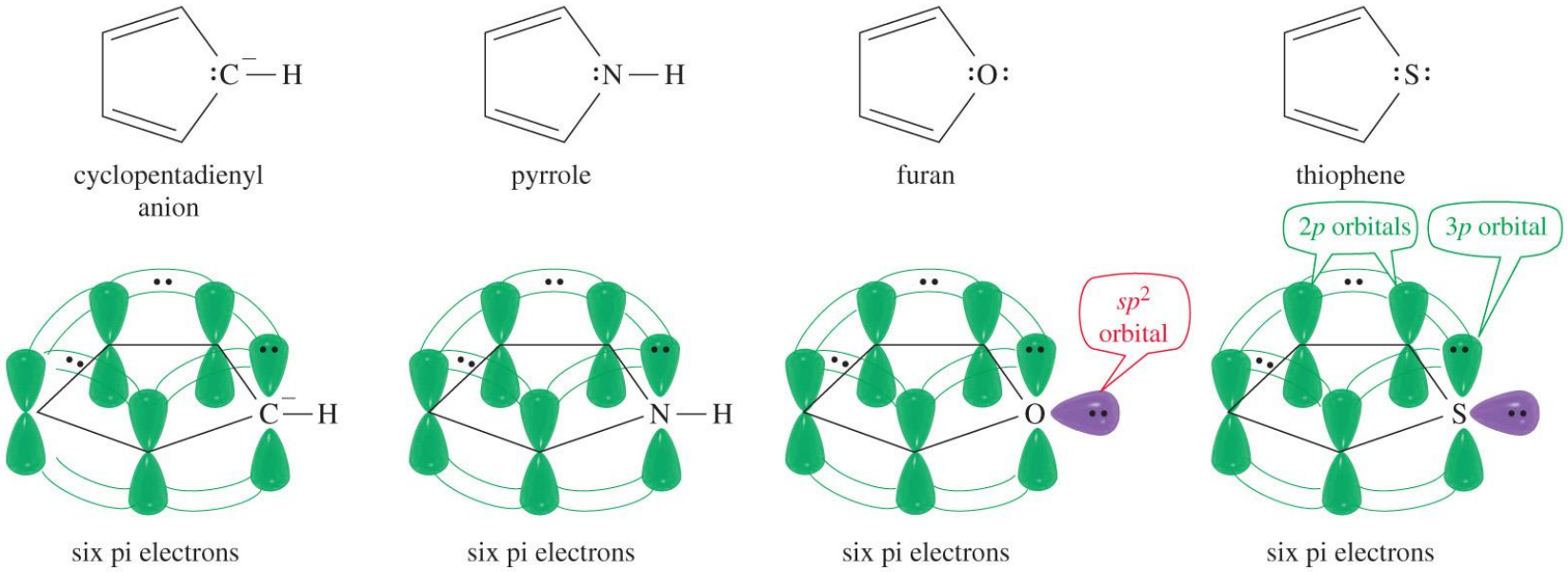


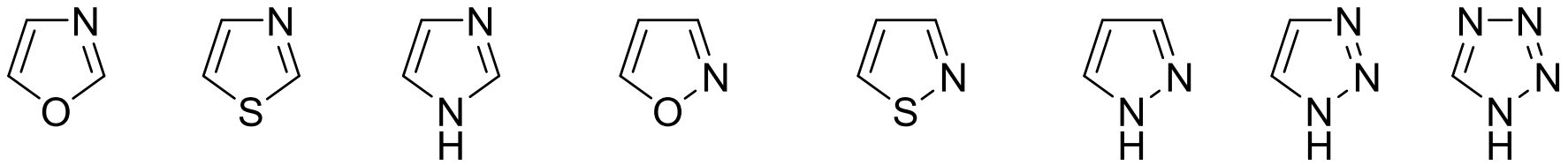
Imidazole has one basic nitrogen and one nonbasic.



Only one of purine's nitrogens is not basic.

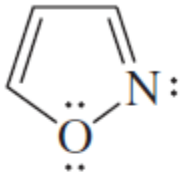
Other Heterocyclics



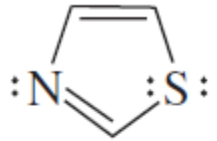


Problem #2

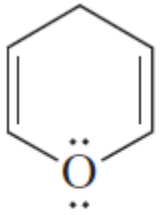
Explain why each compound is aromatic, antiaromatic, or nonaromatic.

(a) 

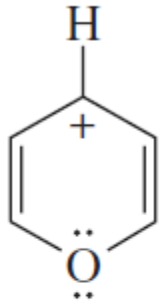
isoxazole

(b) 

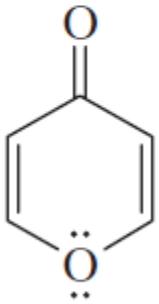
1,3-thiazole

(c) 

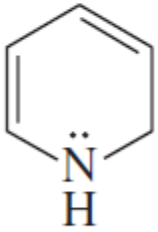
pyran

(d) 

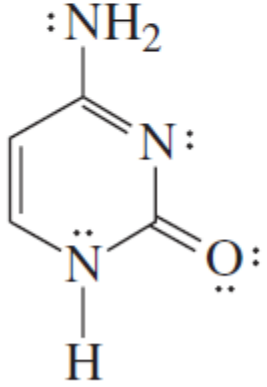
pyrylium ion

(e) 

γ-pyrone

(f) 

1,2-dihydropyridine

(g) 

cytosine

(h)