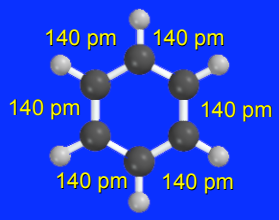
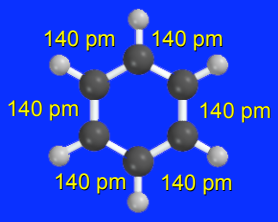
Arenes and Aromaticity
(*Benzene*)

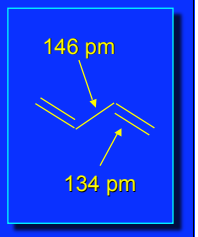
All C—C bond distances = 140 pm



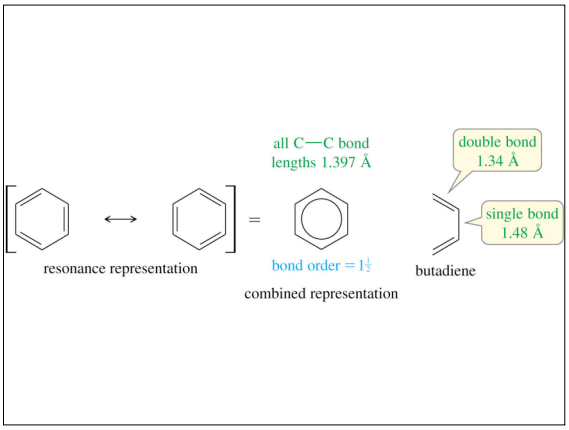
Benzene
empirical formula = CH

All C—C bond distances = 140 pm





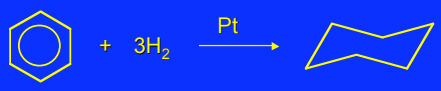
140 pm is the average between the C—C single bond distance and the double bond distance in 1,3-butadiene.



Resonance & Benzene

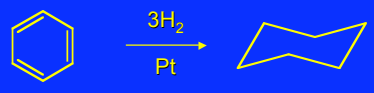
Thermochemical Measures of Stability

heat of hydrogenation: compare experimental value with "expected" value for hypothetical "cyclohexatriene"

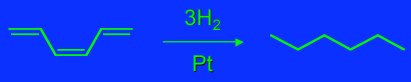


$\Delta H° = -208$ kJ

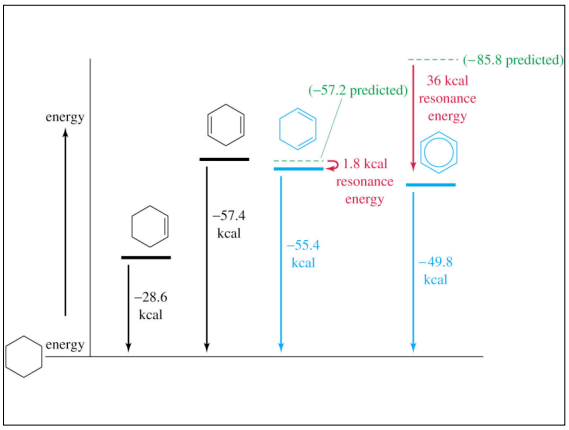
Cyclic conjugation versus noncyclic conjugation



heat of hydrogenation = -208 kJ/mol (-49 kcal/mol)

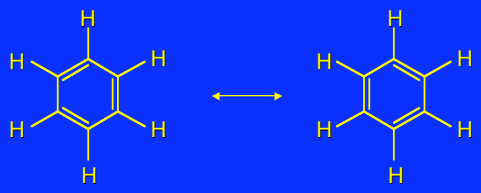


heat of hydrogenation = -337 kJ/mol (-85.8 kcal/mol)



Resonance & Benzene

express the structure of benzene as a *resonance hybrid* of the two Lewis structures. Electrons are not localized in alternating single and double bonds, but are delocalized over all six ring carbons.

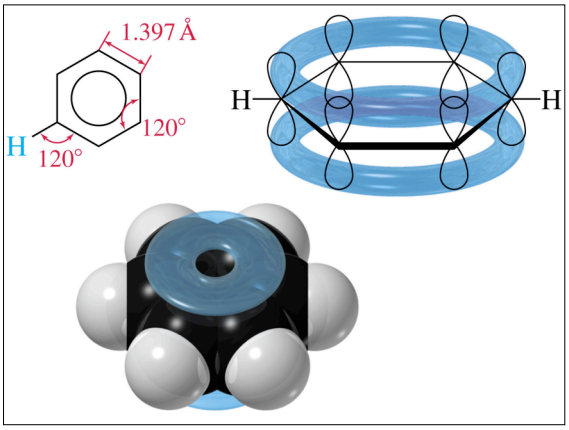


Resonance & Benzene

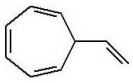
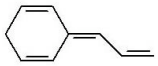
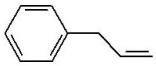
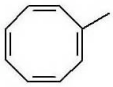
Circle-in-a-ring notation stands for resonance description of benzene (hybrid of two resonance structures)

Question

- Which of the following compounds has a double bond that is conjugated with the π system of the benzene ring?
- A) *p*-Benzyltoluene
- B) 2-Phenyl-1-decene
- C) 3-Phenylcyclohexene
- D) 3-Phenyl-1,4-pentadiene
- E) 2,4,6-trichloroanisole



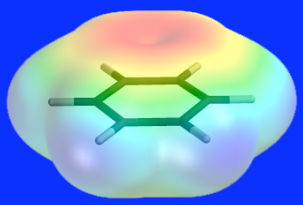
Question

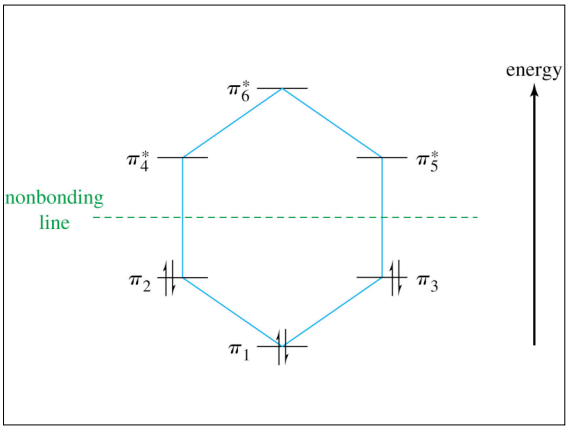
- Which of the following has the smallest heat of combustion?
- A)  B) 
- C)  D) 

The π Molecular Orbitals of Benzene

Orbital Hybridization Model of Bonding in Benzene

High electron density above and below plane of ring



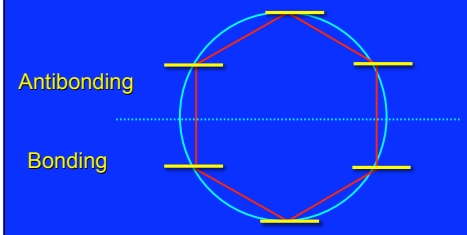


Hückel's Rule

Frost's circle is a mnemonic that allows us to draw a diagram showing the relative energies of the π orbitals of a cyclic conjugated system.

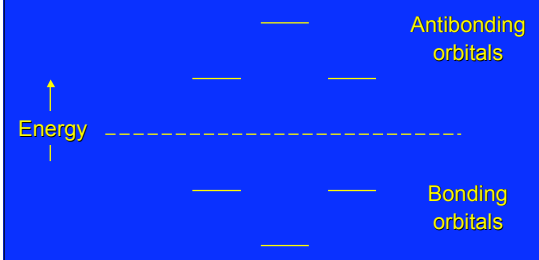
1) Draw a circle.
2) Inscribe a regular polygon inside the circle so that one of its corners is at the bottom.
3) Every point where a corner of the polygon touches the circle corresponds to a π electron energy level.
4) The middle of the circle separates bonding and antibonding orbitals.

Frost's Circle



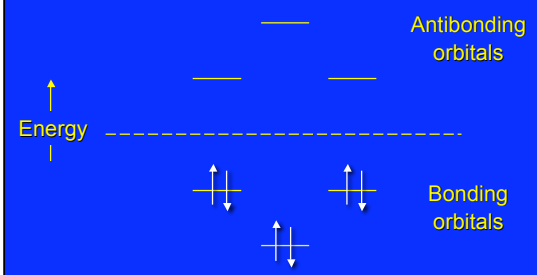
π MOs of Benzene

Benzene MOs

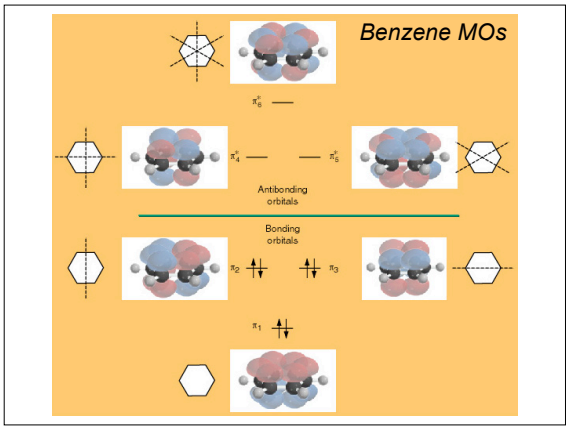


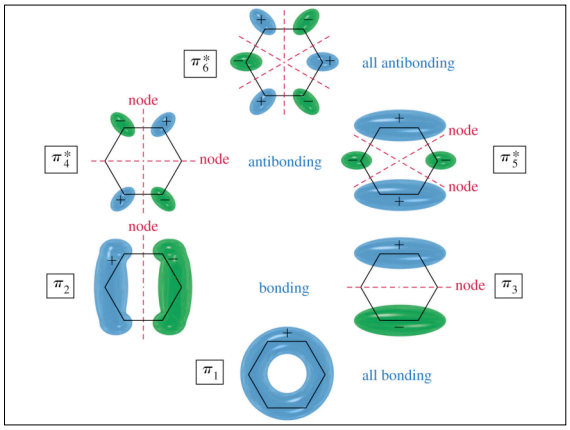
6 *p* AOs combine to give 6 π MOs
3 MOs are bonding; 3 are antibonding

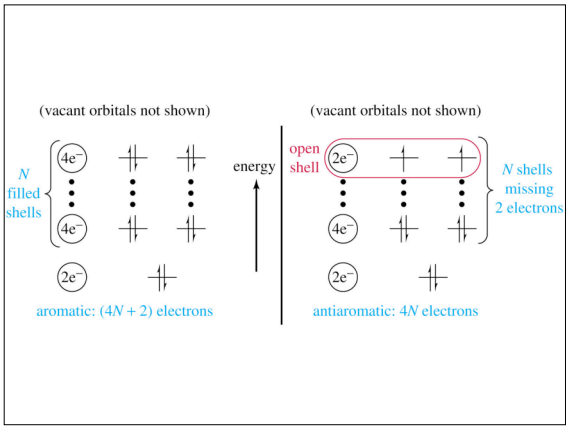
Benzene MOs



All bonding MOs are filled
No electrons in antibonding orbitals

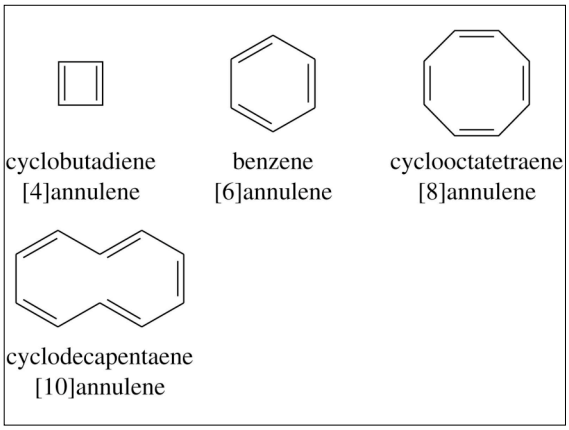






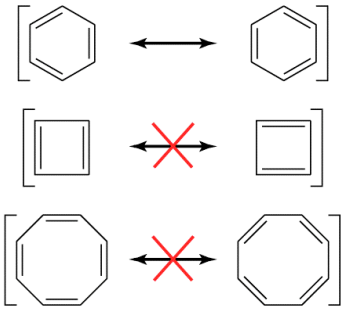
Hückel's Rule: Annulenes

the additional factor that influences aromaticity is the number of π electrons



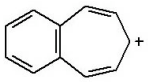
Aromatic vs. "anti-aromatic"

A. Deniz, et. al., *Science*, 5 November 1999



Question

- How many π electrons does the compound shown have?
- A) 5
- B) 8
- C) 10
- D) 12



Hückel's Rule

Among planar, monocyclic, completely conjugated polyenes, only those with $4N + 2$ π electrons have resonance stability (i.e. They are aromatic; and they are also planar.)

N	*4N+2*
0	2
1	6
2	10
3	14
4	18

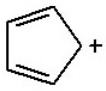
Hückel's Rule

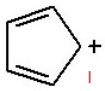
Among planar, monocyclic, completely conjugated polyenes, only those with $4N + 2$ π electrons have resonance stability (i.e. They are aromatic; and they are also planar.)

N	*4N+2*	
0	2	
1	6	benzene!
2	10	
3	14	
4	18	

Question

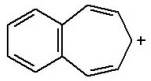
- What is the value of *N* of Huckel's rule for the cyclopentadienyl cation (shown)?
- A) N=1/2
- B) N=1/4
- C) N=1
- D) N=2





I

Question



II

- Which is a true statement based on Huckel's Rule.
- *(Assume that both are planar and that vacant p-orbitals do not interupt conjugation.)*
- A) I is aromatic and II is not.
- B) II is aromatic and I is not.
- C) I and II are aromatic.
- D) I and II are not aromatic.

Hückel's Rule

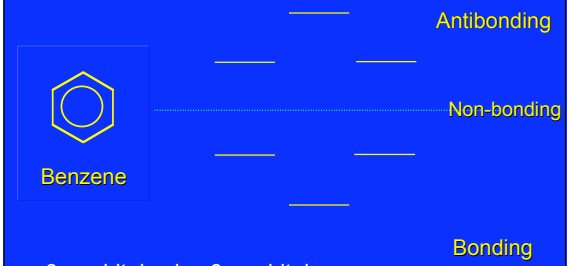
& molecular orbitals

Hückel"s rule applies to: *cyclic, planar, conjugated, polyenes*

the π molecular orbitals of these compounds have a distinctive pattern

one π orbital is lowest in energy, another is highest in energy, and the others are arranged in pairs between the highest and the lowest

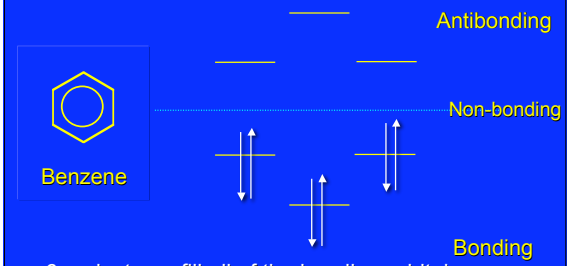
π-MOs of Benzene



6 *p* orbitals give 6 π orbitals

3 orbitals are bonding; 3 are antibonding

π-MOs of Benzene



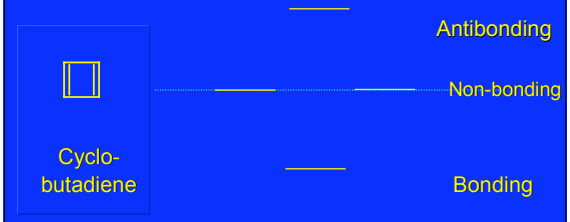
6 π electrons fill all of the bonding orbitals

all π antibonding orbitals are empty

Question

- How many isomers of dibromophenol are aromatic?
- A) 3
- B) 4
- C) 6
- D) 8
- E) none

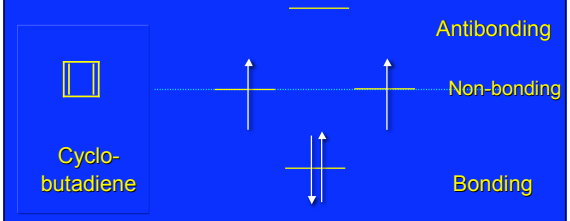
π-MOs of Cyclobutadiene (square planar)



4 *p* orbitals give 4π orbitals

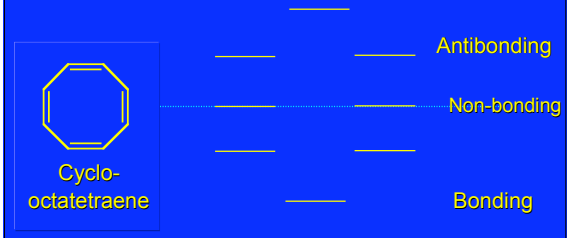
1 orbital is bonding, one is antibonding, and 2 are nonbonding

π-MOs of Cyclobutadiene (square planar)



4 π electrons; bonding orbital is filled; other 2 π electrons singly occupy two nonbonding orbitals

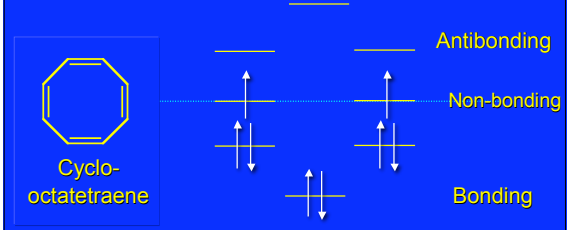
π-MOs of Cyclooctatetraene (square planar)



8 *p* orbitals give 8 π orbitals

3 orbitals are bonding, 3 are antibonding, and 2 are nonbonding

π-MOs of Cyclooctatetraene (square planar)



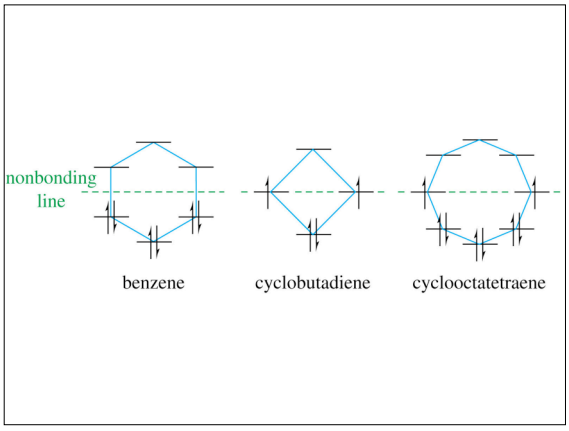
8 π electrons; 3 bonding orbitals are filled; 2 nonbonding orbitals are each half-filled

π-Electron Requirement for Aromaticity

4 π electrons — not aromatic

6 π electrons — aromatic

8 π electrons — not aromatic

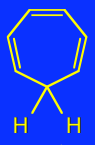


Completely Conjugated Polyenes

6 π electrons; completely conjugated

aromatic

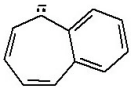
6 π electrons; not completely conjugated



not aromatic

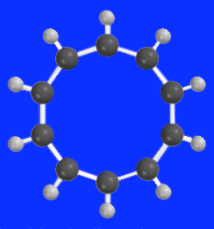
Question

- The compound shown is classified as



- A) non-aromatic
- B) aromatic
- C) anti-aromatic
- D) none of the above

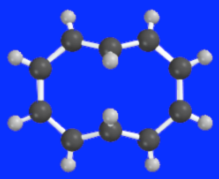
[10]Annulene



predicted to be aromatic by Hückel's rule, but too much angle strain when planar and all double bonds are cis (therefore non-planar)

10-sided regular polygon has angles of 144°

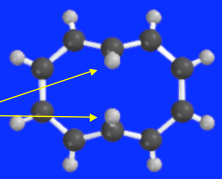
[10]Annulene



incorporating two trans double bonds into the ring relieves angle strain but introduces van der Waals strain into the structure and causes the ring to be distorted from planarity

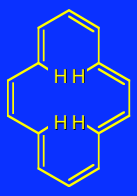
[10]Annulene

van der Waals strain between these two hydrogens



incorporating two trans double bonds into the ring relieves angle strain but also introduces van der Waals strain into the structure and causes the ring to be non-planar

[14]Annulene



14 π electrons satisfies Hückel's rule

van der Waals strain between hydrogens inside the ring & thererfore non-planar

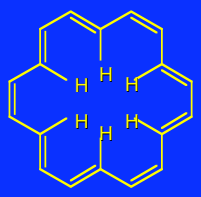
[16]Annulene

16 π electrons does not satisfy Hückel's rule

alternating short (134 pm) and long (146 pm) bonds

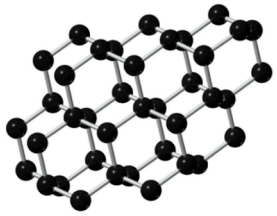
not aromatic

[18]Annulene

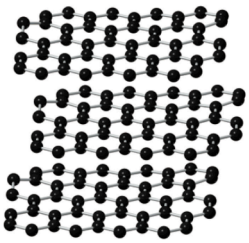


18 π electrons satisfies Hückel's rule

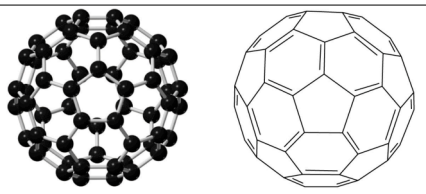
resonance energy = - 418 kJ/mol



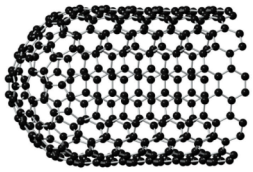
diamond



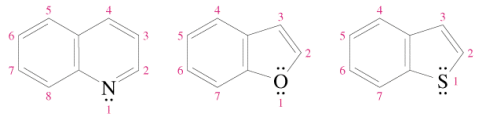
graphite



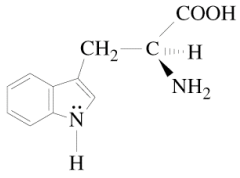
buckyball (C_{60})



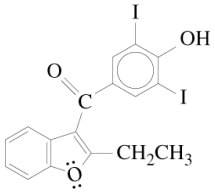
carbon nanotube



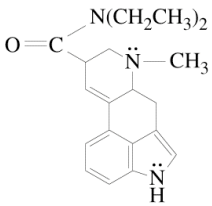
quinoline benzofuran benzothiophene



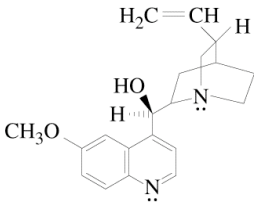
L-tryptophan, an amino acid



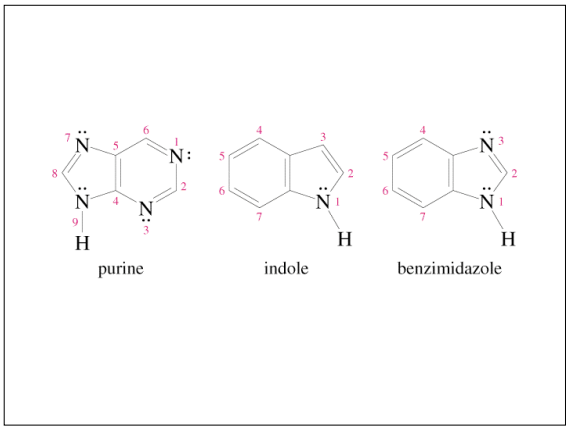
benziodarone, a vasodilator

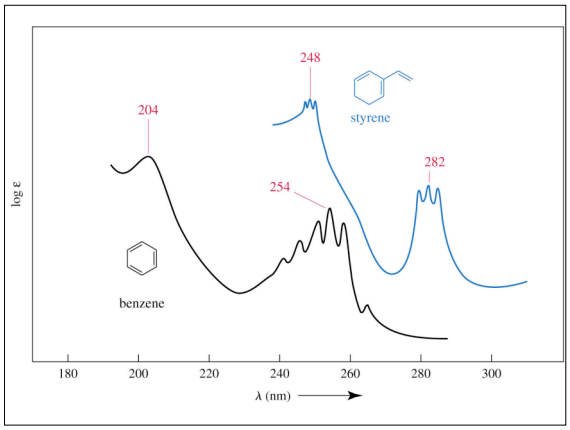


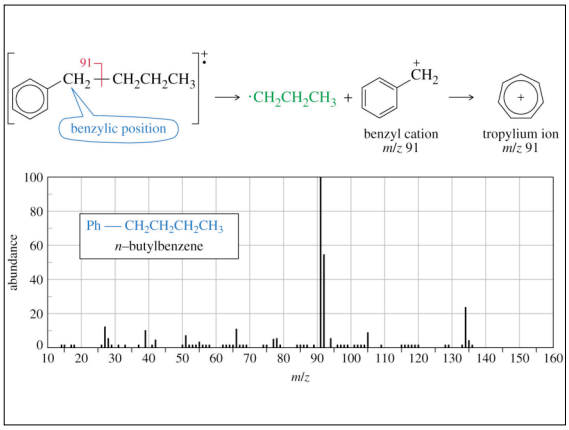
LSD, a hallucinogen



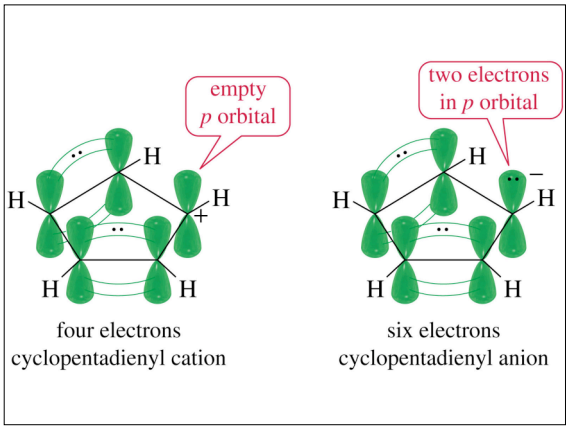
antimalarial drug

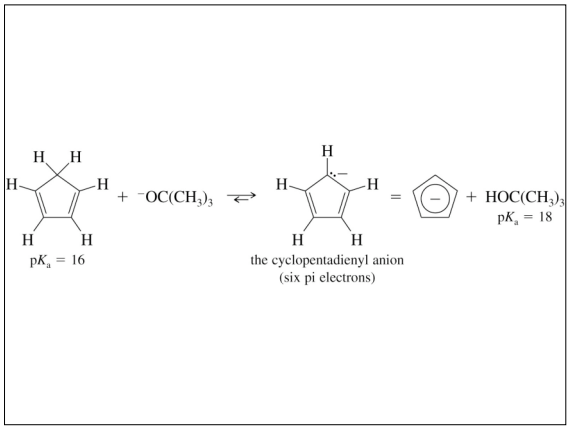


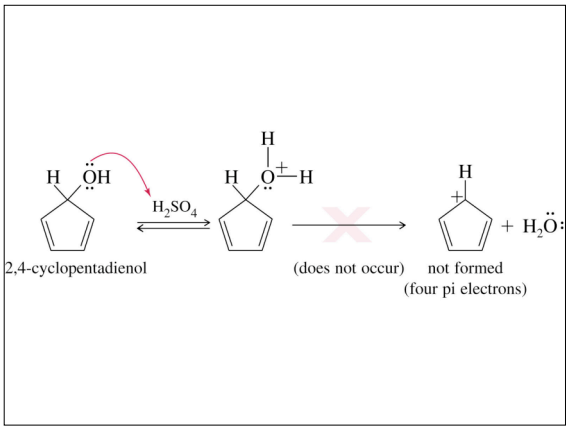


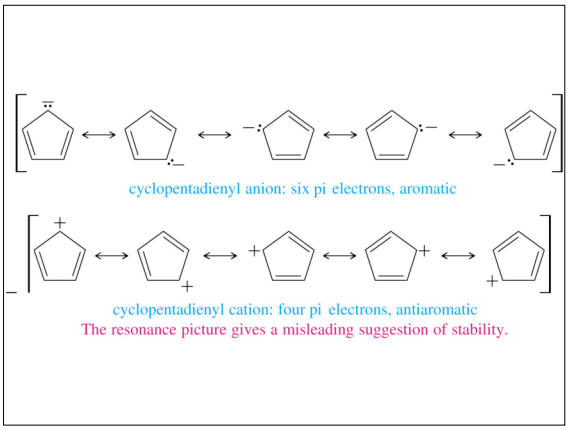


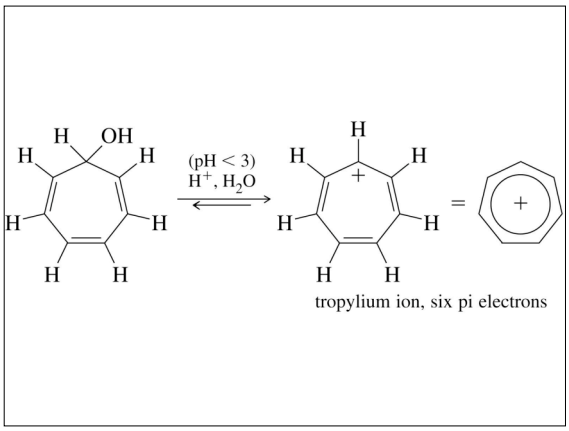
Aromatic Ions

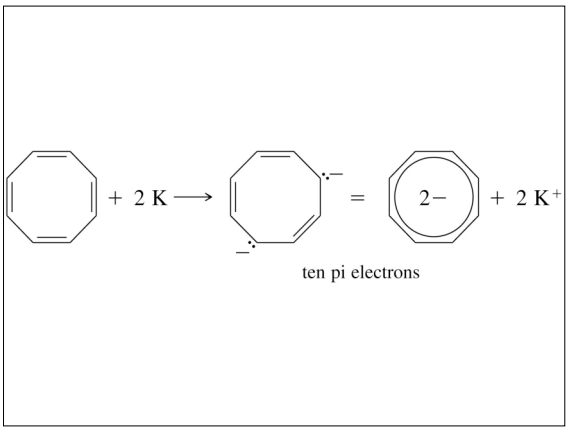




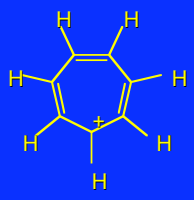






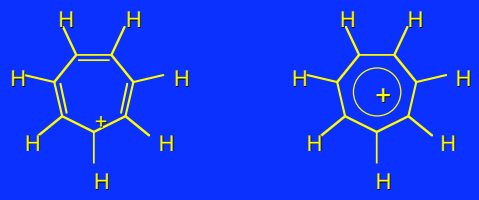


Cycloheptatrienyl Cation

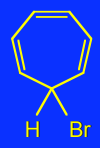


6 π electrons delocalized over 7 carbons
positive charge dispersed over 7 carbons
very stable carbocation
also called tropylium cation

Cycloheptatrienyl Cation



Cycloheptatrienyl Cation



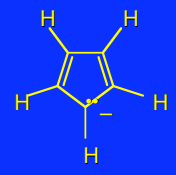
Ionic

Covalent

Tropylium cation is so stable that tropylium bromide is ionic rather than covalent.

mp 203 °C; soluble in water; insoluble in diethyl ether

Cyclopentadienide Anion

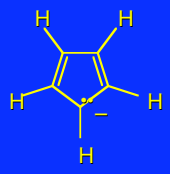


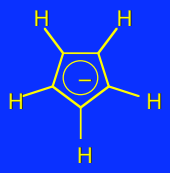
6 π electrons delocalized over 5 carbons

negative charge dispersed over 5 carbons

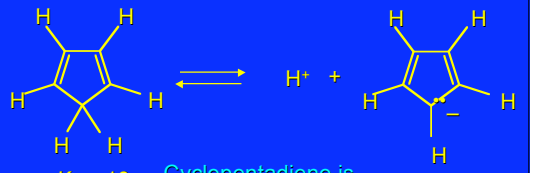
stabilized anion

Cyclopentadienide Anion





Acidity of Cyclopentadiene



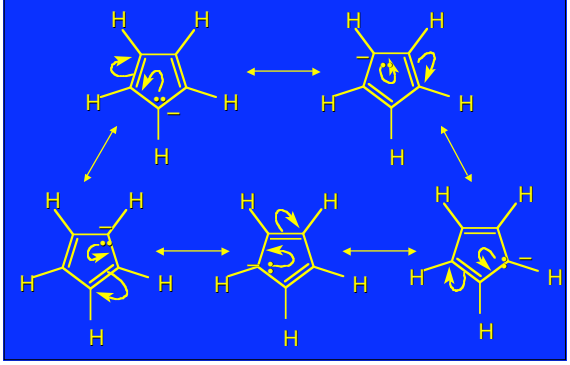
pK_a = 16

$K_a = 10^{-16}$

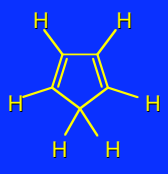
Cyclopentadiene is unusually acidic for a hydrocarbon.

Increased acidity is due to stability of cyclopentadienide anion.

Electron Delocalization in Cyclopentadienide Anion

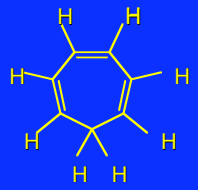


Compare Acidities of Cyclopentadiene and Cycloheptatriene



pK_a = 16

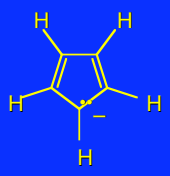
$K_a = 10^{-16}$



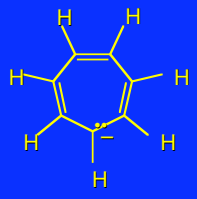
pK_a = 36

$K_a = 10^{-36}$

Compare Acidities of Cyclopentadiene and Cycloheptatriene

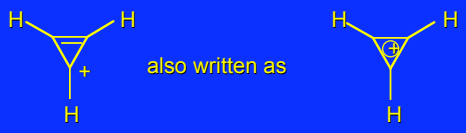


Aromatic anion
6 π electrons



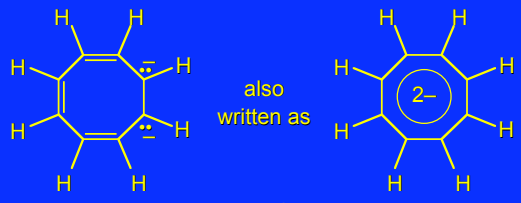
Antiaromatic anion
8 π electrons

Cyclopropenyl Cation



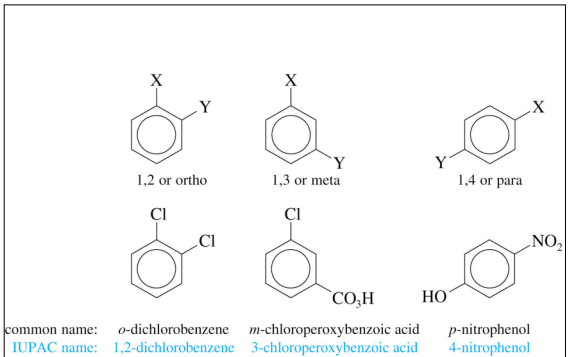
$N = 0$
$4N + 2 = 2\ \pi$ electrons

Cyclooctatetraene Dianion

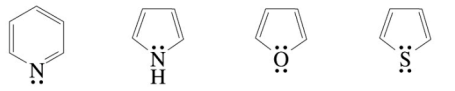


$n = 2$
$4n + 2 = 10\ \pi$ electrons

Heterocyclic Aromatic Compounds

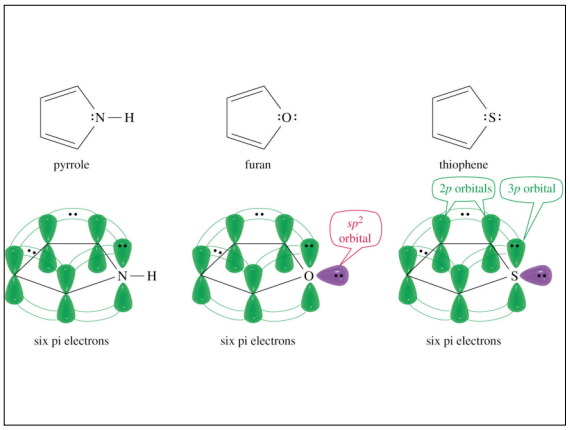


Aromatic Heterocyclic Compounds

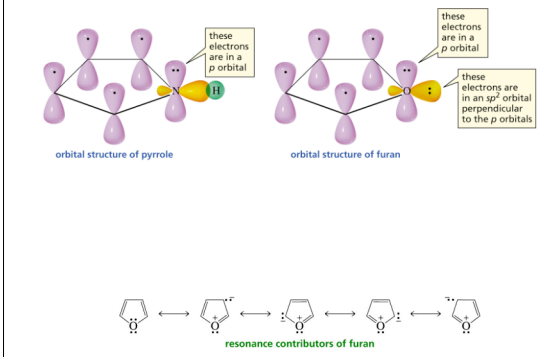


pyridine **pyrrole** **furan** **thiophene**

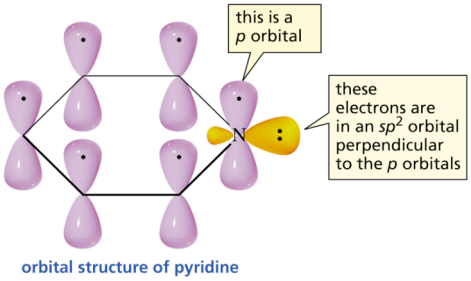
A heterocycleis a cyclic compound in which one or more of the ring atoms is an atom other than carbon.

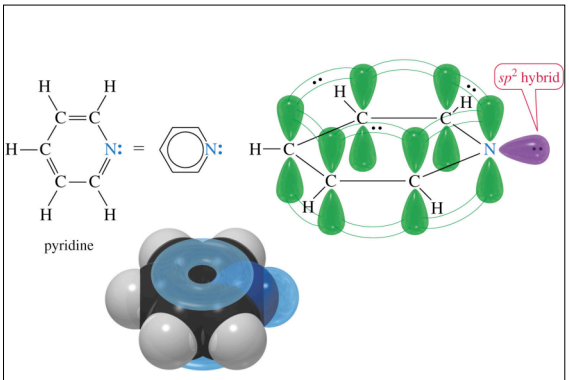


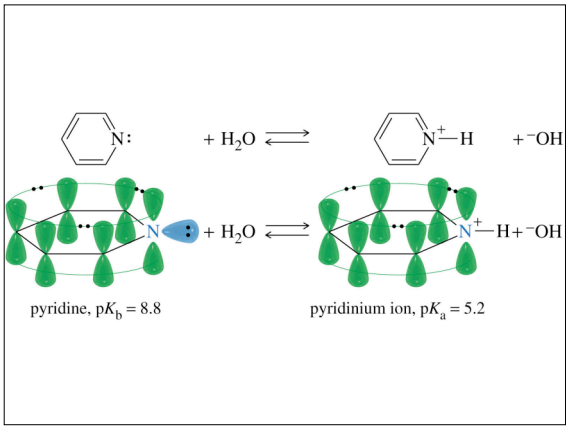
Furan Is Aromatic



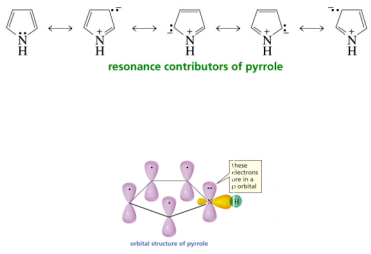
Pyridine Is Aromatic

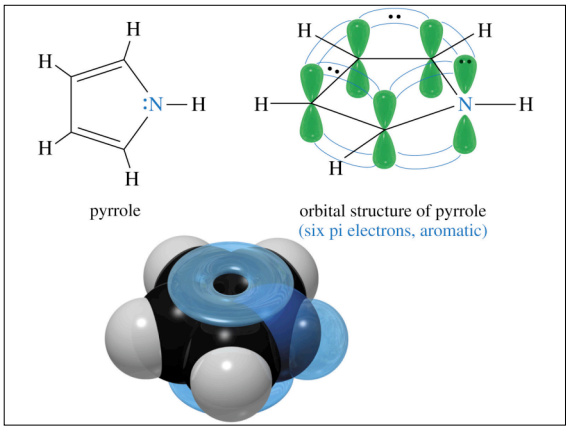


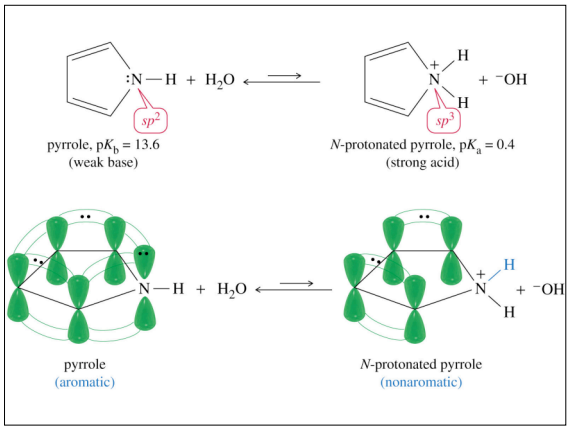




Pyrrole Is Aromatic

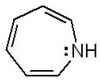




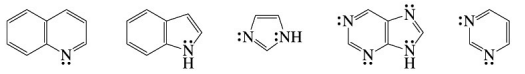


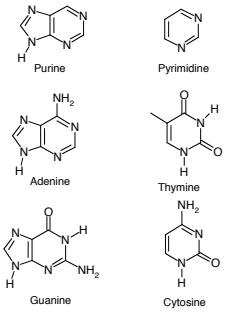
Question

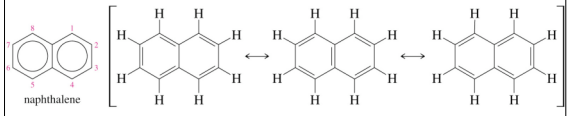
- Which of the following compounds is best classified as an aromatic heterocycle?

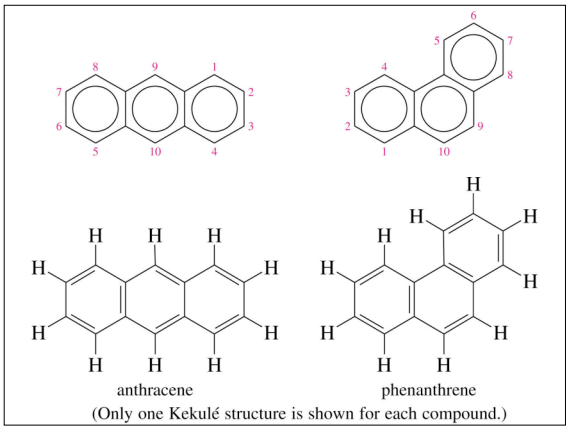
- A)  B) 
- C) Aniline D) Pyridine
- E) All of them

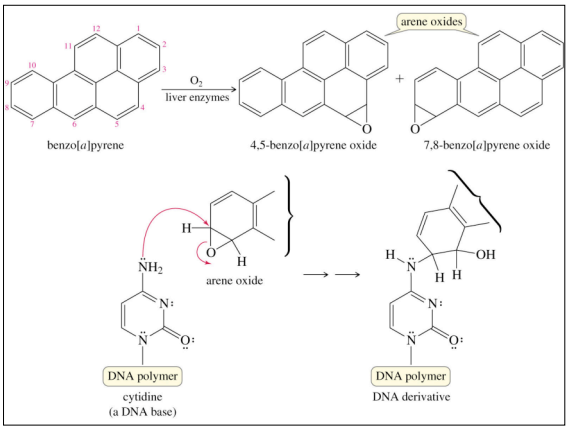
Examples of Important Nitrogen Heterocyclic Aromatic Compounds








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


arene oxides
O2
liver enzymes
benzo[a]pyrene
4,5-benzo[a]pyrene oxide
7,8-benzo[a]pyrene oxide
arene oxide
DNA polymer
cytidine
(a DNA base)
DNA polymer
DNA derivative