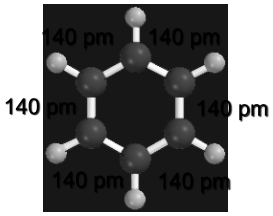
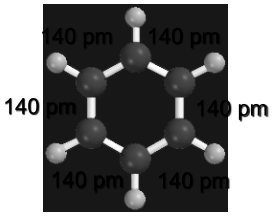
Arenes and Aromaticity
(*Benzene*)

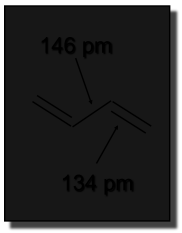
All C—C bond distances = 140 pm



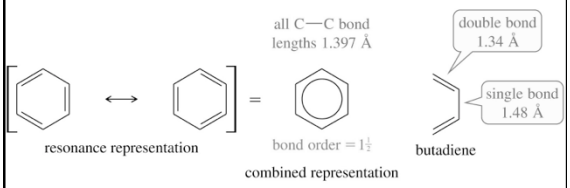
Benzene
***empirical formula* = CH**

All C—C bond distances = 140 pm





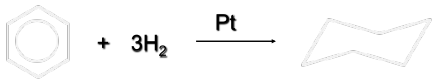
140 pm is the average between the C—C single bond distance and the double bond distance in 1,3-butadiene.



Resonance & Benzene

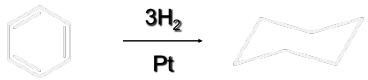
Thermochemical Measures of Stability

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

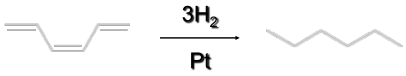


ΔH°= – 208 kJ

Cyclic conjugation versus noncyclic conjugation



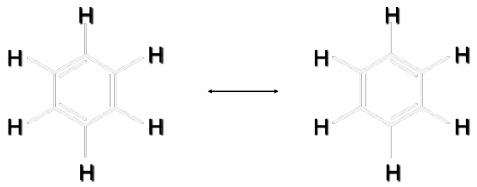
heat of hydrogenation = -208 kJ/mol (-49 kcal/mol)



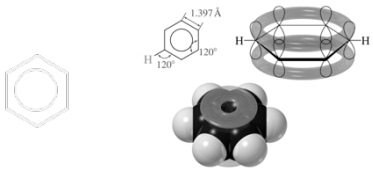
heat of hydrogenation = -337 kJ/mol (-85.8 kcal/mol)

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



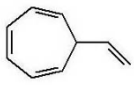
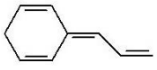
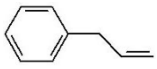
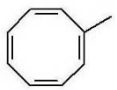
Circle-in-a-ring notation stands for resonance description of benzene (hybrid of two resonance structures)

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

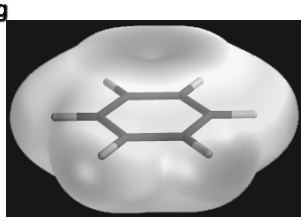
- Predict which of the following has the smallest heat of combustion.

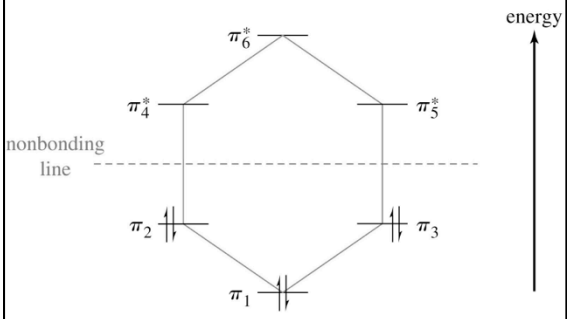
- A) 
- B) 
- C) 


The π Molecular Orbitals of Benzene

Orbital Hybridization Model of Bonding in Benzene

High electron density above and below plane of ring



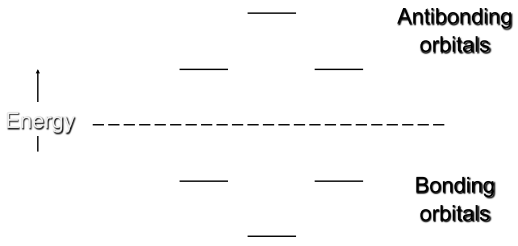


Hückel's Rule

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.

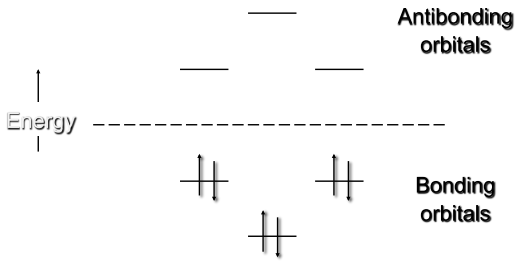
1) Draw a circle.
2) Inscribe a regular polygon inside the circle so that one of its corners is at the bottom.
3) Every point where a corner of the polygon touches the circle corresponds to a π electron energy level.
4) The middle of the circle separates bonding and antibonding orbitals.

Benzene MOs



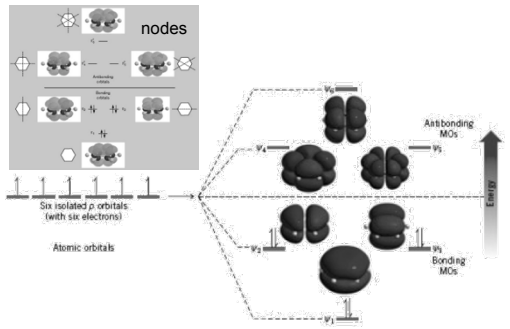
6 *p* AOs combine to give 6 π MOs
3 MOs are bonding; 3 are antibonding

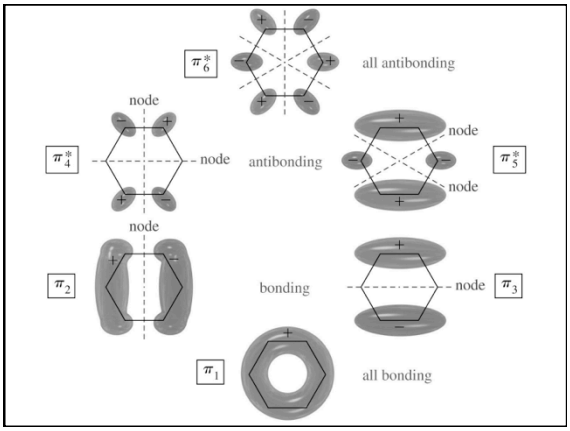
Benzene MOs



All bonding MOs are filled
No electrons in antibonding orbitals

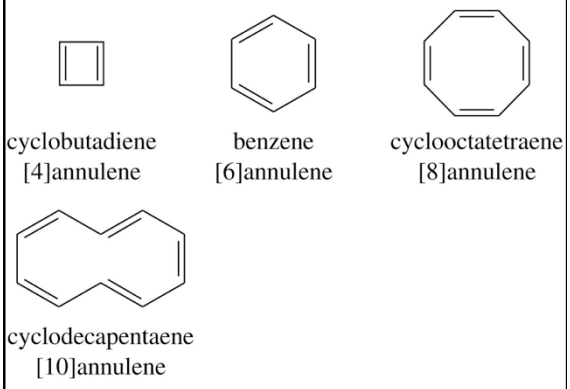
Benzene Molecular Orbitals





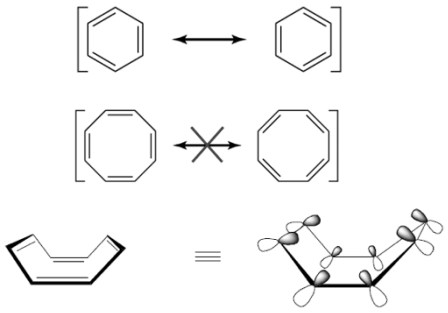
Hückel's Rule:
Annulenes

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



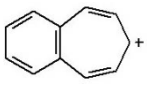
Aromatic vs. "anti-aromatic"

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

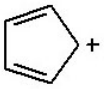
Hückel's Rule

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

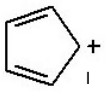
Question

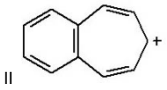
- What is the value of *N* of Huckel's rule for the cyclopentadienyl cation (shown)?



- A) N=1/2
- B) N=1/4
- C) N=1
- D) N=2

Question





- 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.

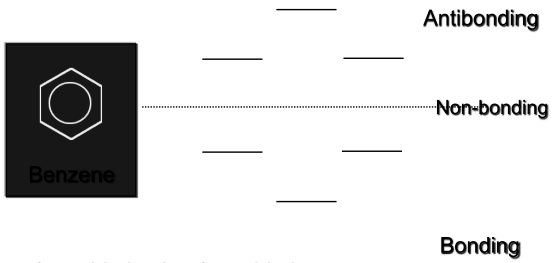
Hückel's Rule
& molecular orbitals

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

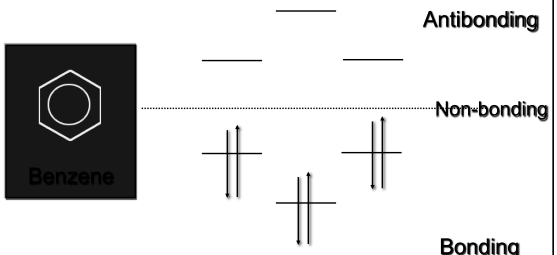
π-MOs of Benzene



6 *p* orbitals give 6 π orbitals

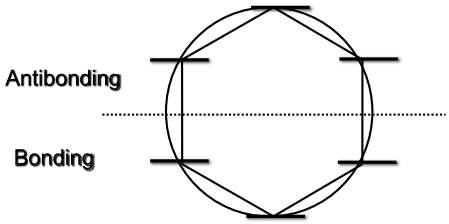
3 orbitals are bonding; 3 are antibonding

π-MOs of Benzene



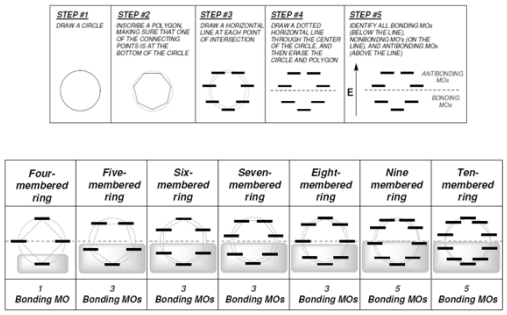
6 π electrons fill all of the bonding orbitals
all π antibonding orbitals are empty

Frost's Circle



π MOs of Benzene

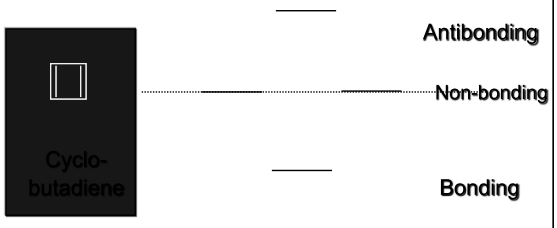
FROST CIRCLES



Question

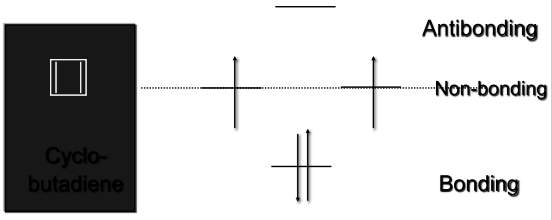
- How many isomers of dibromophenol are aromatic?
- A) 3
- B) 4
- C) 6
- D) 8
- E) none

π-MOs of Cyclobutadiene (square planar)



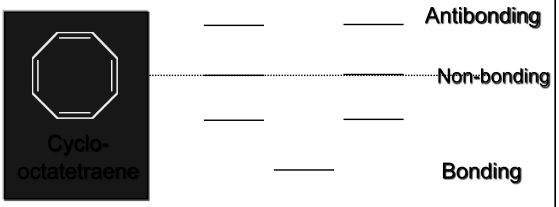
4 *p* orbitals give 4π orbitals
1 orbital is bonding, one is antibonding, and 2 are nonbonding

π-MOs of Cyclobutadiene (square planar)



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

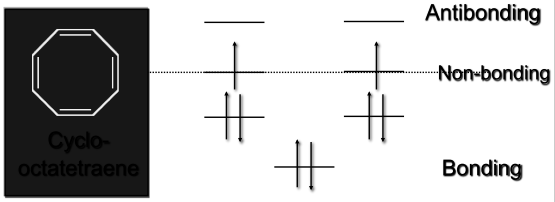
π-MOs of Cyclooctatetraene (square planar)



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

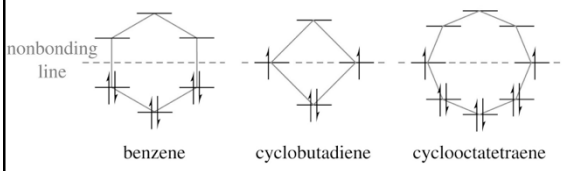
π-Electron Requirement for Aromaticity

4 π electrons — not aromatic

6 π electrons — aromatic

8 π electrons — not aromatic

Anti-aromatic (planar)



Aromatic

Non-aromatic (non-planar)

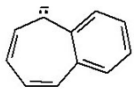
Completely Conjugated Polyenes

6 π electrons; completely conjugated — aromatic

6 π electrons; not completely conjugated — not aromatic

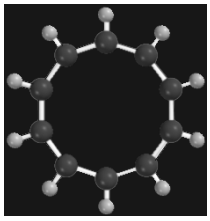
Question

- The planar compound shown below is classified as



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

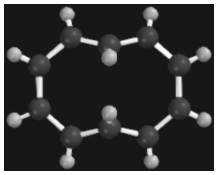
[10]Annulene



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°

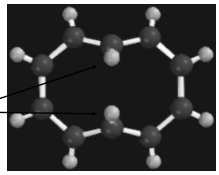
[10]Annulene



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

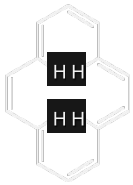
[10]Annulene

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

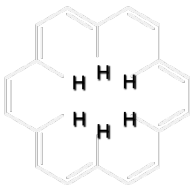
[16]Annulene

16 π electrons does not satisfy Hückel's rule

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

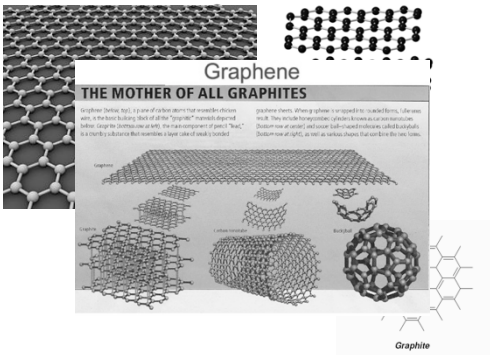
not aromatic

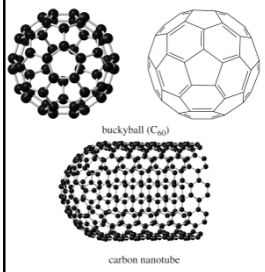
[18]Annulene



18 π electrons satisfies Hückel's rule

resonance energy = - 418 kJ/mol



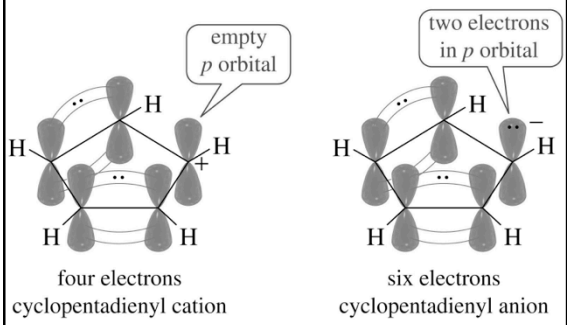


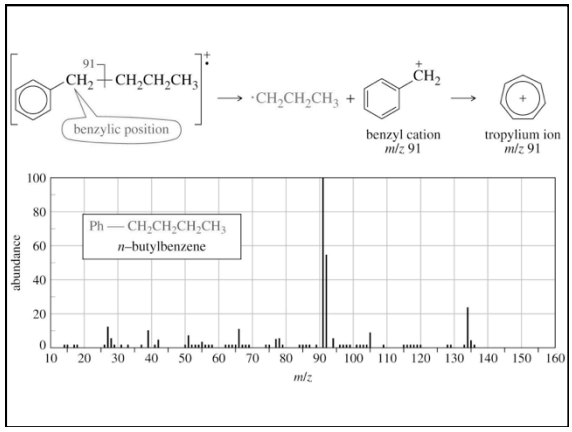
Buckball (Fullerenes) can also be made into tubes.

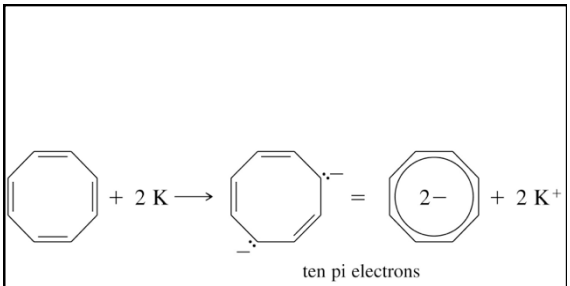
Single, double, and multi -walled carbon nanotubes have many applications:

Conductive Plastics, Energy Storage, Conductive Adhesives, Molecular Electronics, Thermal Materials, Fibres and Fabrics, Catalyst Supports, Biomedical Applications

Aromatic Ions

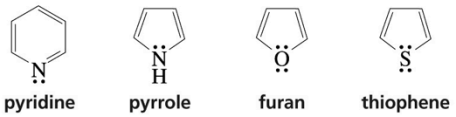




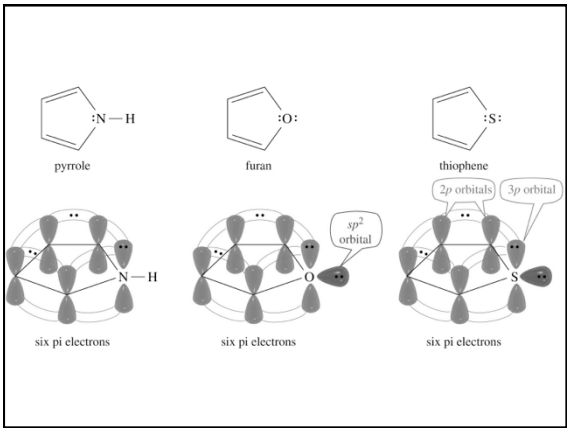


Heterocyclic Aromatic Compounds

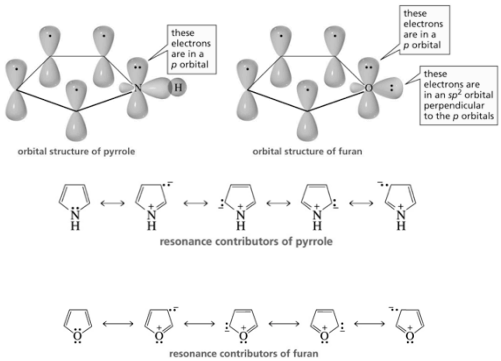
Aromatic Heterocyclic Compounds



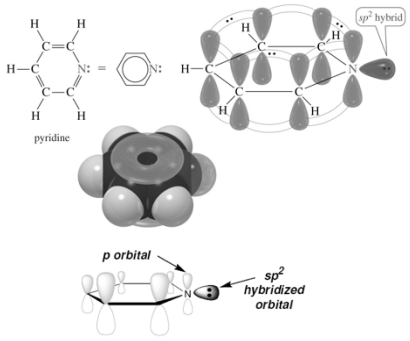
A heterocycleis a cyclic compound in which one or more of the ring atoms is an atom other than carbon.



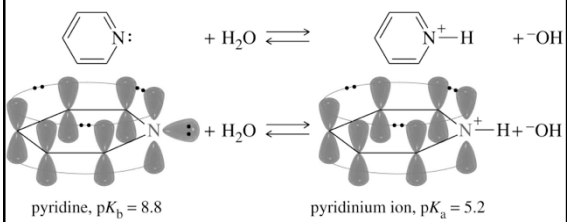
Pyrole & Furan are Aromatic



Pyridine Is Aromatic

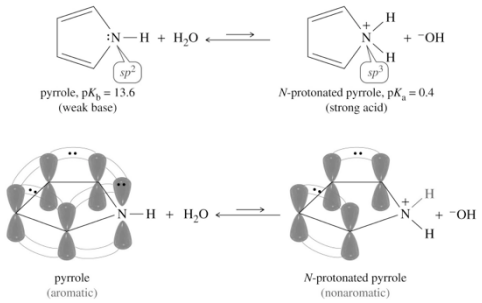


Acid-Base Chemistry & Aromaticity



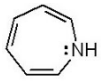
aromatic

Acid-Base Chemistry & Aromaticity

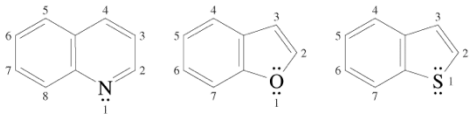


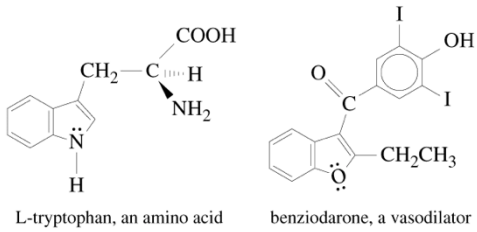
Question

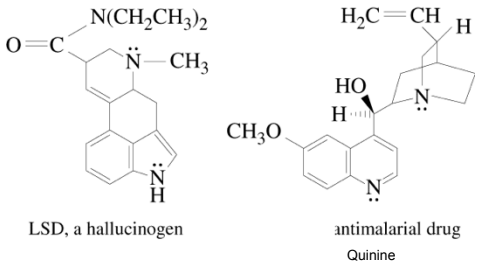
- Which of the following compounds is best classified as an aromatic heterocycle?

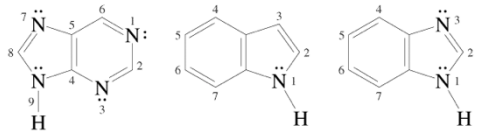
- A)  B) 
- C) Aniline D) Pyridine
- E) All of them

Hetero-bicylic-aromatic compounds

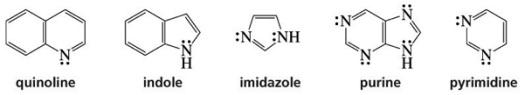


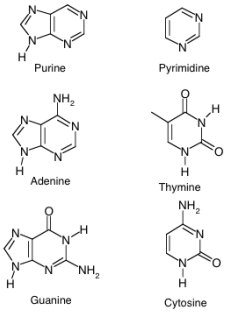




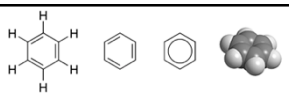


Examples of Important Nitrogen Hetero-bicyclic Aromatic Compounds



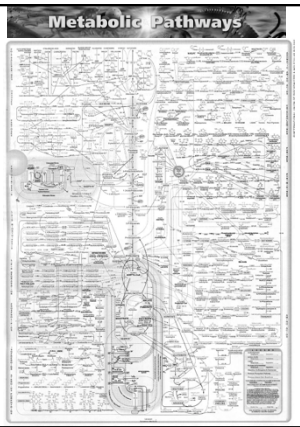


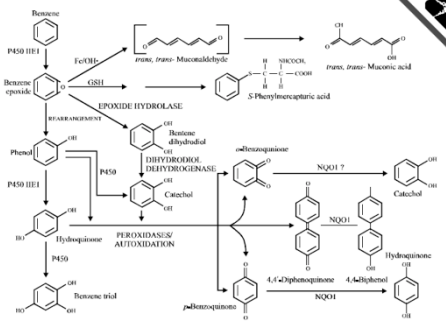
Aromatic Compounds & Cancer

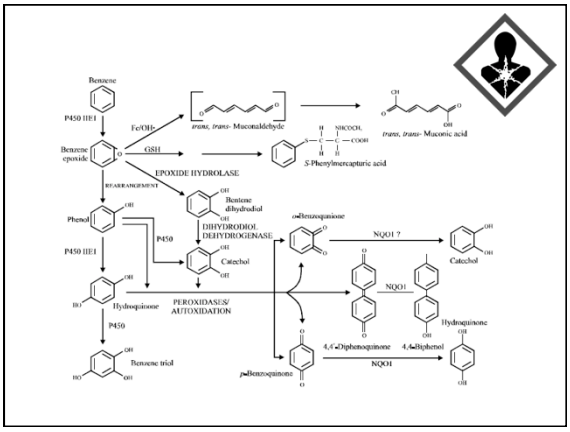


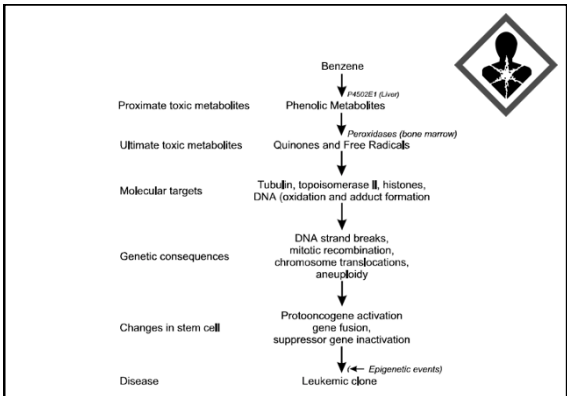
- Benzene is classified as a Group A, human carcinogen by the EPA.
- Increased incidence of leukemia has been observed in humans occupationally exposed to benzene.
- Chronic inhalation has caused various blood disorders, including reduced red blood cell count and aplastic anemia.
- Reproductive effects have been reported for women exposed to high levels by inhalation.
- Adverse effects on the developing fetus have been observed in animal tests.

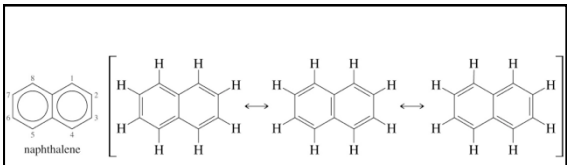
Human Metabolism







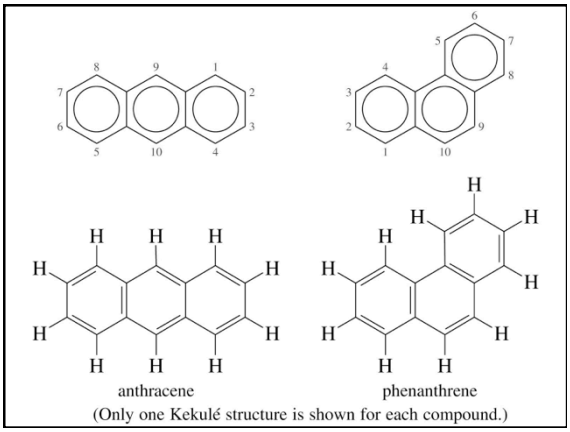




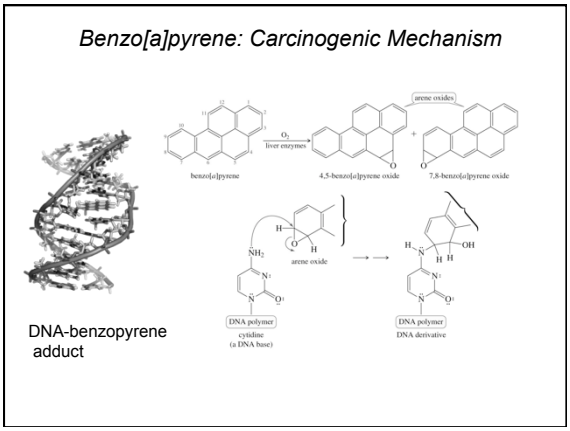
Trace amounts of naphthalene are produced by magnolias, deer, termites, and have been found in meteorites.

It has been used as a common household fumigant which was referred to as “moth balls”. Humans, particularly children have developed hemolytic anemia after ingesting moth balls

Napthalene is regarded to be a possible human carcinogenic and has caused cancer in animal studies.



Benzo[a]pyrene: Carcinogenic Mechanism



DNA-benzopyrene adduct

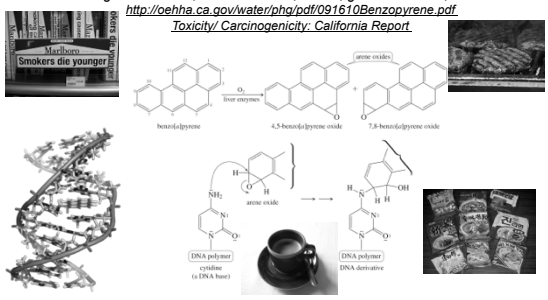
Exposure / Toxicity

http://cebp.aacrjournals.org/content/14/8/2030.long

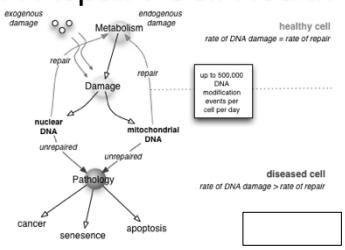
cigarette smoke, ramen noodles, coffee, grilled red meat, water

http://oehha.ca.gov/water/phg/pdf/091610Benzopyrene.pdf

Toxicity/ Carcinogenicity: California Report



DNA Repair / Cell Health



healthy cell

rate of DNA damage = rate of repair

up to 500,000 DNA modification events per cell per day

diseased cell

rate of DNA damage > rate of repair