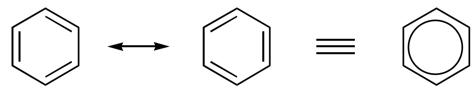
Ch. 16 Aromatic Compounds

C_6H_6

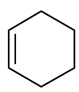
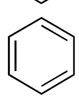


A B C

2 Resonance Structures

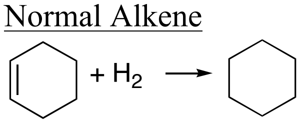
Facts to Accommodate

1. 4 elements of unsaturation
2. All C-C bonds are same length, not alternating (contrary to expectation based on structure **A**)
3. Only 1 isomer of 1,2-dibromobenzene (contrary to expectation based on structure **A**)
4. Unlike alkenes, does not undergo addition reactions (contrary to expectations based on **A**)
5. Extreme stability indicated by combustion or hydrogenation tests

	H_2/Pt	Br_2	HBr	BH_3	$Hg(OAc)_2/H_2O$	Etc.
 D	Reacts	Reacts	Reacts	Reacts	Reacts	
 A	No Reaction	No Reaction	No Reaction	No Reaction	No Reaction	

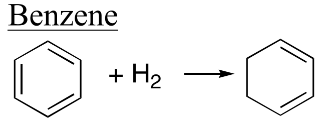
Hydrogenation: Measurement Tests for the Extraordinary Stability of Benzene

Normal Alkene



ΔH = -29 kcal/mol
Strongly Exothermic

Benzene

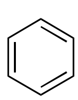
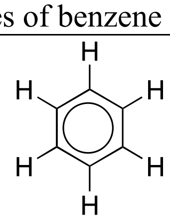
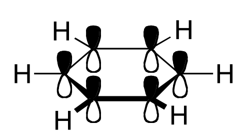
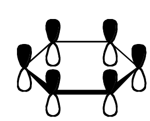


ΔH = +6 kcal/mol
Endothermic

- Hydrogenation is normally very exothermic, but not for benzene
- The less favorable hydrogenation reflects **greater stability**
- The stability difference is over 30 kcal/mol: huge
    - Butadiene gains <4 kcal/mol of stability from it's conjugation

16.3,4 Benzene Molecular, Structural Details, and Molecular Orbitals

1. Some different pictures of benzene

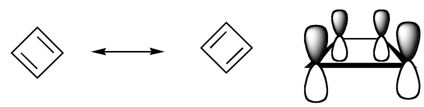
			
a) Simplest **b) Ideal for mechanisms**, helps keep track of the electrons	Illustrates: a) delocalization of b) equivalence of bonds d)complete planarity	**a) Easy to see π-system** b) Helps explain why the C-C bonds are all the same	**a) Easy to see the π-system**, undistracted by the hydrogens

2. Notes on Pictures and Structural Features
1. All 6 carbons are sp^2, with one p orbital each
2. 120º angles, so all 6 carbons and each of their attached hydrogens are all co-planar.
3. Perfectly flat.
4. Perfect 120º angles, no angle strain whatsoever
5. Complete symmetry
6. Each C-C bond is equal in length and strength
7. Each C-C bond is longer than a normal double but shorter than a normal single bond

Normal Bond Lengths:	C-C: 1.54A	C=C: 1.34 A	Benzene CC: 1.39A

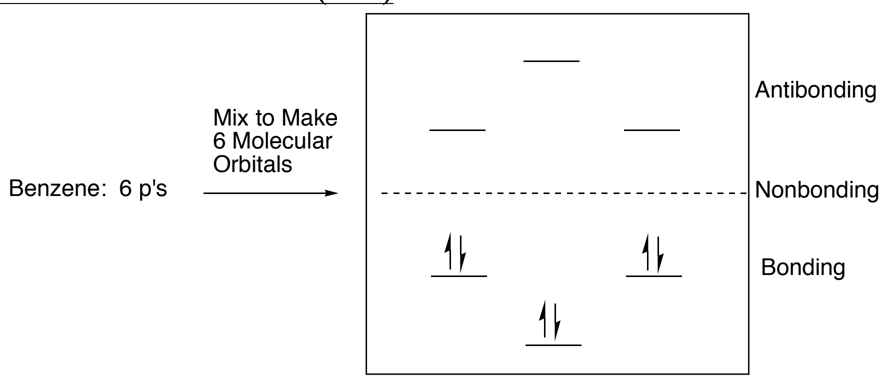
- "1.5" bonds, as we see from resonance.

8. 6 π -electrons are delocalized throughout the ring.
   - Complete racetrack
9. Resonance delocalization, stabilization
10. Note: not all "π racetracks" are stabilized



No extra stability
Actually somewhat destabilized

3. Molecular Orbital for Benzene (11.5)



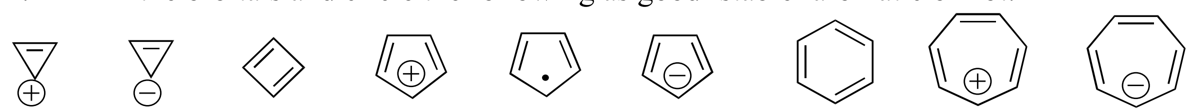
- All and only the bonding molecular orbitals are completely filled. Special stability
- But how can you know what the molecular orbitals will look like for other rings?

Frost Diagram/Polygon Rule: (11.19) For a **complete ring** of **sp^2 centers**,
1. Draw the ring/polygon with a vertex down, basically inside what would be a circle
2. Each apex represents a molecular orbital
3. A horizontal line through the middle of the ring provides the non-bonding reference point
4. Populate the MO's as needed depending on how many π-electrons are available

Molecular Orbital Rules for a cyclic π-system:
1. If all and only bonding molecular orbitals are occupied→ good ("aromatic")
2. If any nonbonding or antibonding MO's are occupied, or if any bonding MO's are not completely occupied → bad, poor stability ("antiaromatic")
   - Below nonbonding line → bonding
   - Above nonbonding line → antibonding
   - On nonbonding line → nonbonding

Practice Problem

1. Draw the MO's for 3-, 4-, 5-, and 6-membered cyclic π systems.
2. Fill in the orbitals and circle the following as good=stable=aromatic or not.



3

4

5

6

NOTE: 5-, 6-, 7-, and 8-membered rings all end up with 3 molecular orbitals below the non-bonding line

(11.19) **Aromatic, Antiaromatic, Nonaromatic**. **Huckel's Rule**: For a **planar**, **continuous ring** of **π-orbitals**, (sp^2 all around):

- If the number of π-electrons = 2,6,10 etc. (4N + 2) → AROMATIC, STABILIZED
- If the number of π-electrons = 4,8,12 etc. (4N) → Anti-aromatic, destabilized

- Why: the 4N+2 rule always goes with favorable Frost diagrams: bonding and only bonding MO's are always filled.

- Generality: Huckel's Rule applies for cycles, bicycles, ionic compounds, and heterocycles.

a. Cycles (one-ring) b. Polycycles (2 or more) c. Ionic rings d. Heterocycles

-

e. Cycles (one-ring) f. Polycycles (2 or more) g. Ionic rings h. Heterocycles

<u>Practice Problems: Classify each of the following as Aromatic (circle them) or not. For those that aren't, are there any that are Antiaromatic? (square them)</u>

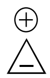
Keys:

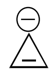
1. Do you have an uninterrupted sp^2 ring?
2. Apply Huckel's Rule: Do you have 2,6,10 etc. π electrons?
3. Applying Huckel's Rule requires that you can accurately count your π-electrons. Be able to count:
   - Anions: contribute 2 π-electrons
   - Cations: contribute 0 π-electrons
   - Heteroatoms (O or N): can provide 2 π-electrons if it helps result in aromatic stability.

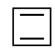
Note: For those that are not aromatic, why not?

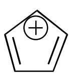
1. Lacks cyclic sp^2 ring
2. Lacks Huckel's rule electron count

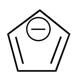
1. 

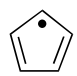
2. 

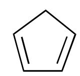
3. 

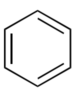
4. 

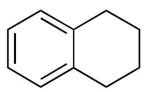
5. 

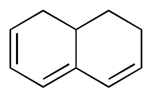
6. 

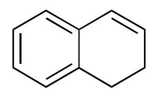
7. 

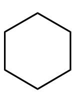
8. 

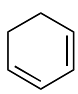
9. 

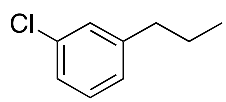
10. 

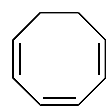
11. 

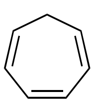
12. 

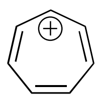
13. 

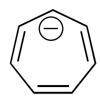
14. 

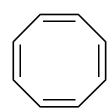
15. 

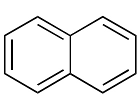
16. 

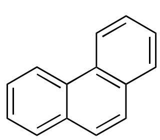
17. 

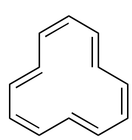
18. 

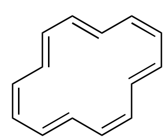
19. 

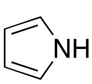
20. 

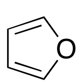
21. 

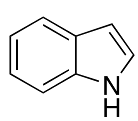
22. 

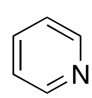
23. 

24. 

25. 

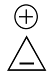
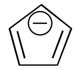
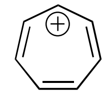
26. 

27. 

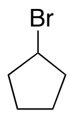
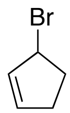
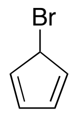
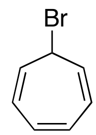
28. 

16.8 Aromatic Ions

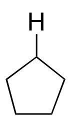
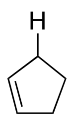
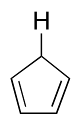
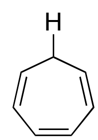
- <u>3 common, important Aromatic Ions</u>

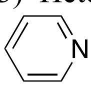
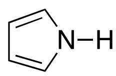
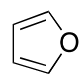
Problem 1: The following substrates have widely differing reactivity toward **<u>H_2O solvolyis</u>**. (The fastest is more than a million times faster than 2nd fastest, and the slowest more than a hundred times slower than the second slowest). Rank the reactivity. (Key: What kind of reaction would happen, and what determines reactivity?)

Problem 2: The following have enormous differences in **<u>acidity</u>**. (10^{-20}, 10^{-42}, 10^{-50}, 10^{-56})
Key:

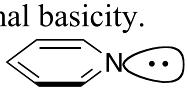
(11.22,23) Heterocyclic Aromatics. Memorize 3.

<u>Pyridine</u>

N-hybridization: sp^2
N-lone-pair: sp^2
N-basicity: reasonably normal

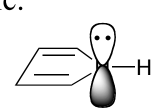
The lone pair is not used in the π-system; the sp^2 points in plane of paper, and has normal basicity.



<u>Pyrrole</u>

N-hybridization: sp^2
N-lone-pair: p
N-basicity: Nonbasic

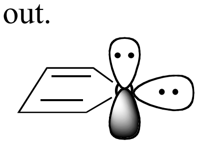
The lone pair is used in the π-system and is counted toward the 6 electrons for Huckel's rule. Because the lone pair is p, pyrrole is nonbasic.



<u>Furan</u>

O-hybridization: sp^2
O-lone-pairs: one p, one sp^2

The p lone pair is used in the π - system and is needed to get the 6 electrons needed for Huckel's rule. But the sp^2 lone pair is in the plane of the ring, extending straight out.



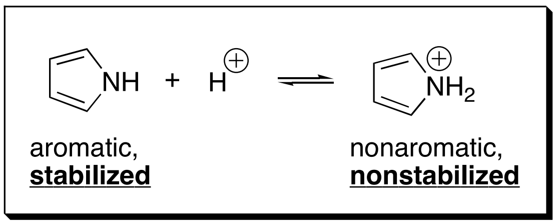
Nitrogens: Atom hybridization, Lone-Pair hybridization, and Basicity

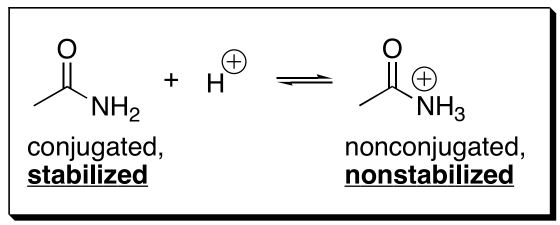
- Amine nitrogens are normally basic, but not when the N-lone pair is p-hybridized
- Rule: If a nitrogen lone pair is p (used in conjugation) → nonbasic
- Nitrogen lone-pair basicity: $sp^3 > sp^2 >>> p$

Situations	N-Atom	N-Lone Pair	N-Basicity
1. Isolated	sp^3	sp^3	Normal
2. Double Bonded	sp^2	sp^2	Normal (a little below, but not much)
3. Conjugated (not itself double bonded, but next to a double bond)	sp^2	p	Nonbasic

Why are p-lone pairs so much less basic?

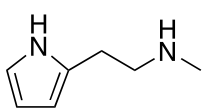
- Because conjugation/aromatic stability in the reactant is lost upon protonation.

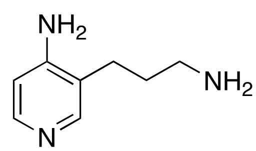


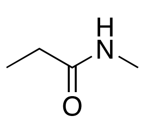


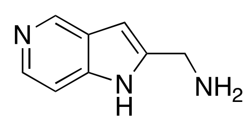
Problem: For each nitrogen, classify:

a) hybridization of the Nitrogen atom
b) hybridization of the Nitrogen lone-pair
c) basicity of the Nitrogen (basic or nonbasic)

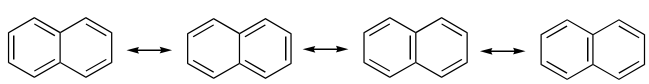
1. 

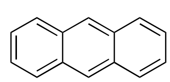
2. 

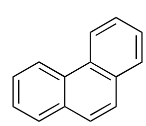
3. 

4. 

16.10 Polycyclic Aromatics (needn't memorize names)


napthalene

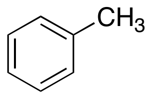

anthracene


phenanthrene

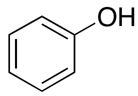
16.13 AROMATIC NOMENCLATURE

1. **Memorize** Special Names.

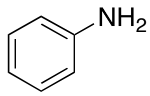
- Six Special Monosubstituted Names You Must **Memorize**



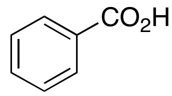
Toluene



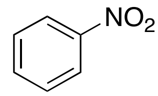
Phenol



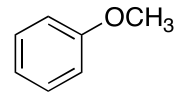
Aniline



Benzoic Acid

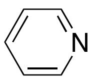


Nitrobenzene



Anisole

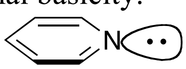
- Three Special Heterocyclic Common Names You Must **Memorize**

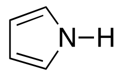


Pyridine

N-hybridization: sp^2
N-lone-pair: sp^2
N-basicity: reasonably normal

The lone pair is not used in the π-system; the sp^2 points in plane of paper, and has normal basicity.

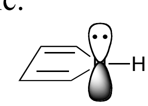


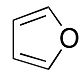


Pyrrole

N-hybridization: sp^2
N-lone-pair: p
N-basicity: Nonbasic

The lone pair is used in the π-system and is counted toward the 6 electrons for Huckel's rule. Because the lone pair is p, pyrrole is nonbasic.

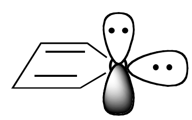




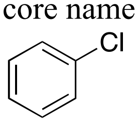
Furan

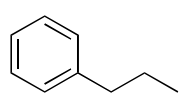
O-hybridization: sp^2
O-lone-pairs: one p, one sp^2

The p lone pair is used in the π -system and is needed to get the 6 electrons needed for Huckel's rule. But the sp^2 lone pair is in the plane of the ring, extending straight out.

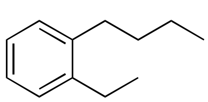


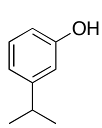
2. Mono-substituted benzenes, if not one of the special memory names: use "benzene" as core name

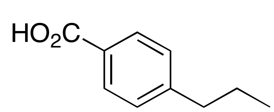




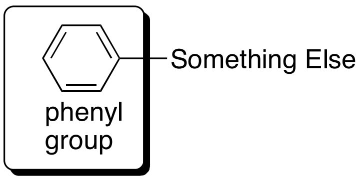
3. Di- or polysubstituted aromatics
   a. If one of the "special" memory names can be used, use that as the core name and number with the special substituent on carbon 1.
   b. Special Terms:
      - "ortho" or o- 1,2 relationship
      - "meta" or m- 1,3 relationship
      - "para" or p- 1,4 relationship

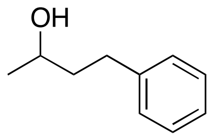
1. 

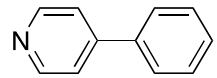
2. 

3. 

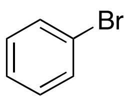
4. As a substituent, benzene is named “phenyl”
   - "phenyl" = C_6H_5- = a benzene group attached to something else, named as a substituent





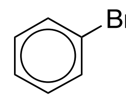


5. Three Shorthands for phenyl

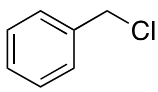


PhBr

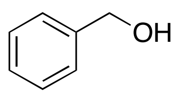
C_6H_5Br



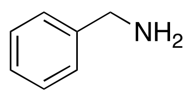
6. “Benzyl” = $PhCH_2$



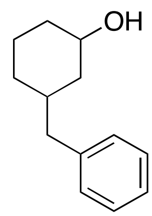
benzyl chloride



benzyl alcohol



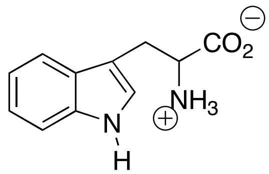
benzyl amine



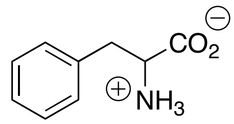
3-benzylcyclohexanol

Some Complex Aromatics in Nature

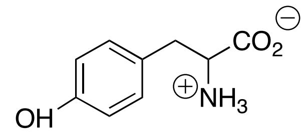
1. Amino Acids. 3 of 22 amino acids found in human proteins are aromatic



Tryptophan



Phenylalanine

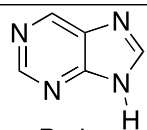


Tyrosine

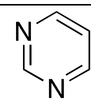
"Essential"-have to eat them, since body can't make the benzene rings

2. Nitrogen Bases: Purine, Pyrimidine, Imidazole.

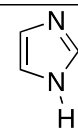
Nitrogen Bases Purine, Pyrimidine, Imidazole. Substituted derivatives of purine and pyrimidine are the stuff of DNA and RNA. The basicity of their nitrogens is crucial to genetics, replication, enzymes, and protein synthesis.



Purine

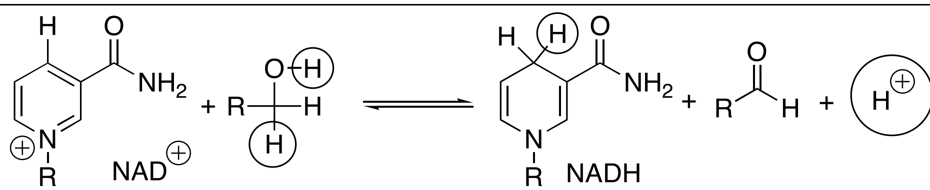


Pyrimidine



Imidazole

3. Nitrogen Bases: Purine, Pyrimidine, Imidazole. Nicotinamide Adenine Dinucleotide (NAD+) and NADH. Important Redox reagents.



4. Polychlorinated Biphenyls (PCB's). High stability as insulators, flame-retardants make them so stable that they are hard to get rid of!