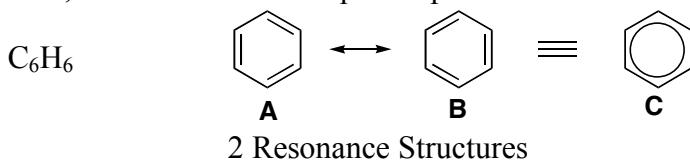


## Ch. 16 Aromatic Compounds

### 16.1,2 Structure and Unique Properties of Benzene

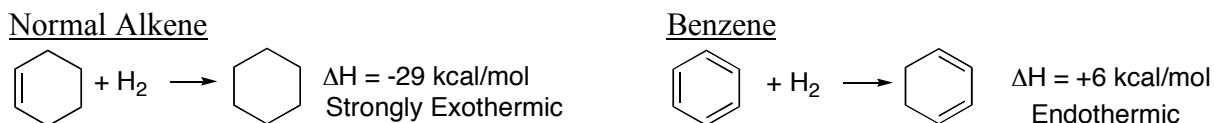


#### Facts to Accommodate

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

	H <sub>2</sub> /Pt	Br <sub>2</sub>	HBr	BH <sub>3</sub>	Hg(OAc) <sub>2</sub> /H <sub>2</sub> O	Etc.
<b>D</b>	Reacts	Reacts	Reacts	Reacts	Reacts	
<b>A</b>	No Reaction	No Reaction	No Reaction	No Reaction	No Reaction	

#### Hydrogenation: Measurement Tests for the Extraordinary Stability of Benzene



- 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 its conjugation

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

#### 1. Some different pictures of benzene

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

**2. Notes on Pictures and Structural Features**

1. All 6 carbons are  $sp^2$ , with one p orbital each
2.  $120^\circ$  angles, so all 6 carbons and each of their attached hydrogens are all co-planar.
3. Perfectly flat.
4. Perfect  $120^\circ$  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: 1.54 Å	C=C: 1.34 Å	Benzene CC: 1.39 Å
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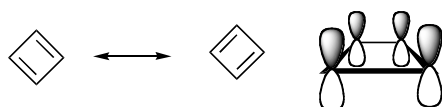
- “1.5” bonds, as we see from resonance.

8.  $6 \pi$  -electrons are delocalized throughout the ring.

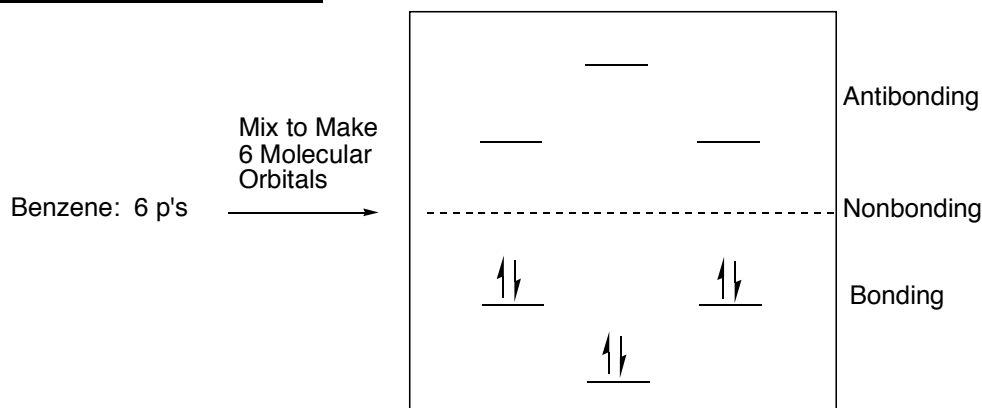
- Complete racetrack

9. Resonance delocalization, stabilization

10. Note: not all “ $\pi$  racetracks” are stabilized



No extra stability  
Actually somewhat destabilized

**3. Molecular Orbital for Benzene**

- 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:** For a **complete ring** of  **$sp^2$  centers**,

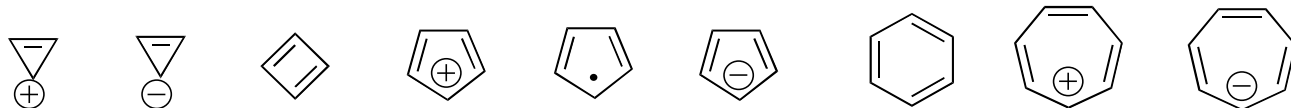
1. Draw the ring/polygon with a vertex down, basically inside what would be a circle
2. Each apex represents a molecular orbital
3. A horizontal line through the middle of the ring provides the non-bonding reference point
4. Populate the MO's as needed depending on how many  $\pi$ -electrons are available

**Molecular Orbital Rules for a cyclic  $\pi$ -system:**

1. If all and only bonding molecular orbitals are occupied  $\rightarrow$  good (“aromatic”)
2. If any nonbonding or antibonding MO's are occupied, or if any bonding MO's are not completely occupied  $\rightarrow$  bad, poor stability (“antiaromatic”)
  - Below nonbonding line  $\rightarrow$  bonding
  - Above nonbonding line  $\rightarrow$  antibonding
  - On nonbonding line  $\rightarrow$  nonbonding

Practice Problem

1. Draw the MO's for 3-, 4-, 5-, and 6-membered cyclic  $\pi$  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

16.5,6, 7 Aromatic, Antiaromatic, Nonaromatic. **Huckel's Rule:** For a **planar, continuous ring** of **p-orbitals**, ( $sp^2$  all around):

- If the number of  $\pi$ -electrons = 2,6,10 etc. ( $4N + 2$ )  $\rightarrow$  AROMATIC, STABILIZED
- If the number of  $\pi$ -electrons = 4,8,12 etc. ( $4N$ )  $\rightarrow$  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

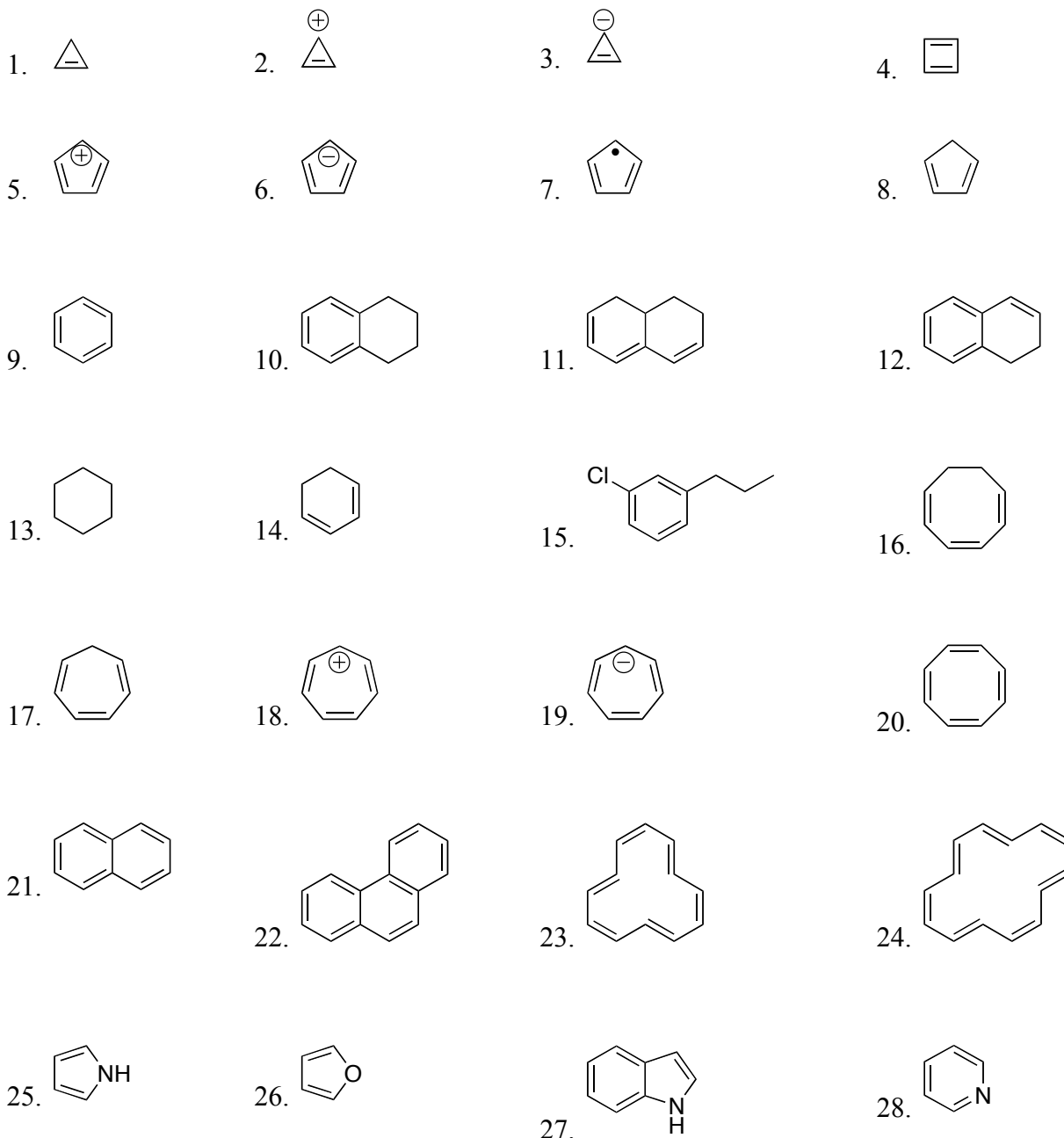
**Practice Problems: Classify each of the following as Aromatic (circle them) or not. For those that aren't, are there any that are Antiaromatic? (square them)**

Keys:

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

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

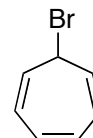
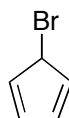
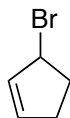
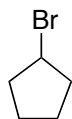
1. Lacks cyclic  $sp^2$  ring
2. Lacks Huckel's rule electron count



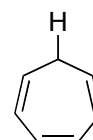
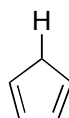
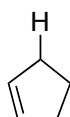
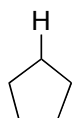
## 16.8 Aromatic Ions

3 common, important Aromatic Ions

Problem 1: The following substrates have widely differing reactivity toward **H<sub>2</sub>O solvolysis**. (The fastest is more than a million times faster than 2<sup>nd</sup> 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 **acidity**. ( $10^{-20}$ ,  $10^{-42}$ ,  $10^{-50}$ ,  $10^{-56}$ )  
Key:

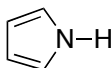
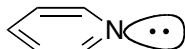


## 15.2 Heterocyclic Aromatics. Memorize 3.

**Pyridine**

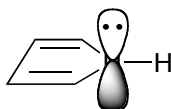
N-hybridization:  $sp^2$   
N-lone-pair:  $sp^2$   
N-basicity: reasonably normal

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

**Pyrrole**

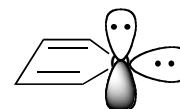
N-hybridization:  $sp^2$   
N-lone-pair: p  
N-basicity: Nonbasic

The lone pair is used in the  $\pi$ -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  $\pi$ -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.



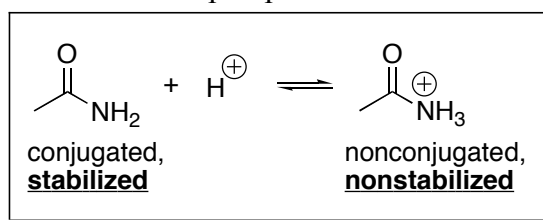
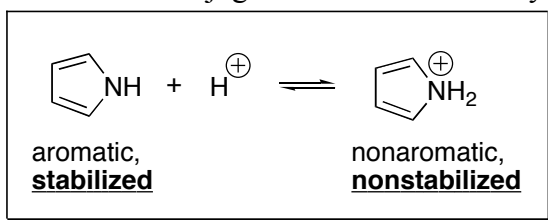
Nitrogens: Atom hybridization, Lone-Pair hybridization, and Basicity

- 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:  $sp^3 > sp^2 \gg p$

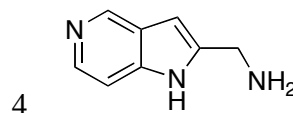
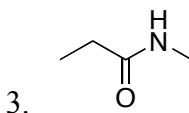
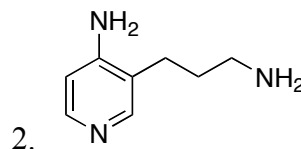
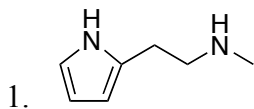
Situations	N-Atom	N-Lone Pair	N-Basicity
1. Isolated	$sp^3$	$sp^3$	Normal
2. Double Bonded	$sp^2$	$sp^2$	Normal (a little below, but not much)
3. Conjugated (not itself double bonded, but next to a double bond)	$sp^2$	p	Nonbasic

Why are p-lone pairs so much less basic?

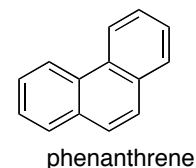
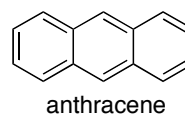
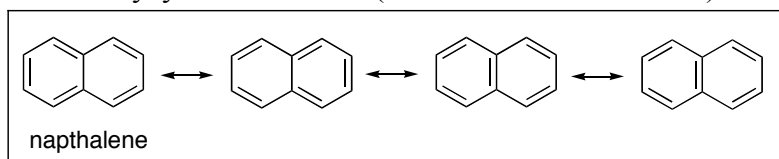
- Because conjugation/aromatic stability in the reactant is lost upon protonation.

**Problem:** For each nitrogen, classify:

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

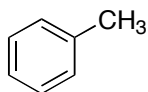
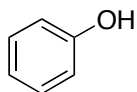
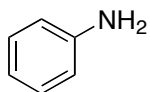
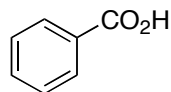
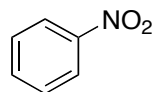
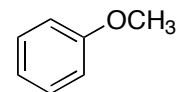


## 16.10 Polycyclic Aromatics (needn't memorize names)



**16.13 AROMATIC NOMENCLATURE**1. **Memorize** Special Names.

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

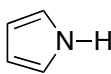
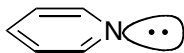
**Toluene****Phenol****Aniline****Benzoic Acid****Nitrobenzene****Anisole**

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

**Pyridine**

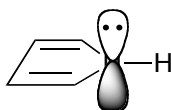
N-hybridization:  $sp^2$   
 N-lone-pair:  $sp^2$   
 N-basicity: reasonably normal

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

**Pyrrole**

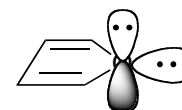
N-hybridization:  $sp^2$   
 N-lone-pair: p  
 N-basicity: Nonbasic

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

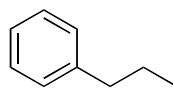
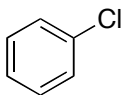
**Furan**

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

The p lone pair is used in the  $\pi$ -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

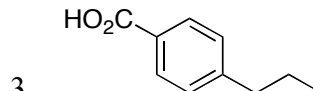
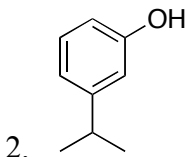
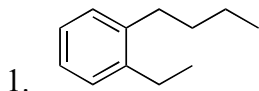


3. Di- or polysubstituted aromatics

- 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.

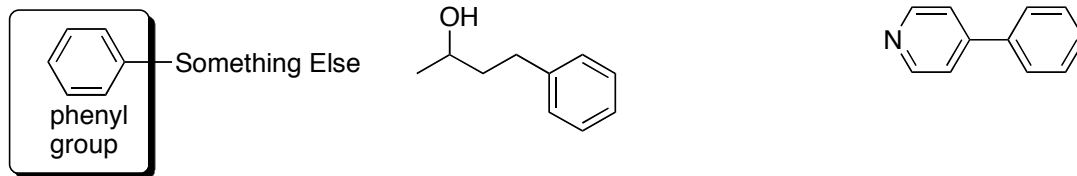
- b. Special Terms:

- "ortho" or o-                      1,2 relationship
- "meta" or m-                      1,3 relationship
- "para" or p-                      1,4 relationship

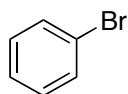


4. As a substituent, benzene is named "phenyl"

- "phenyl" =  $C_6H_5-$  = a benzene group attached to something else, named as a substituent

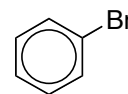


5. Three Shorthands for phenyl

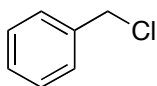


PhBr

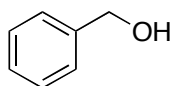
$C_6H_5Br$



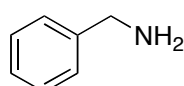
6. "Benzyl" =  $PhCH_2$



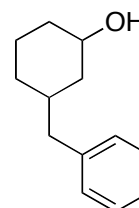
benzyl  
chloride



benzyl  
alcohol



benzyl  
amine

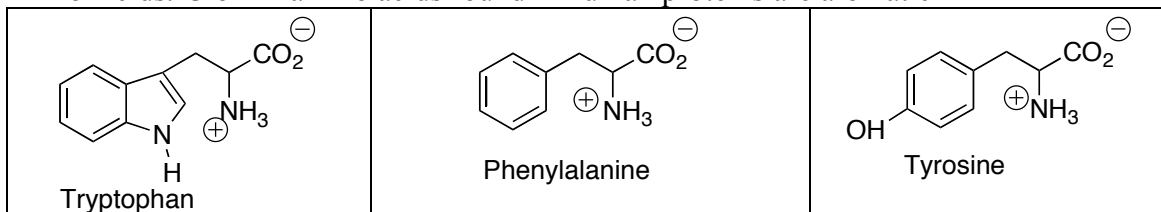


3-benzylcyclohexanol



Some Complex Aromatics in Nature
----------------------------------

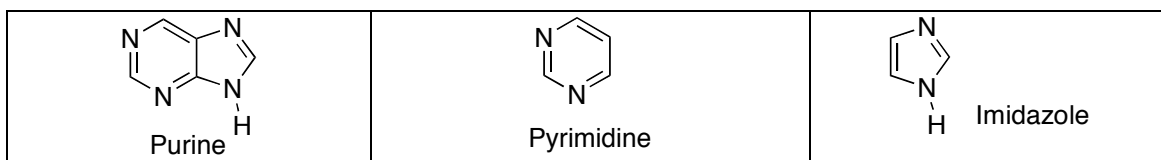
1. Amino Acids. 3 of 22 amino acids found in human proteins are aromatic



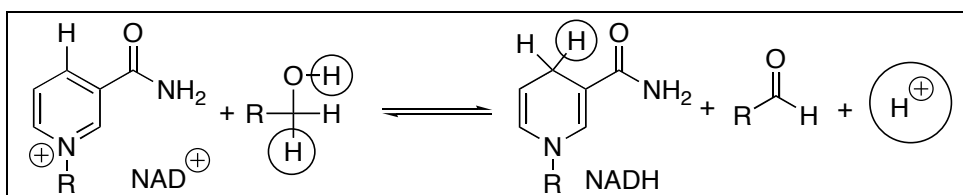
"Essential"-have to eat them, since body can't make the benzene rings

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.



3. Nitrogen Bases: Purine, Pyrimidine, Imidazole. Nicotinamide Adenine Dinucleotide (NAD<sup>+</sup>) 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!

