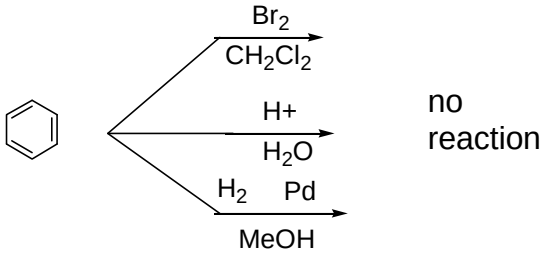
Benzene- highly unsaturated compound (4 degrees of unsaturation).

Resonance structures are also called Kekule' structures:  or  or 

Benzene is an **aromatic** compound- low H/C ratio and has a fragrance

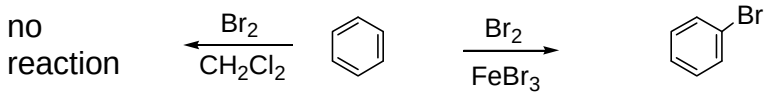
Benzene does not behave like an unsaturated compound:

does not add Br_2 or [ox] with $KMnO_4$
does not add water
does not add H_2 except under forcing conditions



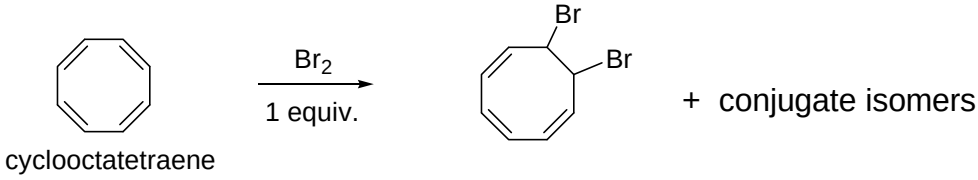
Also $KMnO_4$ does not react with benzene.

Benzene <u>does react</u> with Br_2 in the presence of a catalyst but **gives substitution, not addition**



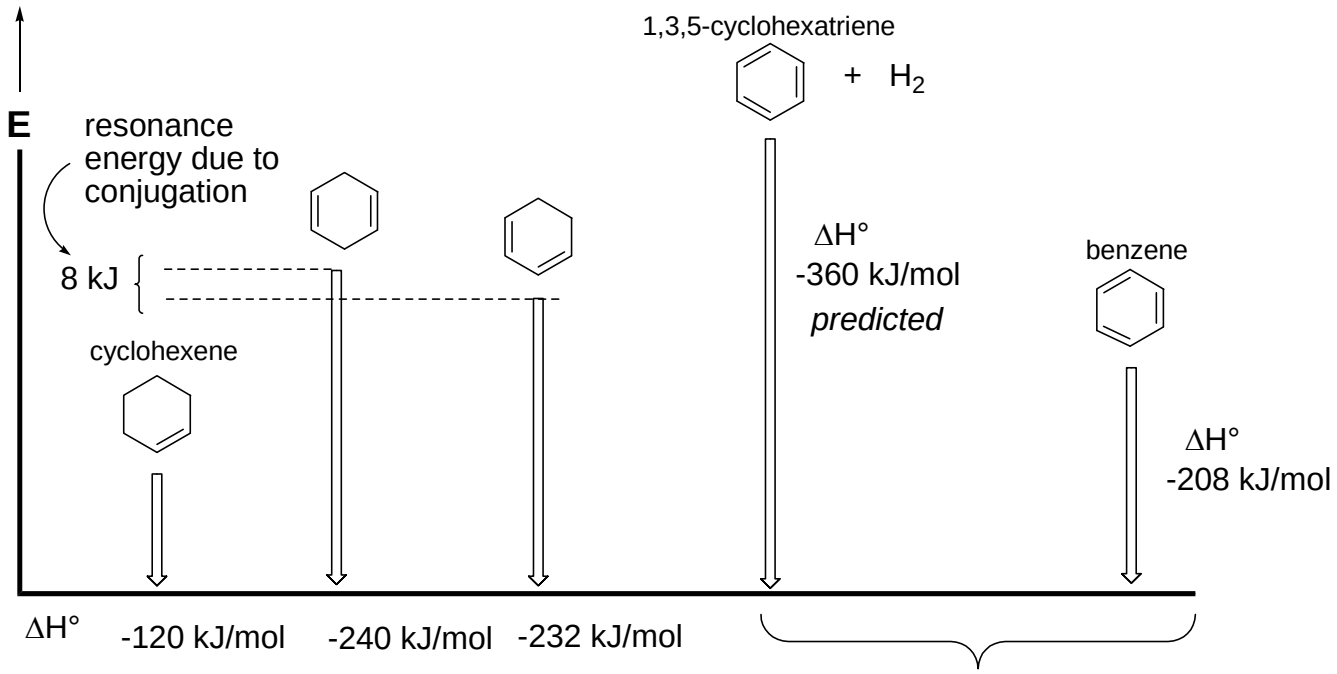
Tendency to undergo substitution instead of addition is another characteristic of aromatic compounds.

Cyclooctatetraene adds Br_2 readily and it reacts with $KMnO_4$
cyclooctatetraene is not aromatic



Alternating single and double bonds in a ring is not necessarily aromatic.

Stability of Benzene- from heats of hydrogenation



Resonance energy = (-360 kJ) - (-208 kJ) = **152 kJ**

Resonance energy- difference between energy released for hydrogenation of benzene and the predicted value for hydrogenation of 1,3,5 cyclohexatriene

Resonance approach and M.O. approach

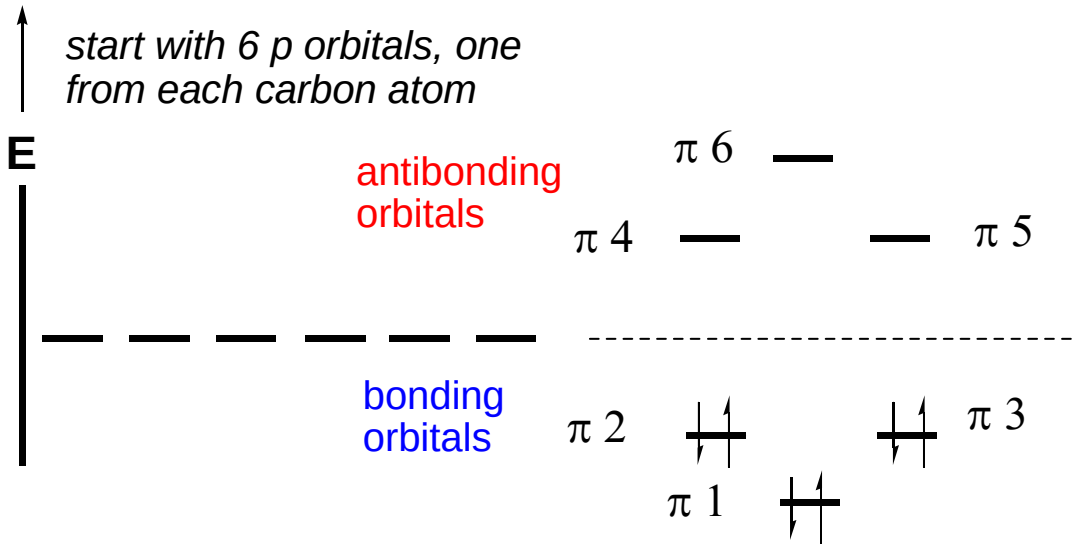
- **Resonance theory** shows that benzene has two Lewis structures
  double-headed arrow is used (not equilibrium arrows!)

More than one equivalent resonance structure implies resonance stabilization.

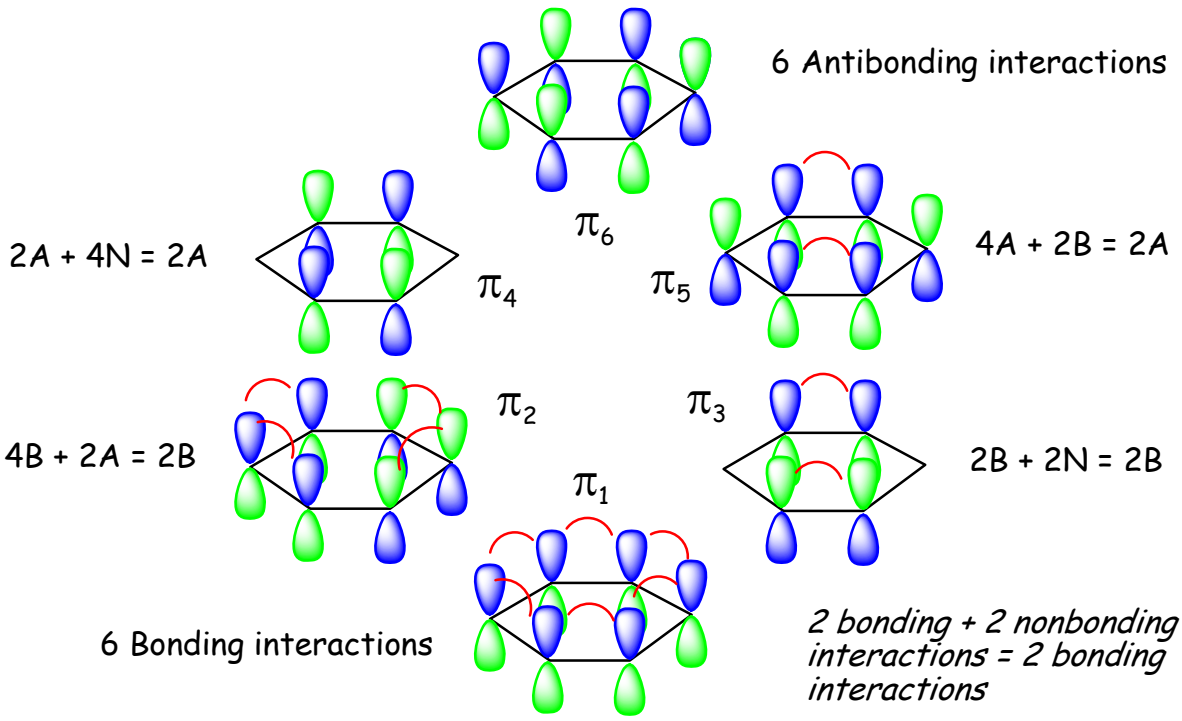
C-C bond length is 1.39 angstroms
Approximately halfway between C-C single bond (1.47) and C=C bond (1.33)

➢ **M.O Approach** *… we combine p orbitals …*

Each carbon is sp^2 hybridized so the *C-C-C* bond angles are all **120°**
Therefore, benzene is **planar**.



Notice from the energy diagram- all the bonding MO are filled: this is called a **closed bonding shell system**.



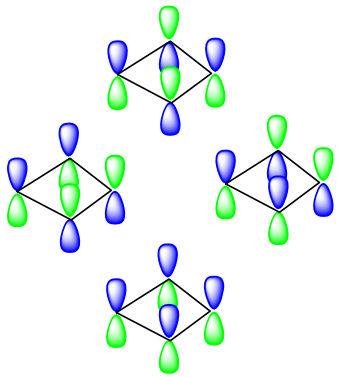
Aromatic compounds meet these criterion:

1. **must be cyclic with conjugated pi bonds**
2. **each atom in ring must have unhybridized p orbital (sp2 or sp)**
3. **p orbitals must overlap to form continuous ring of orbitals**
4. **delocalization of pi electrons must lower the energy of the system**
5. **Huckel's Rule must be met**

If delocalization over the ring increases the energy, then the system is antiaromatic (rule #4)

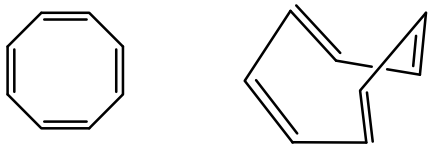
Huckel's Rule: 4n + 2 rule (n = integer 1, 2, 3, etc.)

(4N + 2) = **aromatic (benzene)** **[n = number of π e's in ring system]**
(4N) = **antiaromatic (cyclobutadiene MO diagram)**



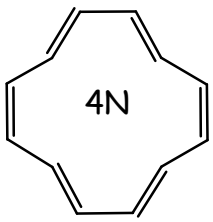
A cyclic compound that does not have continuous overlap is **nonaromatic**.

Cyclooctatetraene- not a planar ring system- nonaromatic

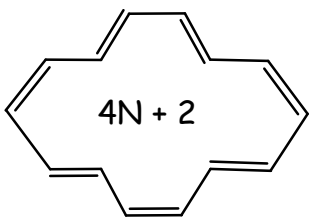


Planar rings with 2, 6, 10, 14 delocalized electrons should be aromatic according to the Huckel numbers.

[12] annulene

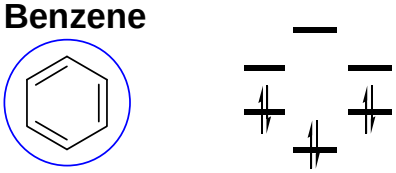


[14] annulene



Frost Circles- polygon rule- M.O. diagram has same shape as the cyclic structure that we draw …

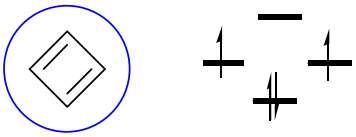
Benzene



closed bonding shell

Benzene is aromatic

Cyclobutadiene

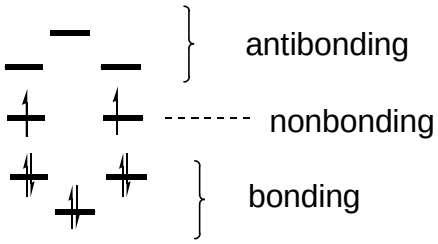


nonbonding orbitals are 1/2 filled

not a closed shell system

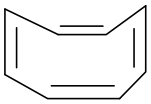
Cyclobutadiene is not aromatic

Cyclooctatetraene



not a closed shell system

Also, this molecule is not planar



tub conformation

Bond lengths for cyclooctatetraene: 1.48 angstroms and 1.34 angstroms (single and double bond lengths)

Annulenes- cyclic structure with alternating single and double bonds.

These are conjugated systems but not necessarily aromatic systems.

Aromaticity determined using Huckel's number and planarity requirement.

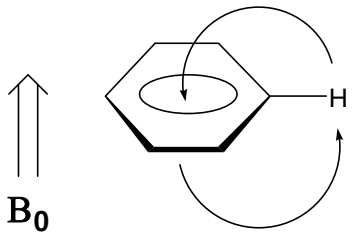
[14]Annulene and [18] Annulene are expected to be aromatic and they are; both have a Huckel number of pi electrons.

[12]Annulene and [16]Annulene are not aromatic since these are not 4n+2

[10]Annulene does have a Huckel number but it is not planar.

NMR Spectrosopy- Evidence for Aromaticity

NMR confirms delocalization of aromatic systems.
Benzene shows a singlet at 7.27 ppm indicating that all H's are equivalent.



Circulating pi electrons generate a ring current.

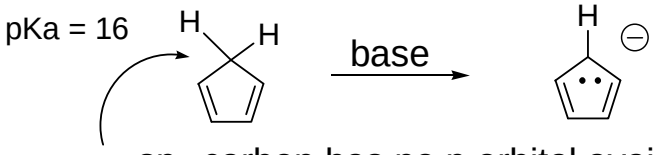
Induced magnetic field adds to the applied field at the position of the protons.

Protons resonate at a lower magnetic field strength; signal is shifted **downfield.**

Deshielding is physical evidence for aromaticity.

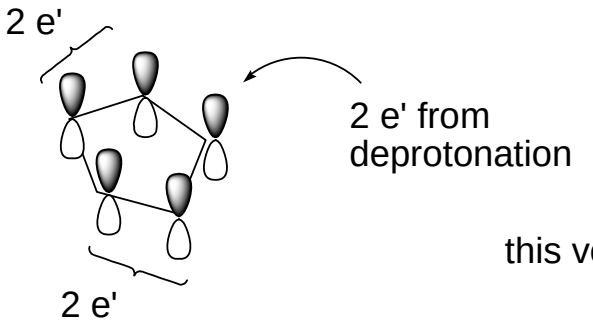
Aromatic Ions

Cyclopentadienyl anion

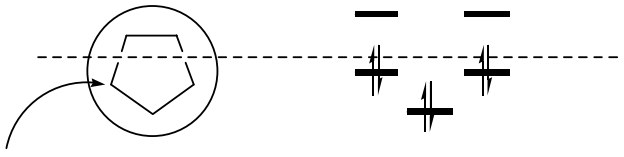


Cyclopentadienyl anion

sp_3 carbon has no p orbital available for delocalization around the ring.

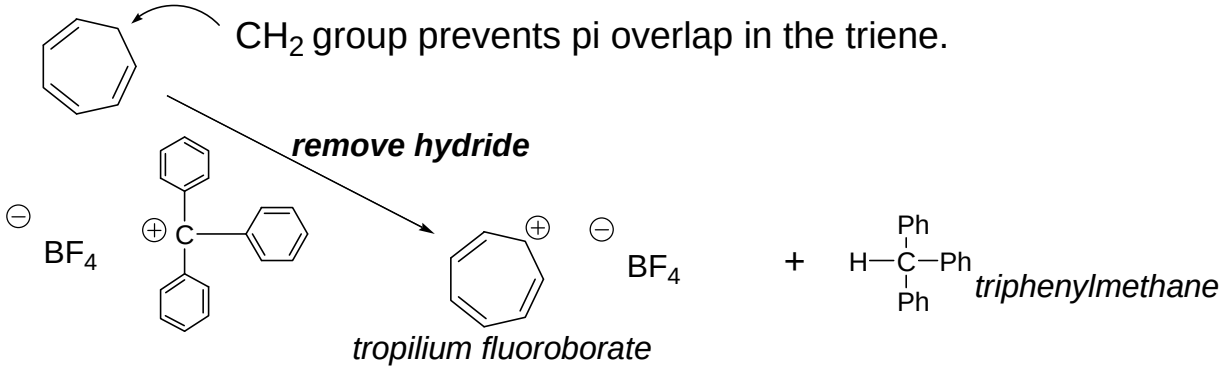


2 e' from deprotonation



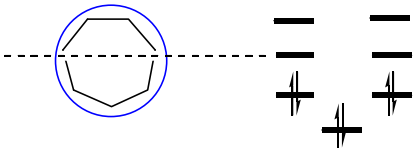
this vertex is below the half-way line

Cycloheptatrienyl cation



Treatment with trityl cation facilitates loss of hydride to give the **tropilium ion.**

Tropilium ion

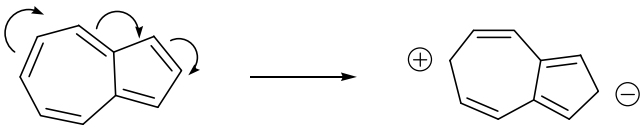


6 pi electrons is a Huckel number and it has a closed bonding shell system.

NMR shows tropilium ion and cyclopentadienyl anion to be aromatic.

Other Aromatic Compounds

Azulene



non-benzenoid aromatic compound

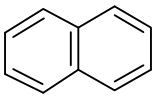
tropilium ion and cyclopentadienyl anion

Resonance form explains the large dipole moment.

Benzenoid aromatics

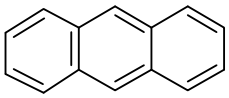
Huckel numbers:

10 e's



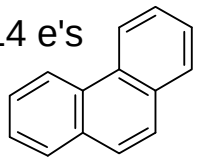
naphthalene

14 e's



anthracene

14 e's

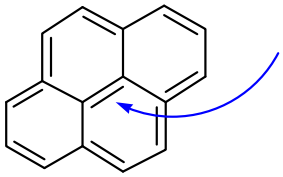


phenanthrene

Remember [10] Annulene, even though it has a Huckel number, is not aromatic because it is not planar.

Pyrene has 16 pi electrons, which is not a Huckel number, but …

pyrene

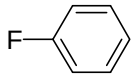


Ignore the internal double bond and we get [14]Annulene which is a Huckel number.

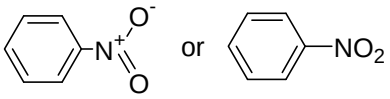
Huckel Rule is for monocyclic systems, so if we ignore the internal olefin, **NMR confirms aromaticity.**

Nomenclature

- monosubstituted- name as a benzene derivative

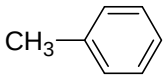


fluorobenzene

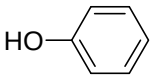


nitrobenzene

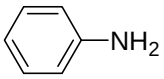
memorize these common monosubstituted benzene compounds:



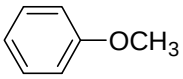
toluene



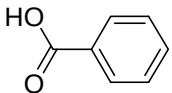
phenol



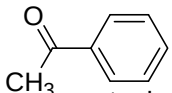
aniline



anisole

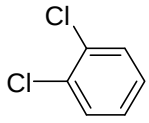


benzoic acid

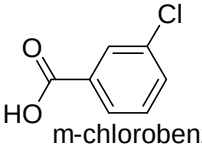


acetophenone

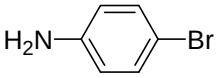
- disubstituted- ortho, meta and para prefixes
  (1,2 1,3 1,4 o, m, p respectively)



o-dichlorobenzene

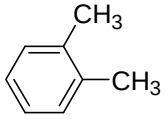


m-chlorobenzoic acid

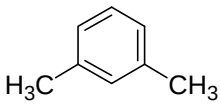


p-bromoaniline

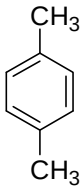
memorize the isomers of dimethylbenzene:



o-xylene

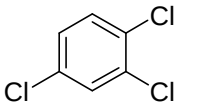


m-xylene



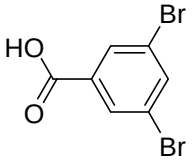
p-xylene

- 3 groups or more- using numbering system



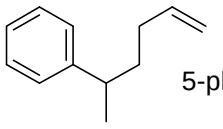
not 1,3,4

1,2,4-trichlorobenzene

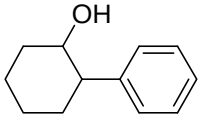


3,5-dibromobenzoic acid

- As a derivative- use prefix **phenyl**



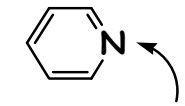
5-phenyl-1-hexene



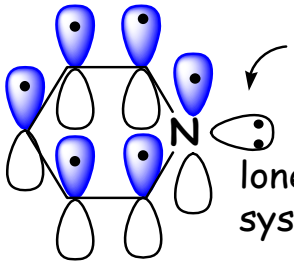
2-phenylcyclohexanol

Heterocyclic Aromatic Compounds

pyridine



sp^2 hybridized



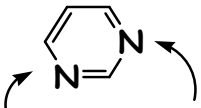
unhybridized p orbital is orthogonal to ring

lone pair is not part of aromatic system- lone pair makes it a base

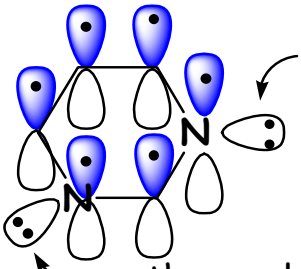
pyridine is a weak base

---

pyrimidine



sp^2 hybridized



unhybridized p orbital is orthogonal to ring

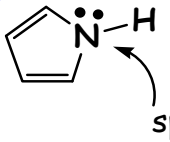
both N are basic sites

pyrimidine is a weak base

orthogonal p orbital

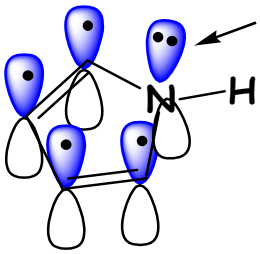
---

pyrrole



sp^2

pyrrole is not basic



lone pair on N is part of aromatic system

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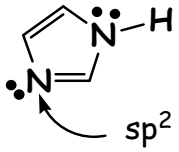
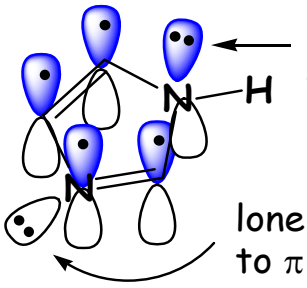
imidazole



sp^2

imidazole is basic



lone pair on this N is part of aromatic system

lone pair on this N is orthogonal to π system and is the basic site

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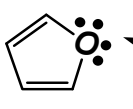
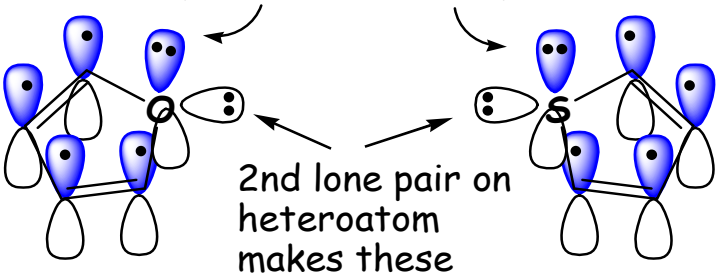
one lone pair on heteroatom is part of aromatic system

furan

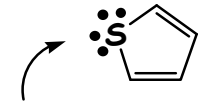


sp^2



2nd lone pair on heteroatom makes these basic compounds

thiophene



sp^2