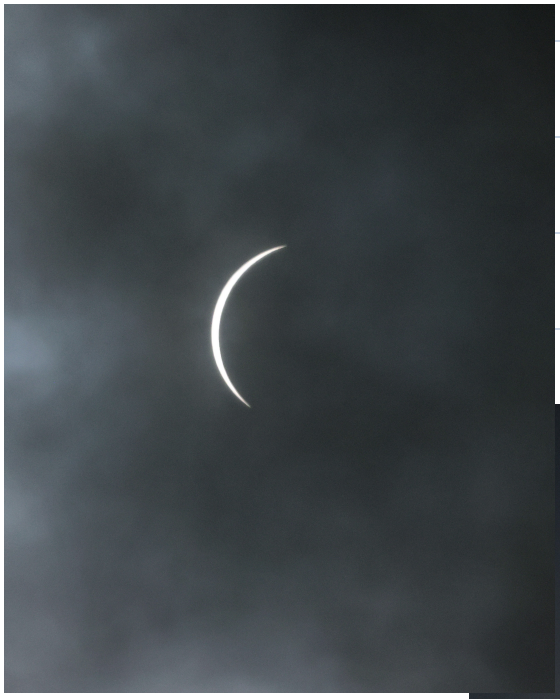
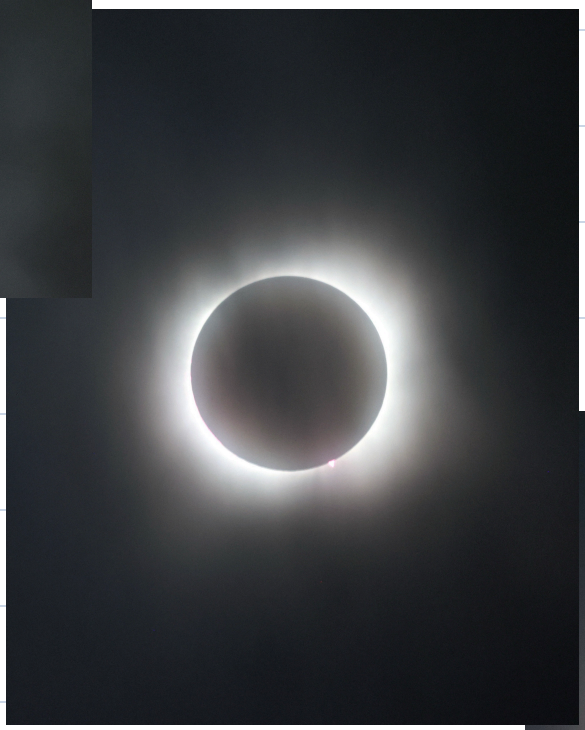
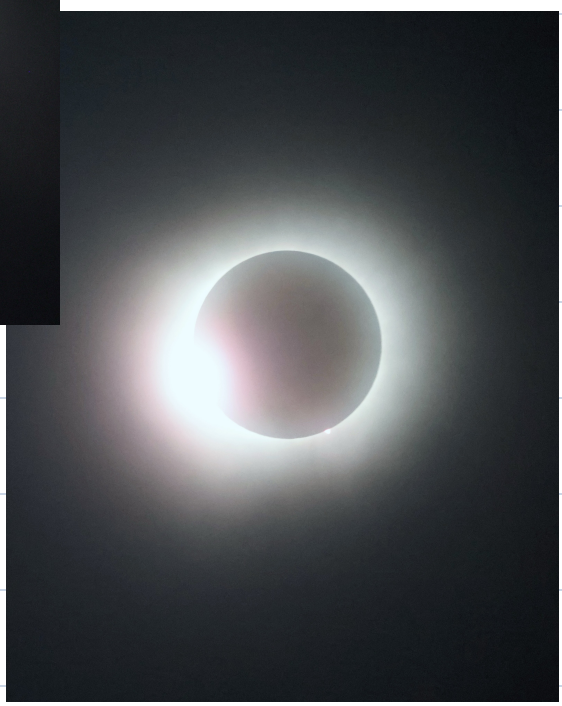






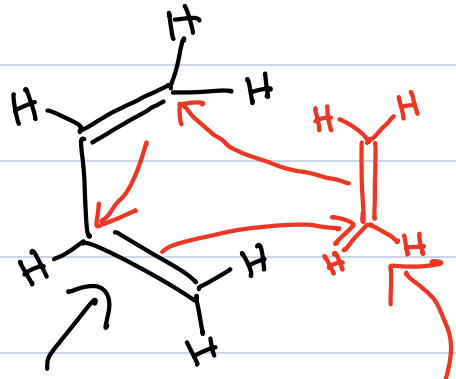
Otto!

↓

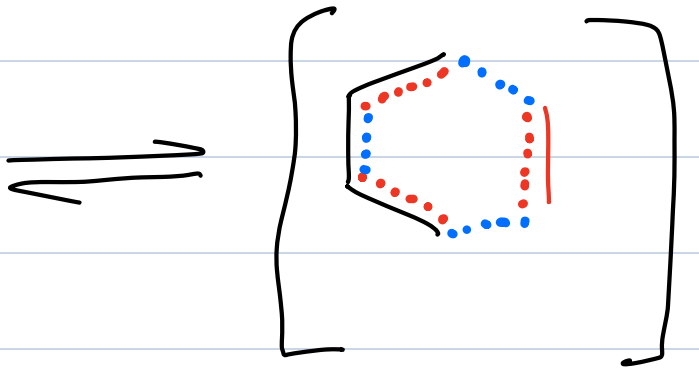
Diels-Alder Reaction

..... bonds being broken

..... bonds forming



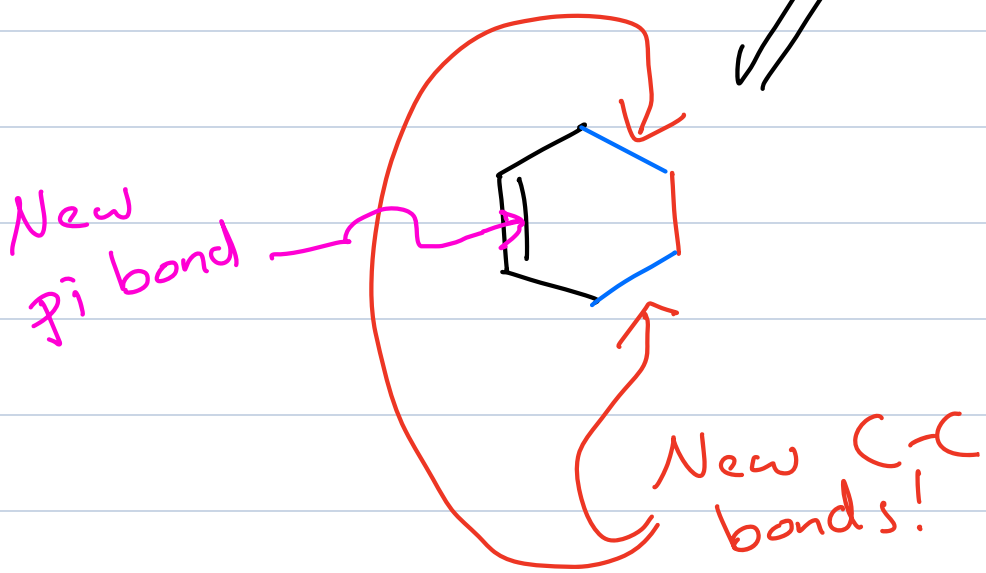
s-cis butadiene



‡

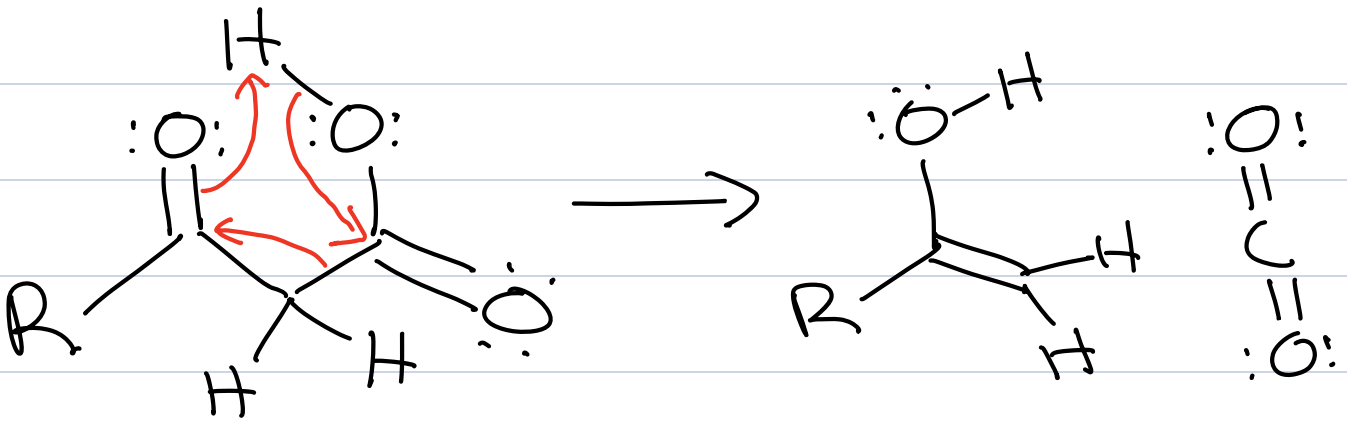
3 π bonds being made or used – all ring atoms are sp^2 hybridized to begin with

"dienophile"



The above reaction gives a poor yield and was used only to illustrate the process → there are many, many known examples of Diels-Alder reactions

You have seen one other example of this type of reaction:



3 π bonds being broken or formed in the transition state → very stable transition state!

Transition state has aromatic character!

That is why β-keto acids and β-diacids decarboxylate when you heat them!

The Golden Rules of Organic Chemistry

Your goal should be to understand, not memorize, the material presented in your organic chemistry course. The following principles should be learned as you begin your study of organic chemistry, then used as a solid foundation for building your understanding throughout the course. These simple ideas explain a great deal about the structures and properties of organic molecules, as well as the characteristic ways in which they react. Thoroughly understanding the following three key principles and related ideas will allow you to develop an intuitive feel for organic chemistry that avoids the necessity of resorting to the far less effective use of extensive memorization.

A. Predicting Structure and Bonding

1. In most stable molecules, all the atoms will have filled valence shells.

2. Five- and six-membered rings are the most stable.

3. There are two possible arrangements of four different groups around a tetrahedral atom.

B. Predicting Stability and Properties

4. The most important question in organic chemistry is "Where are the electrons?"

5. Delocalization of charge over a larger area is stabilizing.

6. Delocalization of unpaired electron density over a larger area is stabilizing.

7. Delocalization of pi electron density over a larger area is stabilizing.

C. Predicting Reactions

8. Reactions will occur if the products are more stable than the reactants and the energy barrier is low enough.

9. Functional groups react the same in different molecules.

10. A reaction mechanism describes the sequence of steps occurring during a reaction.

11. Most bond-making steps in reaction mechanisms involve nucleophiles reacting with electrophiles.

All conjugated systems are extra stable, but there is a certain class that is particularly stable:

Aromatic Rings ⟹ Hückels Rules (definition)

1) All ring atoms are sp^2 hybridized (have a 2p orbital)

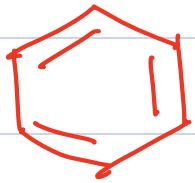
2) Ring is flat

3) Monocyclic

4) 2, 6, 10, 14, 20, 24.... π electrons

$4n+2$ π electrons

$n = 0, 1, 2, 3, 4, 5....$



Benzene

The π electrons of benzene are much less reactive than normal alkenes → benzene only reacts under harsh conditions

All bonds are the same length!

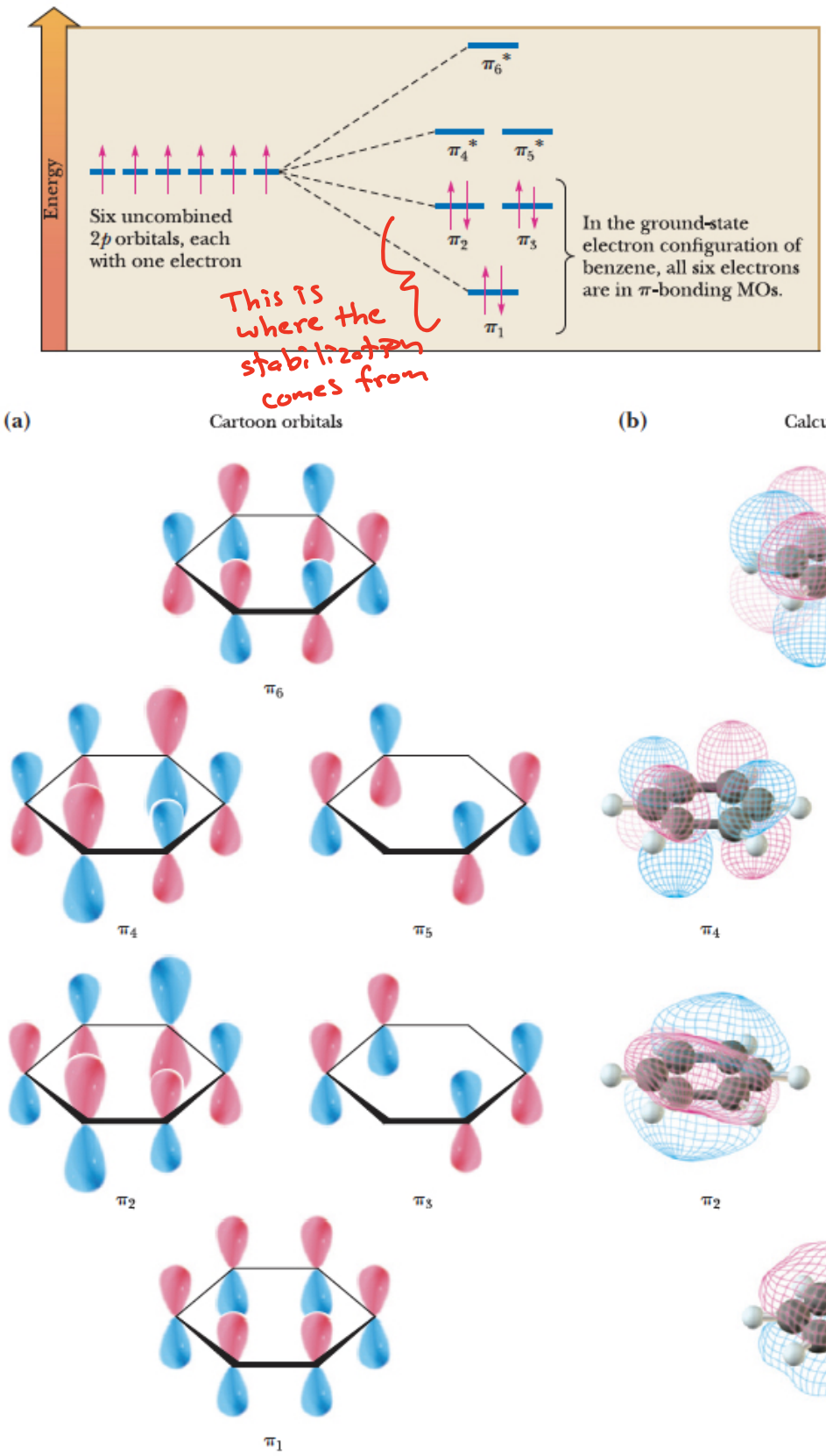


FIGURE 21.2 The molecular orbital representation of the π bonding in benzene.

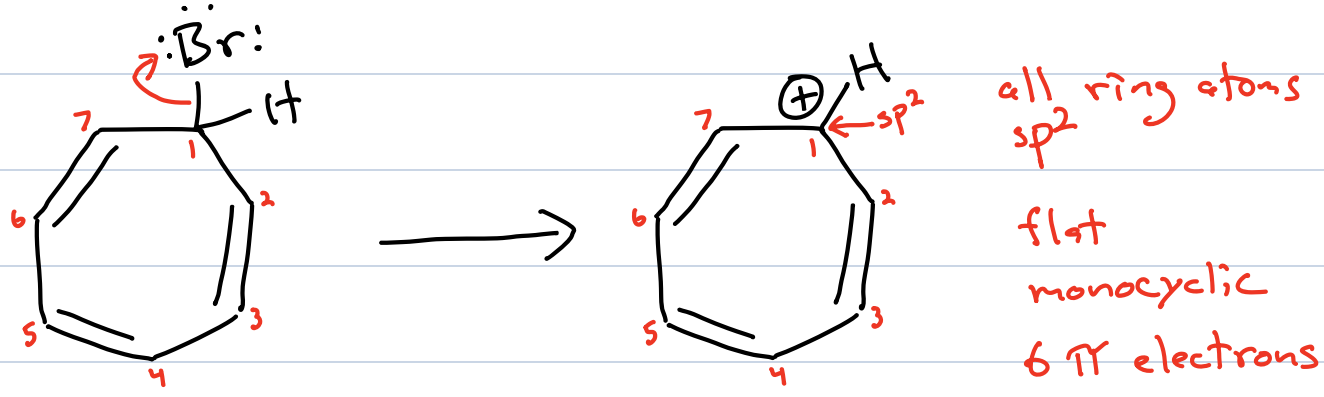
FIGURE 21.3 Orbitals for the π system of benzene. (a) Cartoon representations of the six calculated orbitals that chemists routinely draw. These pictures accentuate the fact that various combinations of parallel $2p$ orbitals lead to the π system of benzene. (b) Calculated orbitals. The three lowest in energy are occupied with electrons (see Figure 21.2). The lowest of these orbitals is the image most chemists use for the π system of benzene: a torus of electron density above and below the ring.

Two Important Consequences of Aromaticity

1) Aromaticity stabilizes ions → anions and cations

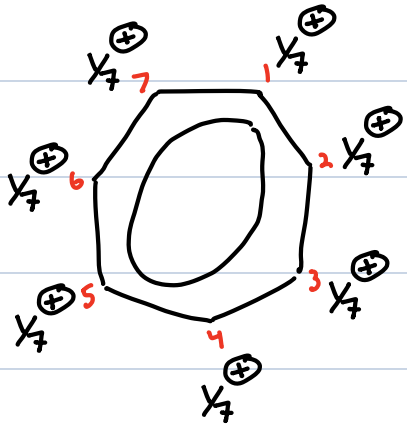
2) Atoms in molecules will be sp^2 if that produces aromaticity

Tropylium Ion



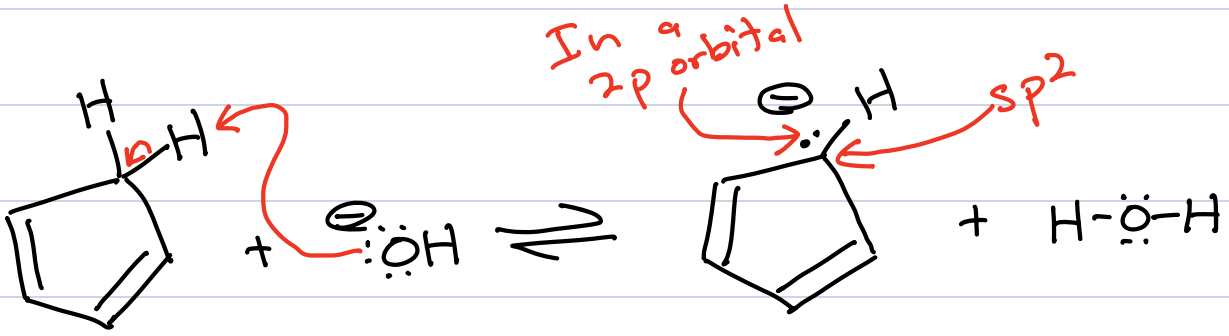
Aromatic!

Super stable cation



All atoms are equivalent → 7 equal contributing structures!

Cyclopentadienyl Anion

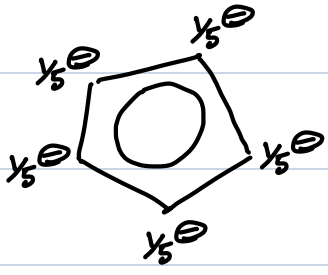


$pK_a = 16$

Aromatic!

Super stable anion

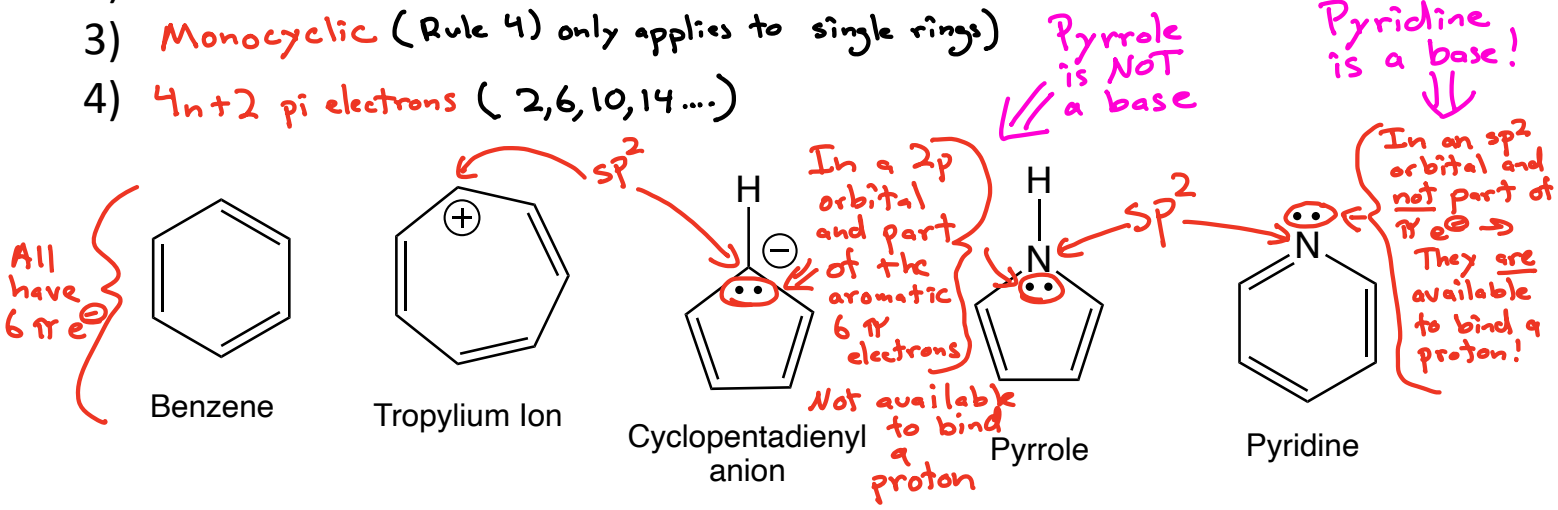
- all ring atoms sp^2
- flat
- monocyclic
- 6 π electrons
  - 2 electrons of lone pair
  - 4 electrons in the 2 π bonds

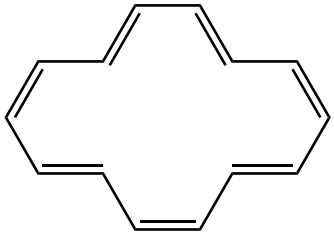


All atoms are equivalent → 5 equal contributing structures!

Hückel's Aromaticity Criteria

1) All ring atoms are sp^2 (they have a 2p orbital)
2) Flat (so the 2p orbitals overlap)
3) Monocyclic (Rule 4) only applies to single rings)
4) 4n+2 pi electrons (2, 6, 10, 14 ....)





Annulene

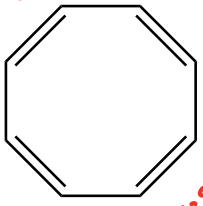
14 π electrons

4 π electrons

Not a stable molecule

Cyclobutadiene

8 π electrons



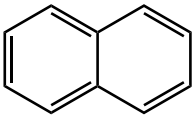
Folds so 2p orbitals do not overlap and avoids antiaromaticity

Cyclooctatetraene

Antiaromatic → These are much less stable than predicted as simple alkenes

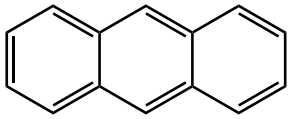
All fused benzene compounds are aromatic no matter the number of π electrons → Not monocyclic so Hückel's 4n+2 rule does not apply!

10 π electrons



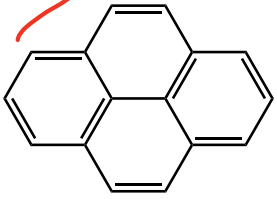
Naphtalene

14 π electrons



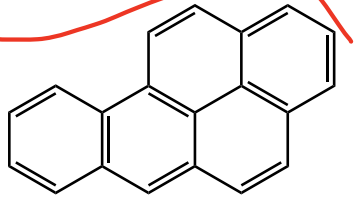
Anthracene

Still aromatic!



Pyrene

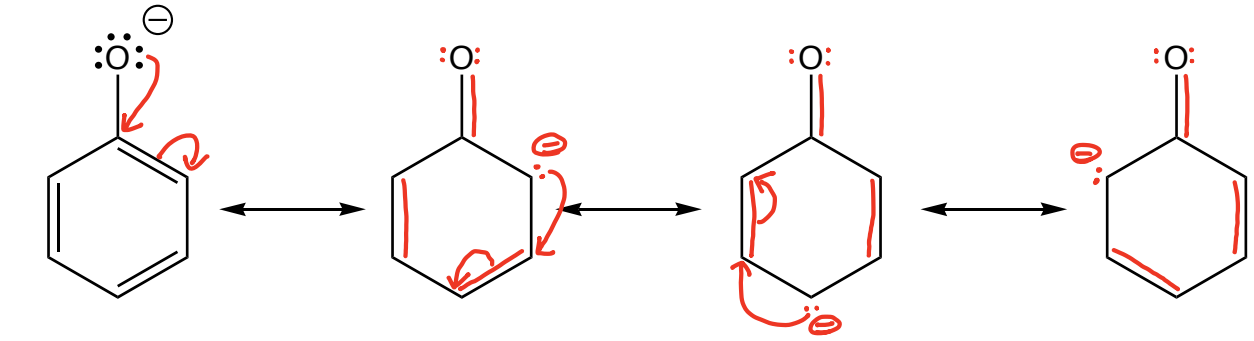
16 π electrons!



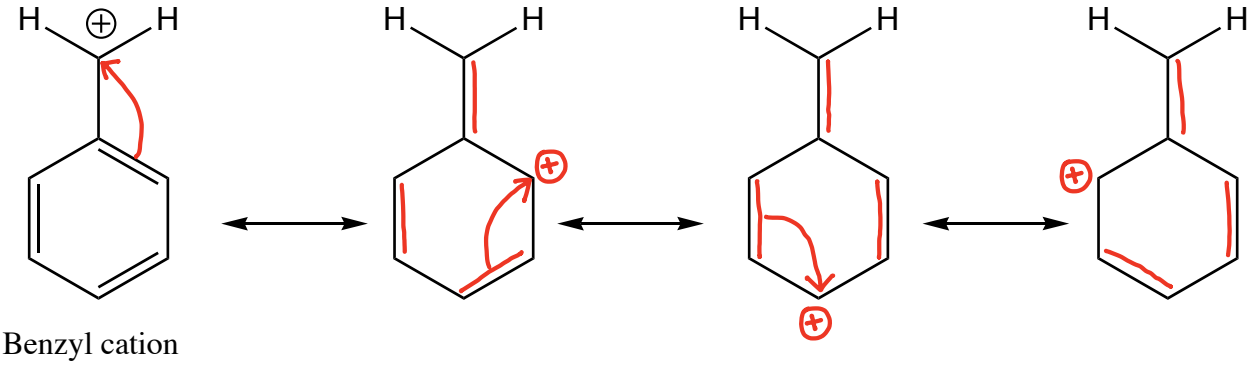
Benzo[α]pyrene

20 π electrons

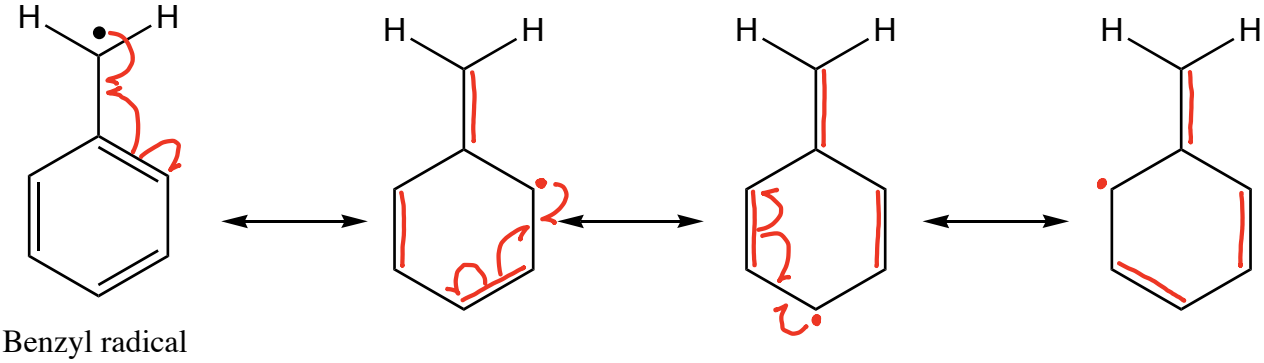
Aromatic resonance stabilization of charged species



Phenoxide anion



Benzyl cation



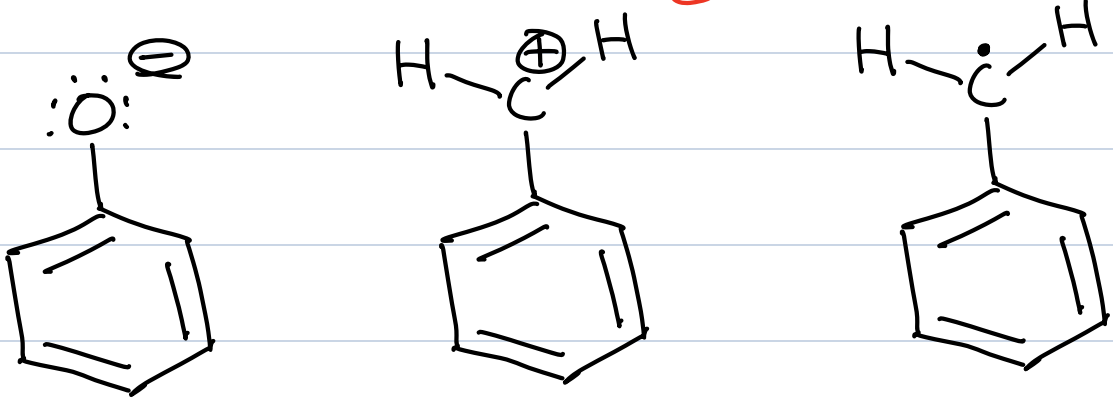
Benzyl radical

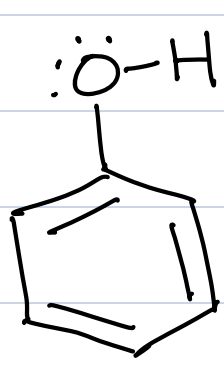
Important takeaways from the contributing structures

1) Benzene rings stabilize anions, cations and radicals (Golden Rules 5, 6 and 7)

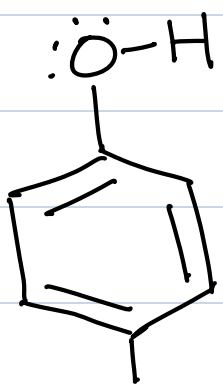
2) Molecules can have electrons on an atom outside the ring delocalized into the π system and the "extra" electrons do not count against the $4n+2$ number of π electrons

Summary → Molecules like those below are all highly stabilized by delocalization into the benzene ring.

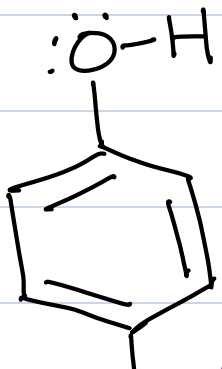




Phenol



Cl



NO_2

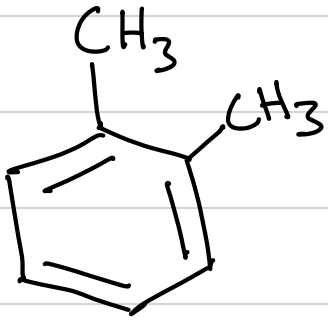
Very electron withdrawing and called a nitro group

$pK_a = 9.95$ $pK_a = 9.0$ $pK_a = 7.15$

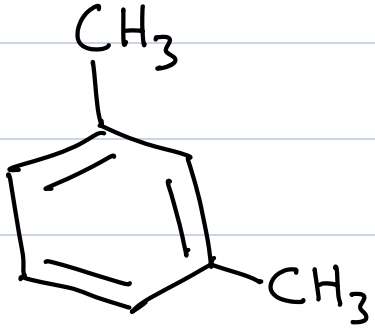
Relative acidity

Electron withdrawing groups on the ring stabilize the deprotonated anion, making OH group more acidic (Inductive effect)

Important terms



ortho



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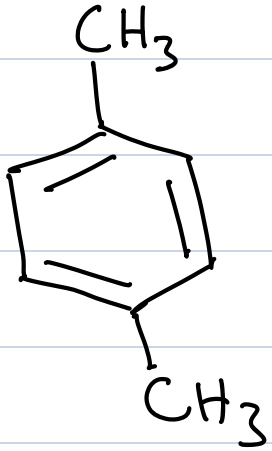

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