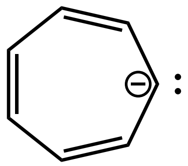
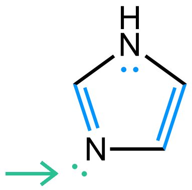
Aromaticity and Benzene Worksheet

1. Identify any aromatic species shown in the set below. For all species, determine how many **π e^-s** are present. For the aromatic species, determine the ***n* value** used in Huckel's Rule. If the system is not aromatic, explain why not.
Note: Lone pairs on heteroatoms are implied.

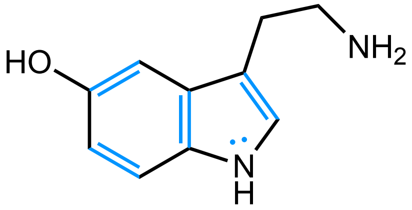


8 π e^-s
anti-aromatic
$4n + 2 \neq 8$
$4n = 8$; $n = 2$

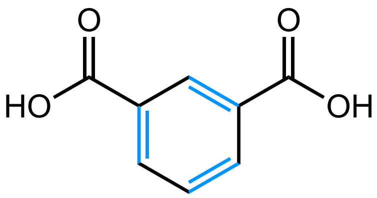
these e-'s are not in a *p* orbital



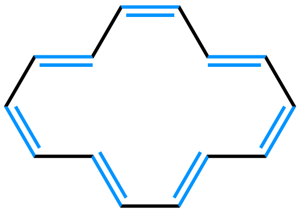
6 π e^-s
aromatic
$4n + 2 = 6$; $n = 1$



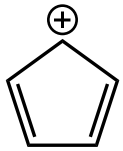
serotonin
10 π e^-s
aromatic
$4n + 2 = 10$; $n = 2$



6 π e^-s
aromatic
$4n + 2 = 6$; $n = 1$

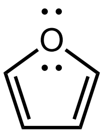


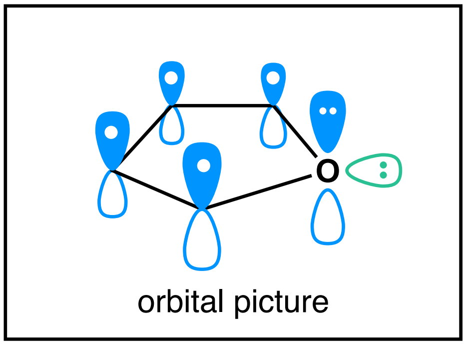
14 π e^-s
aromatic
$4n + 2 = 14$; $n = 3$



4 π e^-s
anti-aromatic
$4n + 2 \neq 4$
$4n = 4$; $n = 1$

2A. Redraw furan (shown below) in a side on view clearly showing the p-orbital overlap that creates this aromatic system. Add electrons into the orbitals to help determine the number of **π** e^-s present.





2B. What is the hybridization of the oxygen atom in furan? **sp^2**

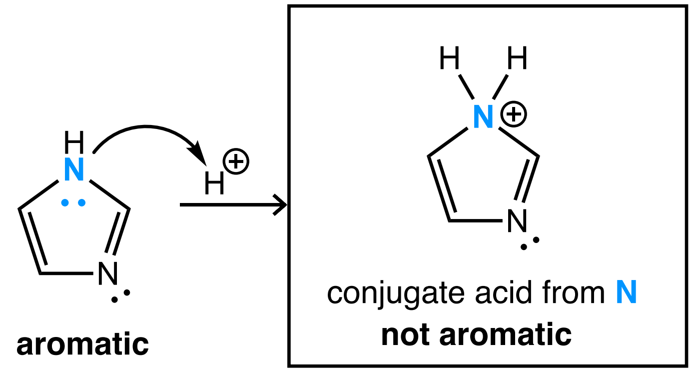
2C. Based on your answer to 2B, what orbitals are the lone pairs on oxygen in?

One lone pair of electrons exists in a ***p*-orbital** that overlaps with the other four *p*-orbitals in the cyclic system. This mandates the second lone pair exist in an **sp^2-hybridized orbital.**

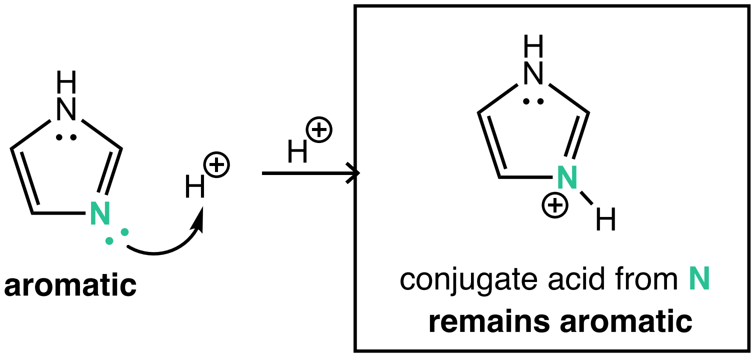
3. Let's consider how aromaticity can influence acid-base chemistry by considering imidazole, an aromatic heterocycle. Aromaticity is an example of a stabilizing effect. Remember that systems that are more stable are often, less reactive.

A. Given that imidazole has two nitrogen atoms, **draw structures for the two possible conjugate acids that can be formed.**

B. Based on your understanding of aromaticity and stability and **explain why one nitrogen atom in imidazole is actually more basic than the other.**



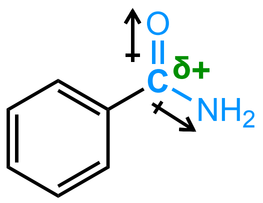
Keep in mind that from question #1, we identified this **lone pair** as part of the aromatic system. Using this lone pair would disrupt the aromatic system and is therefore less likely to happen (**less basic**).



Using the **lone pair** on nitrogen that *is* ***not*** part of the aromatic system leads to a product that is still aromatic. This pathway is more likely to take place (**more basic**).

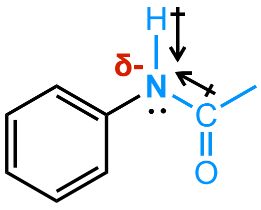
4. The connection to benzene is important to pay attention to when considering directing effects. Two amides are shown below, but notice **one is connected through a C—C bond whereas the other is connected through a C—N bond**.

A. Determine the directing effects of the group in compound **A** and compound **B**. Draw structures of the carbocation intermediates that support your prediction.



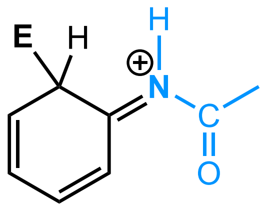
Compound **A**

δ+; *meta* director



Compound **B**

δ-; *o*/*p* director



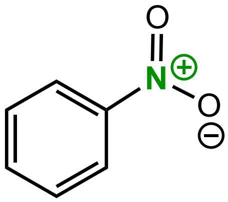
B stabilizes the carbocation intermediate after addition to the *o*- or *p*- position

Compound B is more activated since the N with a lone pair (connected to benzene) is an EDG because it can donate electrons through resonance. In compound **A**, the C=O connected to benzene is an EWG.

5. The substituted benzenes below are shown in order of increasing EAS reactivity. Explain the order.

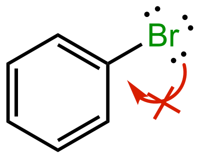
least reactive for EAS → **most reactive for EAS**

Strong EWG



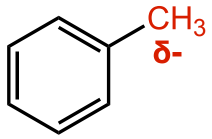
Nitro groups have a full positive charge on N, making them **strong EWGs**.

Weak EWG



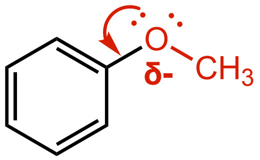
Bromine is a weak EWG. Although it has LPs (like O in OMe), they can not effectively donate to benzene due to poor orbital overlap between C and Br.

Weak EDG



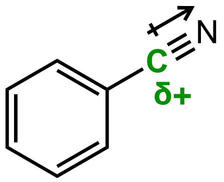
Compared to H, **R (alkyl) groups are weak EDGs** - they possess more electrons than an H atom can

Strong EDG

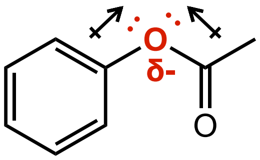


OMe has lone pairs that can effectively donate as a **strong EDG** via resonance (C and O are in the same row = similar orbital sizes)

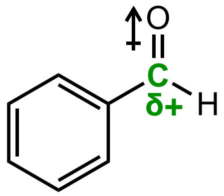
6. **Determine the directing ability** of the groups shown below for **EAS reactions**.



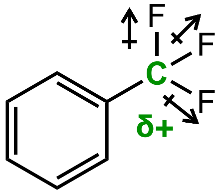
δ+; *meta* director



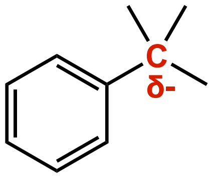
δ-; *o*/*p* director



δ+; *meta* director

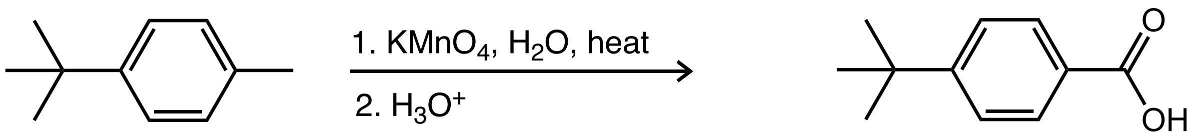


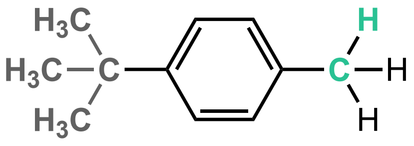
δ+; *meta* director



δ-; *o*/*p* director

7. **Explain why only one R group was oxidized** in the reaction below.



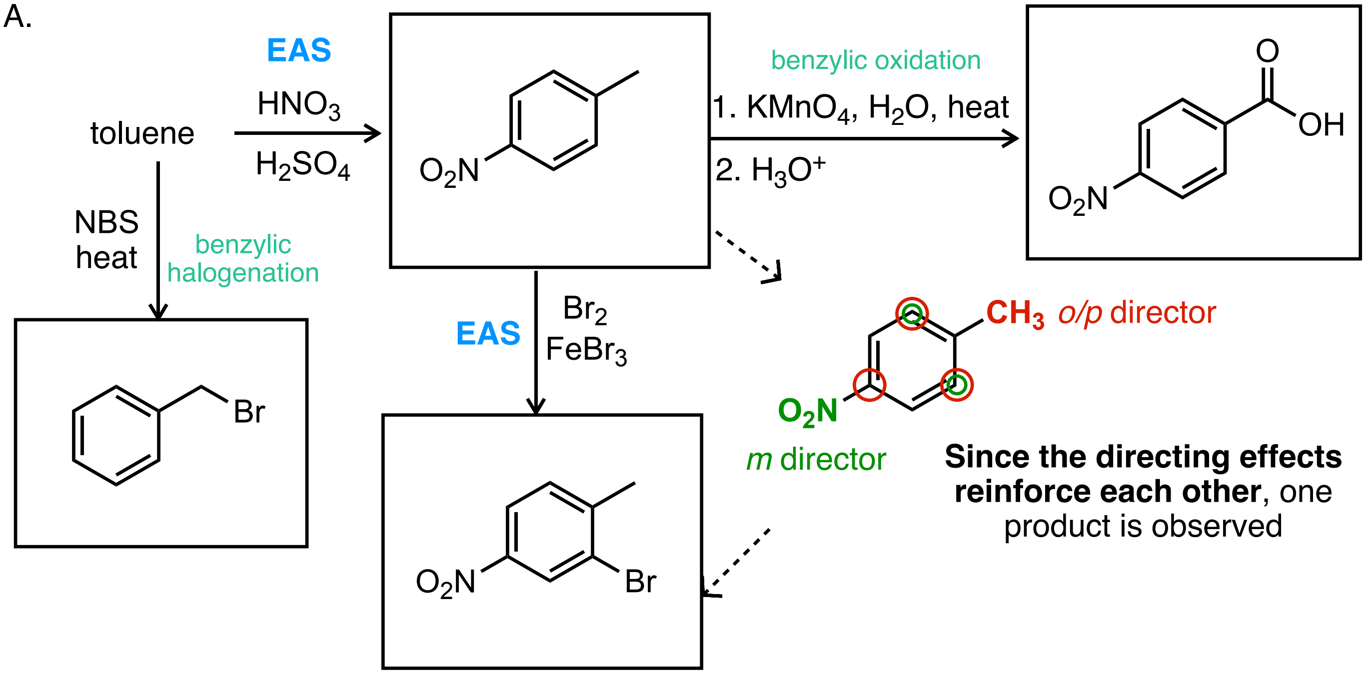


***tert*-butyl**

The *tert*-butyl group does not contain any benzylic C—H bonds, which are required for **benzylic** oxidation, therefore oxidation only occurs at the methyl group.

8. **Draw the structure of the major organic product** generated after each reaction in the series below. In reactions that generate *o*- and *p*- regioisomers, move forward with the *p*-product.

A.



Since the directing effects reinforce each other, one product is observed

B.