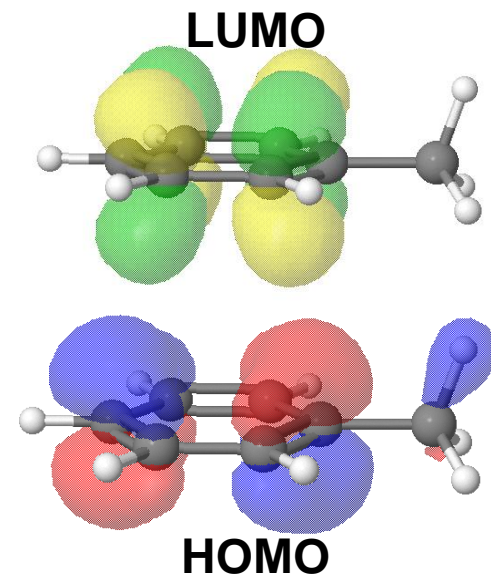
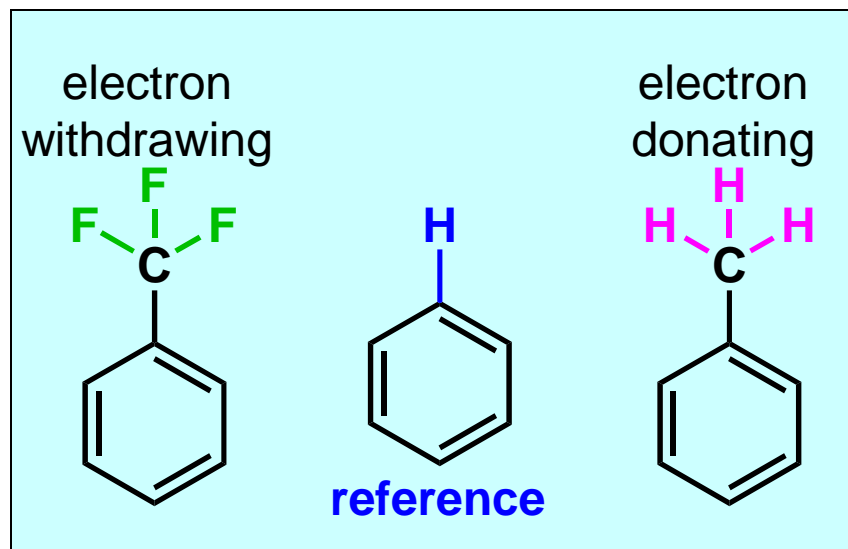
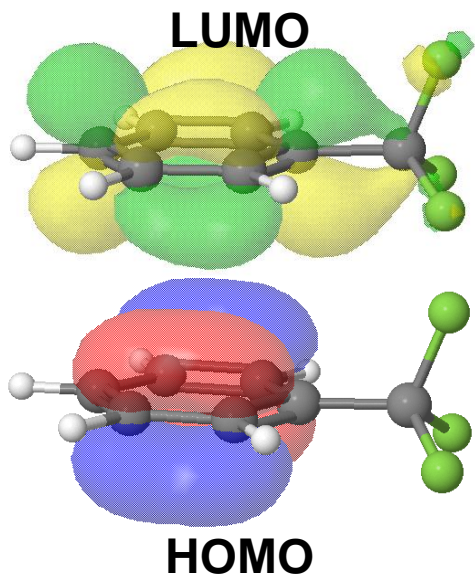


# Substituents Greatly Influence Reactivity and the Stability of the Various Intermediates on the Substitution Pathways

Does the substituent make benzene a **better nucleophile** or **better electrophile**?

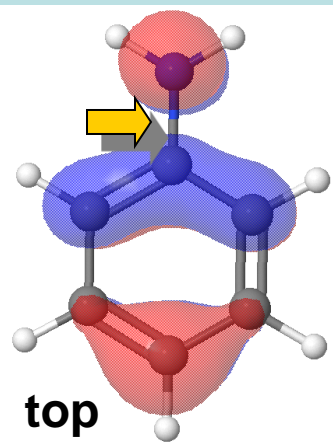
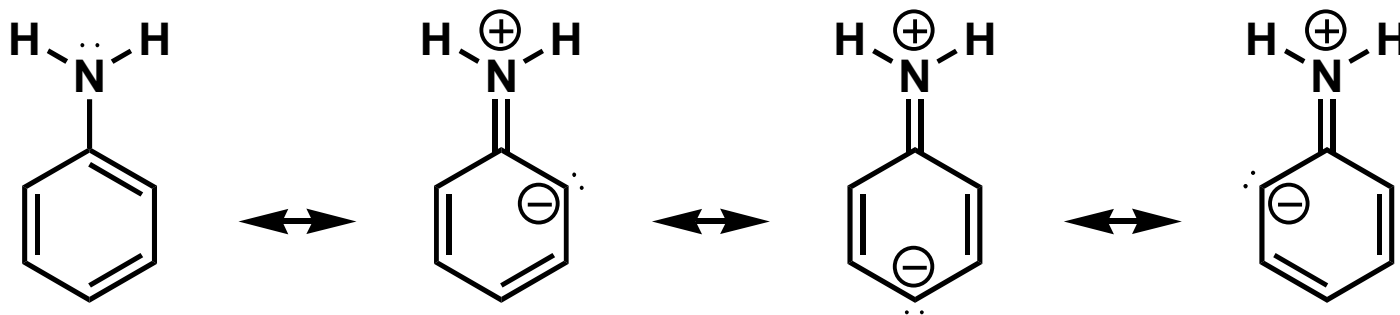
Substituents that interact through  $\sigma$  bonds influence reactivity by what are known as **inductive** effects. Withdrawing substituents accept  $\pi$ -electron density into an appropriately-aligned, low-energy  $\sigma^*$  orbital; in contrast, donating substituents contribute electron density from an appropriately-aligned, high-energy  $\sigma$  orbital. This behavior is revealed below in the frontier orbital pictures. For  $-\text{CF}_3$  (left), the LUMO (but not the HOMO) shows an interaction between the substituent and the  $\pi$ -system. Thus,  $-\text{CF}_3$  lowers the LUMO energy and makes the ring more electrophilic. For  $-\text{CH}_3$  (right), the HOMO (but not the LUMO) shows an interaction between the substituent and the  $\pi$ -system. Thus, a C-H  $\sigma$  bond of  $-\text{CH}_3$  contributes electron density to the HOMO making the ring a better nucleophile.



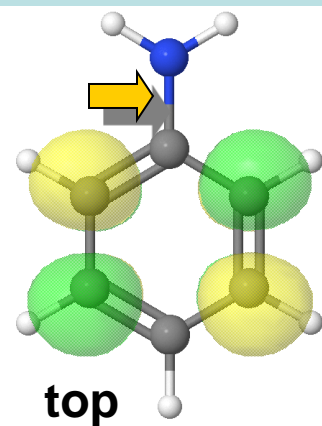
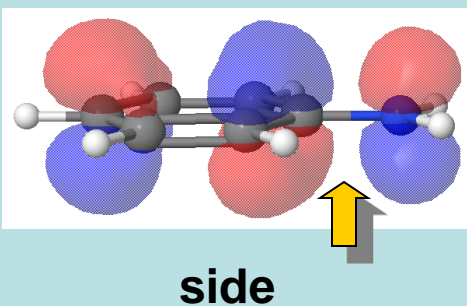
# Substituents with Non-bonding Pairs Donate Electron Density Through an $n \rightarrow \pi^*$ ( $\pi$ -type) Resonance Interaction

Substituents adjacent to a benzene ring can **donate** electron density from an appropriately-aligned, high-energy  $n$  orbital. This behavior is revealed below in the frontier orbital pictures of aniline. Notice that nitrogen is planar (not pyramidal) for maximum  $n \rightarrow \pi^*$  overlap. The HOMO (but not the LUMO) shows an interaction between the substituent and the  $\pi$ -system (indicated by the block arrows). Thus, nitrogen's lone pair contributes electron density to the HOMO making the ring a better nucleophile. This is predicted by the resonance contributors. Those atoms sharing the negative charge contribute most to the HOMO and are the most nucleophilic positions.

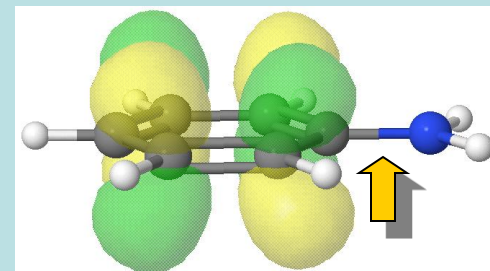
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HOMO



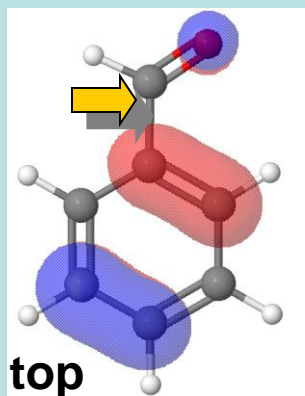
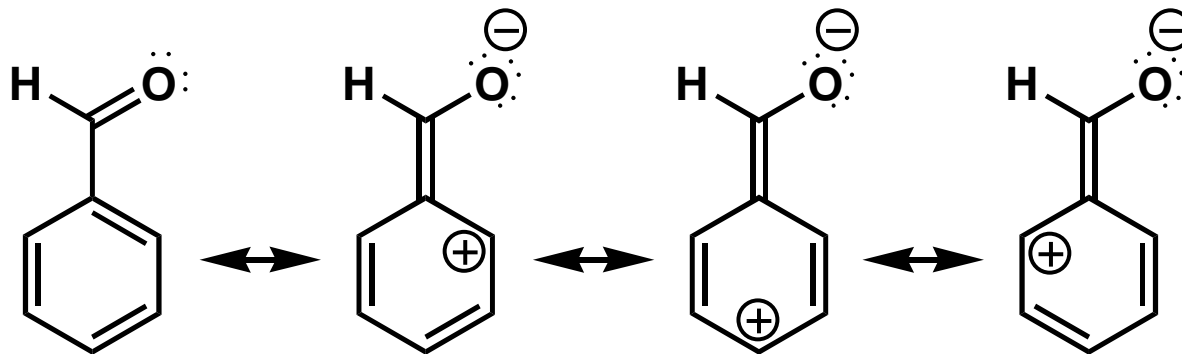
LUMO



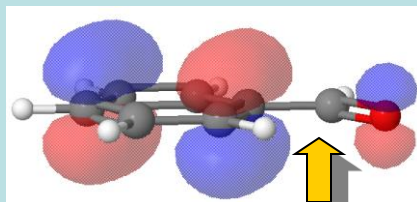
# Substituents with Low-Lying $\pi^*$ Accept Electron Density Through a $\pi \rightarrow \pi^*$ ( $\pi$ -type) Resonance Interaction

Substituents adjacent to a benzene ring can **accept**  $\pi$  electron density into an appropriately-aligned, low-energy  $\pi^*$  orbital. This behavior is revealed below in the frontier orbital pictures of benzaldehyde. Notice that the carbonyl and ring atoms are coplanar for maximum  $\pi$ -type overlap. The LUMO (but not the HOMO) shows an interaction between the substituent and the  $\pi$ -system (indicated by the block arrows). Thus, the C=O lowers the LUMO energy and makes the ring more electrophilic. This is predicted by the resonance contributors. Those atoms sharing the positive charge contribute most to the LUMO and are the most electrophilic positions.

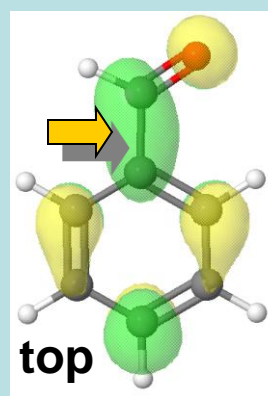
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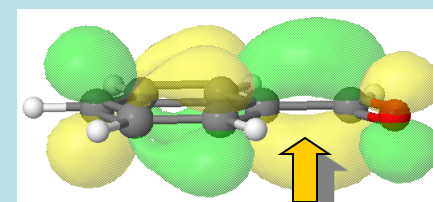
HOMO



side



LUMO



side