Four Mechanistic Pathways for Aromatic Substitution: I. Electrophilic Aromatic Substitution

\[
\begin{align*}
\text{H} & \quad \text{E}^+ \\
\text{[A}_E\text{]} & \\
\rightarrow & \\
\text{H} & \quad \text{E}^+ \\
\text{[D}_E\text{]} &
\end{align*}
\]

resonance stabilized cationic intermediate

\[
\begin{align*}
\text{H} & \quad \text{E} \\
\text{H} & \quad \text{E} \\
\text{H} & \quad \text{E} \\
\end{align*}
\]

MO pictures of the cationic intermediate

The LUMO shows positions of electron deficiency

this filled orbital shows a $\sigma \rightarrow a \pi$-type interaction
Four Mechanistic Pathways for Aromatic Substitution: II. Nucleophilic Aromatic Substitution

The HOMO shows positions of surplus electron density

resonance stabilized anionic intermediate
Four Mechanistic Pathways for Aromatic Substitution:
III. Substitution via Arenediazonium Ion

Two views of the aryl cation’s LUMO

The LUMO shows positions of electron deficiency

The unsubstituted carbon of the aryl cation approaches $sp$ hybridization and distorts the ring’s geometry
Four Mechanistic Pathways for Aromatic Substitution: IV. Substitution via Benzyne Intermediate

\[
\text{[E2]} \quad \text{Cl}^\text{N}H_2, NH_3 (l), -33 \text{ kC} \quad \text{H}N_2 + \text{Cl}^\text{N}H_2, NH_3 (l), -33 \text{ kC} \quad \text{NaNH}_2, \text{NH}_3 (l), -33 \text{ kC} \quad \text{Cl}^\text{N}H_2 + \text{NH}_3 + \text{Cl}^- \\
\]

The LUMO shows positions of electron deficiency.