1) Give two advantages of Molecular Orbital theory over simple Lewis Structure theory for describing the bonding in chemical compounds.

Give one disadvantage of MO theory. (4.5pts)

2) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (14.5pts)
3) Briefly explain your choice of one of the anti-aromatic compounds (3pts)

4) State one piece of experimental evidence which indicates that benzene does **not** really consist of alternating double and single carbon-carbon bonds. (2pts)

5) Using the polygon rule, draw out and decide whether the following species are aromatic or anti-aromatic. (8pts)
6) Predict the products in the following reactions (if you believe no reaction will occur, indicate this!), paying attention to regio/stereochemistry where applicable. (21 pts)

\[
\text{O} \quad \text{NC} \equiv \text{CN} \quad \xrightarrow{\text{heat}} \quad \text{HNO}_3, \text{H}_2\text{SO}_4
\]

\[
\text{Cl} \quad \xrightarrow{\text{HCl}} \quad \text{H}_2\text{C} = \text{CH}_2 \quad \xrightarrow{\text{mCPBA}} \quad \text{A} \quad \xrightarrow{\text{HCl}} \quad \text{B}
\]

\[
\text{Excess NaOH}
\]

\[
\text{NO}_2 \quad \xrightarrow{\text{Br}_2, \text{FeBr}_3} \quad \text{CO}_2\text{H} \quad \xrightarrow{\text{heat}} \quad \text{Br}
\]

\[
\text{CH}_2\text{CH}_2\text{Br} \quad \xrightarrow{\text{KMnO}_4, \text{heat}} \quad \text{Br} \quad \text{CH}_2\text{CH}_2\text{Br}
\]
7) The below compound displays aromaticity.

Choose a nitrogen atom, and describe its hybridization and electron contribution to the aromatic $\pi$ system.

Which nitrogen would be protonated first in dilute sulfuric acid?

Which nitrogen is the most basic? (12pts)
8) Give reagents and conditions to accomplish the following transformations. (18pts)

\[
\begin{align*}
\text{SO}_3\text{H} &\quad \rightarrow &\quad \text{CH}_2\text{CH}_3 \\
\text{CH}_2\text{-OH} &\quad \rightarrow &\quad \text{CH}_2\text{-O-CH}_2\text{CH}_3 \\
\text{C}_6\text{H}_6 &\quad \rightarrow &\quad \text{A} \\
\text{C}_6\text{H}_6 &\quad \rightarrow &\quad \text{NO}_2 \\
\text{C}_2\text{H}_4 &\quad \rightarrow &\quad \text{Br-C}_2\text{H}_4 \\
\text{C}_6\text{H}_6 &\quad \rightarrow &\quad \text{A} \\
\text{C}_6\text{H}_6 &\quad \rightarrow &\quad \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}
\end{align*}
\]
9) The addition of (1 equivalent of) HF to 1,3-butadiene generates a mixture of products.

\[ \text{HF} \quad \text{2 Products} \]

Draw the products, and mechanistically account for the mixture of products.

Which product would you expect to dominate as the temperature of the reaction is raised? (10pts)
10) Why is it accurate to explain the rates and orientation preferences of benzene derivatives in electrophilic aromatic substitution reactions based on the stabilities of the sigma complexes formed?

State and justify whether this is equally valid for nucleophilic aromatic substitution reactions? (7pts)
*Bonus question* (up to 2pts)

Fluoride ion is considered a poor leaving group in (almost all) nucleophilic substitution reactions. Yet NAS reactions (such as the one below) readily proceed with fluoride as the leaving group - why?

\[
\begin{align*}
\text{F} & \quad \text{NO}_2 \\
\text{NO}_2 & \quad \text{NaOH} \quad \rightarrow \\
\text{NO}_2 & \quad \text{OH} \\
\text{NO}_2 & \quad \text{NO}_2
\end{align*}
\]
1) Give two advantages of Molecular Orbital theory over simple Lewis Structure theory for describing the bonding in chemical compounds.

- More accurate description of π bonding in conjugated systems
- Describes aromaticity/anti-aromaticity
- Explains cycloadd. reactions
- Explains π-excitation

Give one disadvantage of MO theory. (4.5pts)

- Complicated

2) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (14.5pts)
3) Briefly explain your choice of one of the anti-aromatic compounds (3pts)

\[ \text{B is } sp^2, \text{ empty } p \text{ orbital} \Rightarrow 4\pi \]

4) State one piece of experimental evidence which indicates that benzene does \textbf{not} really consist of alternating double and single carbon-carbon bonds. (2pts)

- All C-C bond lengths are equal
- Molecule is regular hexagonal in shape
- Unreactive to \( Br_2 \) or \( KMnO_4 \)

5) Using the polygon rule, draw out and decide whether the following species are aromatic or anti-aromatic. (8pts)

(cyclopentadienyl cation)

(cyclopropenyl cation)

\( 4\pi \) = aromatic

Closed shell

\( 4\pi \) = anti-aromatic

Not closed shell, diradical

4 each
6) Predict the products in the following reactions (if you believe no reaction will occur, indicate this!), paying attention to regio/stereochemistry where applicable. (21 pts)

- \[
\begin{align*}
\text{Heat} & \quad \text{Heat} \\
\text{HNO}_3, \text{H}_2\text{SO}_4 & \quad \text{HCl}
\end{align*}
\]

- \[
\begin{align*}
\text{mCPBA} & \quad \text{Excess NaOH}
\end{align*}
\]

- \[
\begin{align*}
\text{Br}_2, \text{FeBr}_3 &
\end{align*}
\]

- \[
\begin{align*}
\text{Heat} &
\end{align*}
\]

- \[
\begin{align*}
\text{KMnO}_4, \text{Heat} &
\end{align*}
\]
7) The below compound displays aromaticity.

Choose a nitrogen atom, and describe its hybridization and electron contribution to the aromatic π system.

This molecule is 10 π Hückel aromatic.

A This N is sp² hybridized.
N has 5 valence electrons:
2x1 e⁻ for σ bonds
1 e⁻ for π bond
2e⁻ for lone pair

B This N is sp² hybridized.
N has 5 valence electrons:
3x1 e⁻ for σ bonds
2e⁻ for lone pair

The lp does not contribute to the π system. It is in an sp² hybrid orbital and points away from the ring.

Which nitrogen would be protonated first in dilute sulfuric acid?

Which nitrogen is the most basic? (12pts)
8) Give reagents and conditions to accomplish the following transformations. (18pts)

- $\text{SO}_3\text{H}$
  - $\text{H}_2\text{O},\text{heat}$
  - $\text{CH}_2\text{CH}_3$

- $\text{CH}_2\text{-OH}$
  - $\text{ONa}$
  - $\text{CH}_3\text{CH}_2\text{I}$
  - $\text{CH}_2\text{-O-CH}_2\text{CH}_3$

- $\text{C}_6\text{H}_6$
  - $\text{FeBr}_3,\text{Br}_2$
  - $\text{HNO}_3/\text{H}_2\text{SO}_4$
  - $\text{B}_4\text{H}_10$
  - $\text{Br}$

- $\text{CH}_2\text{=CH}_2$
  - $\text{Br}_3,\text{hv}$
  - (or $\text{NBS, peroxide}$)
  - $\text{Br}$

- $\text{C}_6\text{H}_6$
  - $\text{HCl}$
  - $\text{Zn(Hg)}$
  - $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Ph}$
9) The addition of (1 equivalent of) HF to 1,3-butadiene generates a mixture of products.

\[ \text{HF} \rightarrow \text{2 Products} \]

Draw the products, and mechanistically account for the mixture of products.

Which product would you expect to dominate as the temperature of the reaction is raised? (10pts)

Red product, most stable, thermodynamic product
10) Why is it accurate to explain the rates and orientation preferences of benzene derivatives in electrophilic aromatic substitution reactions based on the stabilities of the sigma complexes formed?

The energy difference between the reactants and transition state governs the rate of reaction. The T.S. energy can be approximated to be the σ complex energy since this step is ENASTHERMIC, and Hammond's postulate says that species close in energy will be similar in structure.

State and justify whether this is equally valid for nucleophilic aromatic substitution reactions? (7pts)

This is equally valid for NAS since the RDS is ENASTHERMIC too, and so all the above arguments still apply. 2
*Bonus question* (up to 2pts)

Fluoride ion is considered a poor leaving group in (almost all) nucleophilic substitution reactions. Yet NAS reactions (such as the one below) readily proceed with fluoride as the leaving group - why?

Expulsion of $F^-$ is an exothermic process here, not occurring in the RDS. The poor leaving group ability of $F^-$ does not affect the rate, and thus reaction proceeds. (T.S for expulsion of $F^-$ is "σ-complex-like", i.e., strength of C-F bond not a factor.)

See Problem 17-22 in the book, Chapter 17, p762