Name:
If you do not wish to have your graded exam placed outside my office please check here______

1) Provide one reason why Molecular Orbital Theory is so important.

Provide structures of two compounds or species whose bonding is not accurately described by a Lewis Structure. (4pts)

2) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (15pts)
3) Briefly explain your choice of one of the anti-aromatic compounds (3pts)

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

(cyclopentadienyl anion)

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

- 5-membered heterocycle with a COOH group and a CO2H group.
- Phenyl F.
- Ethyl ether.
- Nitro group in benzene.
- Cyclopentyne.
- Diphenyl ether.
6) The below compound displays aromaticity.

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

Which nitrogen would be protonated first in concentrated sulfuric acid?

Which nitrogen is the most basic? (12pts)
7) Give reagents and conditions to accomplish the following transformations. (18pts)
8) The addition of (1 equivalent of) Br$_2$ to 1,3-butadiene generates a mixture of products.

\[ \text{\begin{tikzpicture}[baseline=0.5cm]
  \node (start) at (0,0) {\text{\ce{C\equiv\text{C}}}};
  \node (end) at (1,0) {\text{\text{Br-Br} \rightarrow \text{2 Products}}};
  \draw[->] (start) -- (end);
\end{tikzpicture}} \]

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

Which is the kinetic product?

Which product would you expect to dominate as the temperature of the reaction is raised? (9pts)
9) Devise synthetic schemes to generate the products from the starting material, bearing in mind more than one step is obviously required. (10pts)

\[ \text{CH}_3 \quad \rightarrow \quad \text{NO}_2 \quad \text{Br} \quad \text{CO}_2\text{H} \]

b) \quad \rightarrow \quad \text{CH}_2\text{CH}_3 \quad \text{Br}

*Bonus question* (up to 2pts)
If the \(-\text{NH}_2\) group is such a powerful electron donor (\(\pi\) donor) and therefore activating and ortho/para directing, why is the below reaction very slow, and why does the substituent end up in the Meta position?

\[ \text{NH}_2 \quad \text{HNO}_3 \quad \text{H}_2\text{SO}_4 \quad \rightarrow \quad \text{NH}_2 \quad \text{NO}_2 \]
1) Provide one reason Molecular Orbital Theory is so important.
- Accurately describes it bonding in conjugated systems
- Accurately explains aromaticity and anti-aromaticity
- Predict "allowed" or "forbidden" pericyclic reactions

Provide structures of two compounds or species whose bonding is not accurately described by a Lewis Structure. (4pts)

2) Indicate which of the following molecules are aromatic, non-aromatic or anti-aromatic. (Assume all the molecules are planar). (15pts)
3) Briefly explain your choice of one of the anti-aromatic compounds (3pts)

\[ \text{B (or Al) has 3 valence e's, } \]

\[ \text{:: } \text{S}^2 \text{:: 4T is antiaromatic} \]

\[ \text{overlapping } \pi \text{ orbitals} \]

\[ \text{4N } \pi \text{ electrons } \text{=} \text{antiaromatic} \]

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

\[ \text{(cyclopropenyl cation)} \]

\[ \text{(cyclopentadienyl anion)} \]

\[ \text{BOTH AROMATIC} \]

\[ \text{(FILLED BONDING LEVELS } \]

\[ \text{- CLOSED SHELL MOLECULES } \]
5) Predict the products in the following reactions (if you believe no reaction will occur, indicate this!), paying attention to regio/stereochemistry where applicable. (21pts)
6) The below compound displays aromaticity.

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

Nitrogen A is \( sp^2 \) hybridized and contributes 1\( e^- \) to the \( \pi \) system. It has no lone pairs.

N has 5 valence \( e^- \)s.

\( N^+ \) has 4 valence \( e^- \)s.

The N has 3 \( \sigma \) bonds (\( = 3 e^- \) from N used). This leaves 1\( e^- \) in an unhybridized P orbital to form a \( \pi \) bond with the adjacent carbon.

Nitrogen B is \( sp^2 \) hybridized and contributes 2\( e^- \) to the \( \pi \) system.

\( N \) has 5 valence \( e^- \)s, and it uses 3\( e^- \) for the 3 \( \sigma \) bonds. This leaves 2\( e^- \), and this lone pair is put into a P orbital so it may contribute to the aromatic system, making a total of 4\( +2 = 6 \) \( \pi \) electrons, and thus the system is aromatic.

Which nitrogen would be protonated first in concentrated sulfuric acid?

B, it is the only N with a lone pair. Conc. acid is needed since since protonation destroys the aromaticity.

Which nitrogen is the most basic? (12pts)

B.
7) Give reagents and conditions to accomplish the following transformations. (18pts)

CH₃
\[ \text{CH₃} \quad \text{CH₂CH₃} \]
\[ \text{CH₂CH₃} \]
\[ \text{CO₂H} \]
\[ \text{CO₂H} \]

\[ \text{Br₂} \quad \text{FeBr₃} \]
\[ \text{Br} \]
\[ \text{NO₂} \]
\[ \text{NO₂} \]

\[ \text{Br₂} \quad \text{FeBr₃} \]
\[ \text{Br} \]
\[ \text{Cl} \]
\[ \text{Cl} \]

\[ \text{HNO₃} \quad \text{H₂SO₄} \]
\[ \text{Br₂} \quad \text{FeBr₃} \]
\[ \text{Br} \]
\[ \text{NO₂} \]
\[ \text{CH₃CH₂CH₂CF₃} \]
\[ \text{CH₂CH₂CH₂CF₃} \]

\[ \text{C₆H₅} \quad \text{HCl} \]
\[ \text{C₆H₅} \quad \text{HCl} \]

\[ \text{C₆H₅} \quad \text{CH₃CH₂CH₂CF₃} \]
\[ \text{C₆H₅} \quad \text{CH₃CH₂CH₂CF₃} \]
8) The addition of (1 equivalent of) Br₂ to 1,3-butadiene generates a mixture of products.

\[
\begin{align*}
\text{Br-Br} & \quad \text{2 Products} \\
\end{align*}
\]

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

Which is the kinetic product?

Which product would you expect to dominate as the temperature of the reaction is raised? (9pts)
9) Devise synthetic schemes to generate the products from the starting material, bearing in mind more than one step is obviously required. (10pts)

a)

\[
\begin{align*}
\text{CH}_3 & \quad \rightarrow \quad \text{NO}_2 \\
& \quad \rightarrow \quad \text{CO}_2\text{H}
\end{align*}
\]

b)

\[
\begin{align*}
\text{CH}_2\text{CH}_3 & \quad \rightarrow \quad \text{Br}
\end{align*}
\]

*Bonus question* (up to 2pts)

If the –NH\textsubscript{2} group is such a powerful electron donor (π donor) and therefore activating and ortho/para directing, why is the below reaction very slow, and why does the substituent end up in the Meta position?

The –NH\textsubscript{2} gets protonated in the acidic media, creating a –NH\textsuperscript{+} substituent, which is e- withdrawing because of its +1 charge, & is deactivating & meta directing.