C H E M 6 3 5 3 — M I D T E R M I:  
A R O M A T I C I T Y, A R O M A T I C S U B S T I T U T I O N S,  
P E R I C Y C L I C R E A C T I O N S  
Given in class period on 02/17/2010

Name:__________________ _______________________

U H S t u d e n t I D #:__________________ _______________________

Question 1:____/30  
Question 2:____/30  
Question 3:____/40  
Question 4:____/60  
Question 5:____/30  
Question 6:____/10  
Total:_________/200

This exam should have eight (8) pages.  
If it does not, ask Ognjen for a replacement immediately.
Question 1—30 points

Using the frontier molecular orbitals (FMO) analysis, predict the stereochemistry of the pericyclic reaction given below. Classify the reaction by the number and type of interacting electrons, and by its geometry (for example, Diels-Alder reaction would be $[4_e+2_c]$).
Question 2—30 points

Using Clar's concept of "filled" and "empty" hexagonal aromatic circuits, qualitatively predict the bond lengths in fully conjugated polycyclic aromatic hydrocarbons of the following geometries:

Classify all bonds into three categories: long (single), short (double), or intermediate (delocalized).
Question 3—40 points

The Friedel-Crafts alkylation of anisole (shown below) is catalyzed by strong Lewis acids such as AlCl₃:

\[ \text{Ph} - \text{OMe} + \text{t-Cl} \xrightarrow{\text{AlCl}_3} \text{Ph} - \text{OMe} \]

The following information has been obtained about the mechanism of this reaction:

i. At low concentrations of anisole, the reaction is first order in [anisole] and is inhibited by added AlCl₄⁻.

ii. At low concentrations of anisole, addition of AlCl₄⁻ enriched in the isotope ^{37}\text{Cl} results in exchange of labeled chloride into the t-butyl chloride starting material.

iii. At high concentrations of anisole, the rate becomes independent of [anisole] and added AlCl₄⁻ has a negligible effect on the rate of formation of product.

Provide a mechanism for this Friedel-Crafts reaction and show that the rate law for your mechanism is consistent with each one of the above observations.
Question 4—60 points

Provide a full orbital correlation diagram for the following cycloaddition. Clearly identify the symmetry element being preserved during the reaction and label all orbitals as symmetric or antisymmetric with respect to that symmetry element. Correlate the orbitals of the starting materials with their counterparts in the product. Is the reaction allowed or forbidden?
Question 5 — 30 points (10+10+10)

Provide arrow-pushing mechanisms for the following reactions:

\[
\begin{align*}
\text{CH}_3 & \quad \text{H}_3\text{C} \\
\text{O} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{C} & \quad \text{C} \\
\end{align*}
\]

\[
\text{0.01M HCl} \quad 25^\circ\text{C}
\]

\[
\begin{align*}
\text{OH} & \quad \text{CH}_3 \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\end{align*}
\]
Question 6—10 points
Predict the preferred position for nitration of quinoline (formula shown below). Explain your choice.

\[
\begin{array}{c}
  \text{N} \\
  \text{\begin{array}{c}
    \text{C} \\
    \text{C}
  \end{array}}
\end{array}
\]
If you need extra space, use this page. Clearly specify what problem are you solving here. No external pieces of paper will be graded.