C h e m 6 3 5 3 — M i d t e r m I:
Aromaticity, Aromatic Substitutions,
Pericyclic Reactions
Given in class period on 02/20/2012

Name:________________________________________________________

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

Q u e s t i o n 1:_____/30
Q u e s t i o n 2:_____/30
Q u e s t i o n 3:_____/40
Q u e s t i o n 4:_____/50
Q u e s t i o n 5:_____/30
Q u e s t i o n 6:_____/20
T o t a l :______/200

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

C h e m 6 3 5 3 : P h y s i c a l O r g a n i c C h e m i s t r y
Spring 2012 (January 18th—April 30th 2012)
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 \([\pi_4 + \pi_2]\)).
Question 2—30 points

Using aromaticity arguments, draw the most favorable resonance structures of linear [3]phenylene (left) and angular [3]phenylene (right). Qualitatively predict the bond lengths in the two compounds and order the labeled bonds by decreasing length. Note that the representations below may not be the most favorable resonance structures.
Question 3—40 points (4×10)

Predict the most likely products in the following reactions. Indicate stereochemistry where pertinent.

1. \( \text{NH}_2 \quad \text{COOH} \quad + \quad \text{isoamyl nitrite} \quad \xrightarrow{\text{dioxane}} \quad \) 

2. \( \text{O-\text{ethyl} \quad \text{aryl} \quad \xrightarrow{\text{heat}} \quad} \)

3. \( \text{benzene \quad \text{heteroatom} \quad \xrightarrow{\text{heat}} \quad \text{hint: 2 pericyclic reactions occur}} \)

4. \( \text{F-NO}_2 \quad \text{NO}_2 \quad + \quad \text{NH}_2 \quad \xrightarrow{} \quad \)
Question 4—50 points

Provide a full orbital correlation diagram for the conrotatory electrocyclization of 1,3,5-hexatriene. 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 (20+10)

Provide arrow-pushing mechanisms for the following pericyclic reactions. Remember that [2+2] cycloadditions/cycloreversions are usually forbidden.

![Reaction 1](image1)

![Reaction 2](image2)
Question 6—20 points
Predict the preferred position for nitration of 2,7-naphthyridine (formula shown below). Explain your choice.
If you need extra space, use this page. Clearly specify what problem are you solving here. No external pieces of paper will be graded.