CHEMISTRY 6353: Physical Organic Chemistry
Prof. Ognjen Š. Miljanić

Final Exam
May 7, 2014

Name: ___________________________ Last 4 Digits of Student ID Number: _________
(print legibly) Last First

Read all directions very carefully. Write your answer legibly in the designated spaces and think about what you are doing. Total number of points is 350. This exam is supposed to have eight (8) pages.

1. For each of the following questions, write in a number (or a formula) which you think best represents the quantity you are being asked for. An error of ±20% will be tolerated. 8 × 5 = 40 points

Typical strength of a C–H bond in organic compounds is _____________ kcal mol⁻¹.

Typical distance between the planes of two [π⋯π] stacked rings is _____________ Å.

Generally useful region of the proton (¹H) NMR spectroscopy is between _________ and _________ ppm.

Möbius aromatic compounds have _____________ π-electrons.

One kilocalorie (kcal) is _________________ joules (J).

The pKₐ of acetic acid is approximately _________________.

The difference in length of single and double bonds of benzene is approx. _________________ angstroms.

If a Mₘ of a polymer is 150,000 g mol⁻¹ and its Mᵣ is 100,000 g mol⁻¹, then the PDI is ________________.
2. All-cis-cyclononatetraene (shown below) undergoes a spontaneous electrocyclic ring closure at 25 °C to afford a single product. Suggest a structure for this product and construct full orbital correlation diagram that explains its formation. Then, describe an alternative symmetry-allowed electrocyclic reaction that would lead to an isomeric bicyclononatriene (you can do this without a separate orbital correlation diagram). Explain why the product of this alternative reaction is not observed.

80 points
3. Define, in your own words, the following terms. Be succinct but precise. Use chemical formulas if necessary. 

Homoaromaticity

Conrotatory

Polydispersity Index (PDI)

Macroyclic Effect

Bifurcated Hydrogen Bond

Rotaxane

4. Using qualitative molecular orbital theory, predict the regio- and stereochemical outcome of the following 1,3-dipolar cycloaddition. Show your work. Note: this is an uncatalyzed reaction—NOT a click reaction.

33 points

\[
\begin{align*}
\text{COOEt} & \quad + \quad \text{N}_3 \\
\text{heat} & \\
\end{align*}
\]
5. Calculate the yield of an intact G5 dendrimer composed of the core and branch segments shown below, assuming that every individual reaction proceeds with a 99.5% yield. 30 points
6. Suggest a mechanism by which each of the following three transformations could occur. More than one step is involved in each case.

\[ \text{COOCH}_3 + \text{H}_3\text{CO} \xrightarrow{\text{heat}} \text{H}_3\text{COOC} \text{CH}_3 \]

\[ \text{COOCH}_3 + \text{H}_3\text{CO} \xrightarrow{\text{H}^+} \text{Et} \text{OEt} \]

\[ \text{Et} \text{OEt} \xrightarrow{\text{H}^+} \text{Et} \text{OEt} \]
7. The association constant for the binding of a linear thread $T$ by macrocycle $C$ is 100 M$^{-1}$. Thread $T$ undergoes cyclization in 100% yield to form a copy of $C$. Calculate the relative yields of $C$ and [2]catenane $C\cdot C$ assuming that $C$ and $C\cdot C$ are equally stable and that reaction of $T$ to form $C$ is a fast unimolecular process that is not affected by binding to $C$. $T$ and $C$ are present in 1:1 mole ratio. Show your work. 40 points
8. Provide a mechanistic explanation for the observed high enantioselectivity in this reaction. 25 points