Test I

100 points total

This test is short answer and problem solving. Please be as complete as possible in your answers—partial credit is available, so it is to your advantage to write your ideas, even if you aren’t able to completely solve the problem. Make sure to show your work!

1. (18 points)

a. Which of the above compounds are isomers of B (more than one is possible)?
   \[ D_1 E \]

b. What are the most important intermolecular forces in compounds C and E?
   \[ C: \text{H-bonding} \quad E: \text{Dipole-Dipole} \]

c. Name the functional group present in each of the above compounds.
   A: ether  B: ketone  C: alcohol  D: alcohol  E: aldehyde

2. (23 points)

a. Complete the Lewis structure of the following molecule, by including lone pairs and/or multiple bonds. Draw two additional important resonance structures. Indicate non-zero formal charges, when necessary. Number the resonance structures from most stable (1) to least stable (3).

   \[
   \begin{array}{c}
   H \quad C \quad \text{N} = \text{N} \quad \text{O} \quad \text{C} \quad \text{H} \\
   H \quad \text{N} \quad \text{N} \quad \text{O} \quad \text{C} \quad \text{H} \\
   \end{array}
   \]

Answer the remaining questions with respect to the most stable resonance structure you determined in part a.

b. Estimate the following bond angles:
   - C-N-C 120°
   - H-C-N 109°
   - N-C-O 180°

c. Indicate the atomic (or hybrid atomic) orbitals used to make up the following bonds:
   - methyl C-N  \( C_{sp^3} - N_{sp^2} \) σ bond
   - C-H  \( C_{sp^3} - Hs \) σ bond
   - N-central C  \( N_{sp^2} - C_{sp^3} \) σ bond + \( N_{sp} - C_p \) π bond

d. Draw a wedge-dash picture showing the overall shape of the most stable resonance structure of this molecule. Make sure to consider the geometry around each atom. Considering the relative importance of your resonance structures in part a, indicate the presence of a net dipole moment, if any exists, by drawing an arrow on your picture.
3. (15 points) Suppose you had samples of two white solids, A and B, which could be either trans-stilbene or succinimide (right). Because they have identical melting points, they cannot be distinguished by melting point.

a. Explain how trans-stilbene (180.25 g/mol), the molar mass of which is almost twice that of succinimide (99.09 g/mol), could have a melting point identical to succinimide. Answers that do not include a discussion of intermolecular forces are not complete.

Trans-stilbene has stronger dispersion forces than succinimide because it is a larger molecule. Succinimide makes up for its weaker dispersion forces with dipole-dipole and H-bonding intermolecular forces. As a result, the two compounds have comparable intermolecular forces and melting pt.

b. You predict that the compounds may be identified by TLC, so you spot a TLC plate (silica gel) with samples A and B and develop it with ethyl acetate. After visualization, the plate looks like that drawn at right. Which compound, A or B, is likely to be succinimide? Explain.

A. Succinimide is more polar than trans-stilbene and it also has the ability to hydrogen bond to the plate. The intermolecular forces between succinimide and the plate are stronger, making it more difficult for ethyl acetate to drag the compound up the plate.

c. Show how you would calculate the Rf value for spot A (indicate the distances you would measure on the plate and set up the equation). How do you predict the Rf value would change (increase or decrease), if you used 80% hexane:20% ethyl acetate to develop the plate? Explain.

\[ R_f = \frac{a}{b} \]

The Rf value would decrease by using the less polar, 80:20 hexane:ethyl acetate solution as eluent. This is because a less polar solvent would be less effective at competing against the strong intermolecular forces that the compounds have with the plate.
4. (24 points) Consider the two isomers and their enthalpies of combustion, shown below.

\[ \Delta H_{\text{comb}}^\circ = -1247.38 \text{ kcal/mol} \quad \Delta H_{\text{comb}}^\circ = -1245.66 \text{ kcal/mol} \]

a. Provide an acceptable IUPAC name for each of the above isomers.

\text{trans-1,3-dimethylcyclohexane} \quad \text{cis-1,3-dimethylcyclohexane}

b. Write a balanced equation for the combustion reaction of either of the isomers above.

\[ C_8H_{16} + 12O_2 \rightarrow 8CO_2 + 8H_2O \]

c. Use the enthalpies of combustion to calculate the difference in energy between the two isomers. Which isomer is lower in energy?

\[ \Delta E = \Delta H_{\text{comb}} \text{ cis} - \Delta H_{\text{comb}} \text{ trans} \]
\[ = -1245.66 - (-1247.38) = 1.72 \text{ kcal/mol} \]

The \textit{cis} isomer is lower in energy.

d. Draw the lowest energy chair conformation of each isomer.

\[ \text{cis} \quad \text{trans} \]

\[ \text{cis} \quad \text{trans} \]

e. Explain how you could use your answer in part c to determine the strain associated with a \text{CH}_3 group in the axial position.

The difference in energy between the \textit{cis} and \textit{trans} isomers is due to the strain associated with a methyl group in the axial position. Therefore, the energy difference calculated in part c is equal to the strain energy of a methyl group in the axial position (1.72 kcal/mol).
5. (20 points) 
   a. The strain energy of the twist boat conformer of cyclohexane is 5.5 kcal/mol. Calculate K for the conversion of twist boat $\rightarrow$ chair cyclohexane at 298 K ($R = 1.987 \text{cal/mol}^\circ\text{K}$).

   \[
   \Delta G = \text{strain chair} - \text{strain twist boat} \\
   = 0 - 5.5 \text{ kcal/mol} = -5.500 \frac{\text{cal}}{\text{mol}}
   \]

   \[
   \Delta G = -RT \ln K \Rightarrow -5.500 = (1.987)(298) \ln K
   \]

   \[
   9.29 = \ln K
   \]

   \[
   K = 11,000
   \]

   b. What percent of cyclohexane is in the twist boat conformation at equilibrium?

   \[
   K = \frac{\text{chair}}{\text{twist boat}} = \frac{11,000}{1}
   \]

   \[
   \% \text{ twist boat} = \frac{1}{11,001} \times 100 = 0.01\%
   \]

   (if $K = 500$: \% twist boat = $\frac{1}{501} \times 100 = 0.2\%$)

   c. For the compound below, the most stable conformation is not a chair, but rather a twist boat. Explain this observation. (The strain of an axial tert-butyl group is 4.9 kcal/mol.)

   ![Compound Diagram]

   If the compound were in a chair conformation, one tert-butyl group would have to be in the axial position. The molecule adopts a twist boat instead, because in this conformation, both tert-butyl groups can be pseudo-equatorial.