MO Energies and Reaction Rates
Chemistry 200 – Fall 2004 – Assignment #10
Due: November 5, 2004, high noon

Go through each of the problems below, and then present the answers using Microsoft Word. If structures are required, follow the directions in each problem, and copy and paste the structure into Word. Data should be presented in a format that is easily comprehensible to the reader. Be sure to answer all of the questions in each problem. You must submit a hard-copy of this problem set to Dr. Caran, AND a digital copy (as a single Word format document) in the digital drop-box on Blackboard. As always, your digital copy must be named using your JMU email username in the following way: username_C200_10.doc.

The Diels-Alder Reaction

Diels-Alder reactions typically involve an electron-rich diene and electron-poor dienophile, which react to form a cyclohexene, as shown below.

Electron-donating groups (EDG) increase the energy of the highest occupied molecular orbital (HOMO) of the diene, while electron-withdrawing groups (EWG) decrease the energy of the lowest unoccupied molecular orbital (LUMO) of the dienophile. The above pattern of substituents decreases the difference in energy between the HOMO of the diene and the LUMO of the dienophile (the “HOMO-LUMO gap”), thus increasing the rate of the reaction.

In this assignment, we will use Spartan to look at the effect of the placement one or more EDGs on the diene and one or more EWGs on the dienophile. We will then record HOMO and LUMO energies, respectively, in order to predict relative reaction rates. We will also compare some of our calculated values to actual reaction rates, and look at the effect of using Lewis Acid catalysts.
Note: Dienes must be in the s-cis conformation (and not the s-trans conformation) in order to undergo a Diels-Alder reaction.

1. Electron Donating Groups on the Diene

Build each of the molecules below in Spartan. Be sure to build it in the s-cis (and not the s-trans) conformation. Calculate the equilibrium geometry of each one with a PM3 basis set (semi-empirical). Record and report the HOMO energy of each molecule. (To do this, click display→properties. If an atom or bond is selected, the dialog will give you the properties of the atom or bond. To see the molecule properties, deselect the atom or bond.) Copy and paste your structures into Word as “ball and spoke” structures. Be sure to label your structures A-M. Answer all of the questions below.

1a. Which is a better EDG according to your calculations for molecules A-M, methyl or methoxy? How do you know?

1b. Does an EDG on the diene affect the HOMO energy to the same degree, no matter where it is on the molecule? For example, does a methyl group on a terminal sp² carbon of the diene (i.e. in B) have the same affect as a methyl group on an interior sp² carbon (i.e. in D)? If it is not the same, in which position does it have a greater affect?

1c. For the molecules with two EDGs on the diene (C, E, F, G, I, K, L, M), does the overall increase in energy of the HOMO equal the sum of the individual substituent effects? Or is it greater or less than the sum of the individual effects? Clearly explain using two examples (including numbers).

1d. What does the HOMO of a diene look like? Open up your file for diene J (2-methoxybutadiene). Calculate the shape of the HOMO of this molecule by selecting Surfaces from the Display menu, and adding a surface to the list (surface: HOMO, property: none). Submit your calculation, and display the
new surface as a transparent surface over a ball-and-spoke model. Copy this image into Word.

2. Electron Withdrawing Groups on the Dienophile

A cyano group (-CN, such as in acrylonitrile) is often used as an EWG on a dienophile. Let’s take a look at the effect of using 1,2,3 or 4 cyano groups directly attached to the double bond of the dienophile in the Diels-Alder reaction with cyclopentadiene (below).

![Diagram of Diels-Alder reaction with acrylonitrile and cyclopentadiene]

In this example, we will be learning how to use the list processing, spreadsheet, and graphing functions of Spartan. We will build all of these molecules in a single file, and run a calculation simultaneously on all of them. We will be building the following six molecules: acrylonitrile (cyanoethylene), trans-1,2-dicyanoethylene, cis-1,2-dicyanoethylene, 1,1-dicyanoethylene, tricyanoethylene and tetracyanoethylene. Build the first molecule by selecting New from the File menu, but all subsequent molecules by selecting New Molecule from the File menu. Build these molecules in the order they are given to you above. This will put all six molecules in the same file, and allow us to access them all in a single spreadsheet. To display the spreadsheet, select Spreadsheet from the Display menu.

Set up your calculation using a Hartree-Fock 3-21G* basis set. Choose Single Point Energy in the menu to the right of “Calculate”. In the menu to the right of “Start from:”, select AM1. This will tell Spartan to first calculate the equilibrium geometry using an AM1 basis set, and then to calculate the energy of that geometry using a 3-21G* basis set. Be sure that “apply globally” is checked on the lower part of the dialog box, so that your calculations are applied to all of the molecules in your file. After clicking OK, submit your job.

While you are waiting for your calculation to complete, type in the experimental data from the table below into the spreadsheet (display → spreadsheet). It turns out that the log of the reaction rate is proportional to the LUMO energy of the dienophile. Enter a title by clicking on a blank cell in the spreadsheet and typing “log(rate)”. Enter the rate data in the appropriate cells in the column.

<table>
<thead>
<tr>
<th>Dienophile</th>
<th>$\log_{10}$(relative rate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>acrylonitrile</td>
<td>0</td>
</tr>
<tr>
<td>trans-1,2-dicyanoethylene</td>
<td>1.89</td>
</tr>
<tr>
<td>cis-1,2-dicyanoethylene</td>
<td>1.94</td>
</tr>
<tr>
<td>1,1-dicyanoethylene</td>
<td>4.64</td>
</tr>
<tr>
<td>tricyanoethylene</td>
<td>5.66</td>
</tr>
<tr>
<td>tetracyanoethylene</td>
<td>7.61</td>
</tr>
</tbody>
</table>

After the calculation has completed, add a new column to your spreadsheet by clicking on the Add... button, and choose E LUMO (the energy of the LUMO), and kcal/mol as your units. Then click OK. To plot your data in Spartan, select Plots from the Display
menu. Plot \( \log(\text{rate}) \) on the x-axis and \( E_{\text{LUMO}} \) on the y-axis, then click \textbf{OK}. The default trend line will be a “cubic spline”. To change this to a linear least squares fit (which is more appropriate to represent this trend), select \textbf{properties} (from the \textbf{Display} menu) and click on the plot you have just drawn. After “Fit:”, select \textbf{Linear LSQ} to change the trendline. Recreate this plot [\( \log(\text{rate}) \) vs \( E_{\text{LUMO}} \)] using Excel by copying the data from the spreadsheet in Spartan and pasting it into Excel. Label your axes, title your plot, and clearly show the data points, trendline, and the equation for the line. Be sure that your axes are on an appropriate scale to show the data, and that your axes cross each other at an appropriate point to display the data. (To make adjustments to these values, right-click on each axis, select \textbf{format axis}, and select the \textbf{scale} tab.)

2a. Report the calculated values of the LUMO energies for the dienophiles.
2b. Copy the Excel plot into your Word document.
2c. Do you see the expected correlation between relative rate and \( E_{\text{LUMO}} \)? Does this make sense, considering the structures of the dienophiles (i.e. the number of EWGs)? Explain.

### 3. The Use of Lewis Acids to Complex the Dienophile

Lewis acids (such as \( \text{BF}_3 \)) are typically used to accelerate the rate of Diels-Alder reactions. They do this by forming a complex with the dienophile, thus lowering the energy of the LUMO. For example, the \( \text{BF}_3 \) complex with acrolein (shown below) reacts faster in a Diels-Alder reaction than acrolein itself.

Note that \textit{trans}-acrolein is a more stable conformation than \textit{cis}-acrolein, shown below. These the C-C single bond has some double-bond character due to the conjugation of the two double bonds, so the rotation around the bond is hindered compared to the free-rotation around a typical C-C single bond.

3a. Build \textit{trans}-acrolein in Spartan, and calculate the value of the LUMO energy of the equilibrium geometry using a PM3 basis set. Also calculate the shape
3b. Build the trans-acrolein-BF$_3$ complex. The best way to do this is to use the expert model kit. In the expert model kit, select C from the periodic table, and trigonal planar from the list of atomic hybrids below. Use this tool to build the carbon framework of trans-acrolein as shown below.

Select O from the periodic table, and bent dicoordinate and add the oxygen. If necessary, set the dihedral angle (using the measure dihedral tool) so that the free valence on oxygen is trans to the CC bond, as shown below. All four atoms should lie in the same plane.

Select B and tetrahedral to add the boron, and F, monocordinate, to add the BF$_3$ unit, as shown below.

Now you simply have to introduce the correct bond types by clicking on the double bond in the expert model kit, and double clicking on the appropriate bonds. The three C’s, four H’s, O, B, and one F should all be in the same plane. The remaining two F’s should be out of the plane.

Calculate the equilibrium geometry using a PM3 semi-empirical calculation, and report the value of the LUMO.

3c. How does the value of the LUMO change when trans-acrolein forms a complex with BF$_3$? Is this consistent with the observation that Lewis acids increase the rate of Diels-Alder reactions? Explain why the incorporation of BF$_3$ in the reaction would increase the reaction rate. (i.e. Why does it lower the LUMO?)
4. Final Questions

4a. Look at all of the dienes in question 1, and the dienophiles in question 2. Which combination of these molecules (one diene, one dienophile) would give you the fastest Diels-Alder reaction, according to your calculations? What is the value of the HOMO-LUMO gap? Draw the reaction (including reactants, and the product) using KnowItAll (don’t worry about stereochemistry).

4b. Look at all of the dienes in question 1, and the dienophiles in question 2. Which combination of these molecules (one diene, one dienophile) would give you the slowest Diels-Alder reaction, according to your calculations? What is the value of the HOMO-LUMO gap? Draw the reaction (including reactants, and the product) using KnowItAll (don’t worry about stereochemistry).