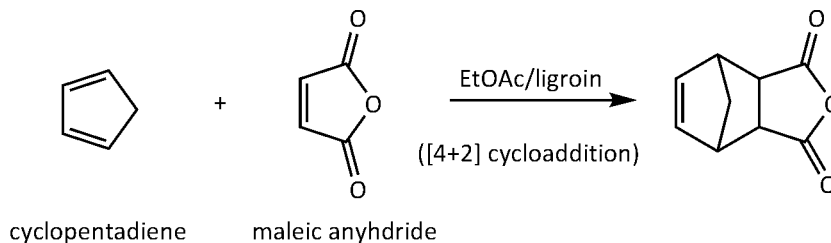## Molecular Modeling and Mechanics – *Endo* vs. *Exo* Diels-Alder Product.

Reading: Pavia (5th edition), *Molecular Modeling and Molecular Mechanics* (p. 106-164).


cyclopentadiene   maleic anyhdride

Overview
The Diels-Alder (D-A) reaction of cyclopentadiene and maleic anhydride proceeds as shown above to give one major product – the endo product is the isolated material. The D-A reaction usually produces the endo product, but why? To explore the basis for this rule, you will investigate the energies associated with this well-known case of the D-A reaction.

Using Spartan Student v7, predict which of the two possible transition states – *endo* or *exo* - is lower in energy and which of the products – *endo* or *exo* – is lower in energy. And predict which product is more stable. To do this build structures for each of the starting materials, both products, the use the tool to predict an initial geometry of the *endo* and *exo* transition states. Minimize the energy for each transition state using the Hartree-Fock, 3-21G basis set and view the output, print and

Procedure
Using Spartan Student v7, start by selecting Build New under the File menu.
Click the rings button and select cyclohexane
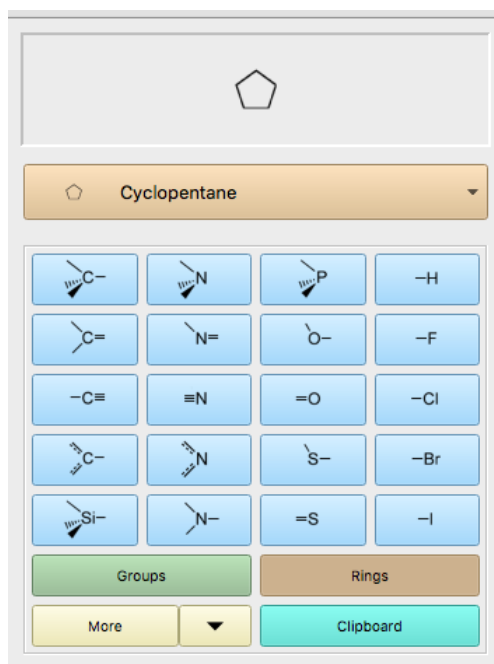
Double-click the left mouse button in the main window. (double-click in another location for each subsequent ring, which you will do later) Use the mouse keys to move and rotate – hold left mouse button and drag to rotate in 3D, hold right mouse button and drag to move across the screen.

To make a double bond out of single bond, select the bond tool and sequentially double-click on the two atoms that need a double bond. The bond tool is the second button from left.
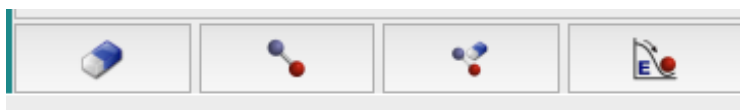
Double-click the first atom of the double-bond, then double-click the second atom. Click the minimize button (far right button) after each new bond is made. To make maleic anhydride, you will need to "convert" two carbons to carbonyls – select the appropriate carbon button (Csp2) and click on the carbons in a cyclopentane ring,
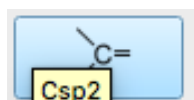
then change the end of the double bond to an oxygen, using the appropriate button (Osp2) and double-click on the end of the double bond.
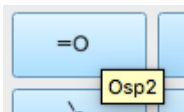
Similarly, change the oxygen in the ring to the one in maleic anhydride by selecting the Osp3 oxygen and double-click on the atom between the two carbonyls that you just made above. Minimize the structure at each stage using the Minimize button above.
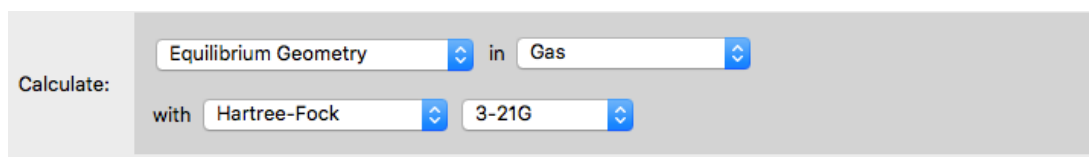
To make a bicyclic compound, start with two separate cyclopentane rings shown in the display. With two rings shown in one display the mouse clicks and dragging will move both at the same time. To move just one ring at a time. especially to orient them better before connecting them, select only one of the rings by doing the following:

a. Hold the left mouse button down, then click the right mouse button and drag a selection box completely around one of the rings (be sure to only select atoms in the ring you intent to move).
b. While holding the Control key, use the left and right mouse buttons to move the selection.

Connect two rings by making bonds between atoms in each ring – this will make the "bridge head connections" of the bicyclic. Just like making a double-bond, simply double-click on the first atom of ring 1, then double-click on an atom in the second ring. Minimize the resulting bicyclic structure with the Minimize button, as before.

Make separate models of 1,3-cyclopentadiene, maleic anydride, and the endo and *exo* and *endo* D-A products. For each model, do the following to do a complete energy and geometry minimization:
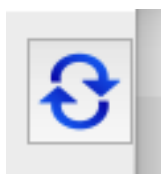
a. Under **Setup** menu, choose **Calculations**
b. In the calculate dialog box, select Hartree-Fock and 3-21G as shown below.
c. Click the **Submit** button – it will prompt you for a file name – give one for the final minimized version of the model.
d. Once the calculation is complete the program will alert you, then under the **Display** menu, select **Output**.
e. Print the output for later (be sure to label the output, since it doesn't show the file your printed it from)

For the *endo* and *exo* transition state (TS) geometry, start with the minimized D-A product structure (open the file you just made above). Select the **Guess Transition State** tool:
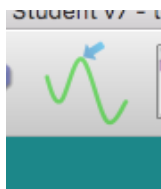
Highlight the bonds that will be "broken" to get to the transition state by clicking on a bond, then click the bond where the electrons will go (electron-pushing mechanism). Continue doing this until you have all three arrows displayed that will lead to the TS. Then click the **Generate Transition State** button,
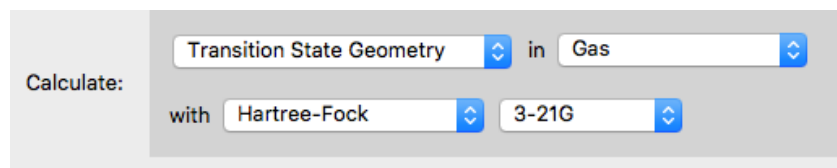

The result should look like the TS for the D-A reaction. Use the mouse to rotate the structure and notice whether the TS looks "correct." You should observe some single bonds shown with a dashed line and some double bonds with similar dashed line.

To minimize the energy of the TS, do the following:

a. Under Setup menu, choose Calculations
b. under the calculate dialog box, select Hartree-Fock and 3-21G as shown below. (This time with Transition State Geometry selected)

c. Click the submit button – it will prompt you for a file name – give one for the final minimized version of the model. Once the calculation is complete the program will alert you, then under the Display menu, select Output. Print the output for later (be sure to label the output, since it doesn't show the file your printed it from)

Calculate: Transition State Geometry   in   Gas
              with   Hartree-Fock   3-21G

To Complete the Experiment (**partial** report to attach to the Diels-Alder experiment)

In total you will need the energies of both starting materials, both TS possibilities and both D-A products. From this data you can construct an energy diagram and show all activation energies (E_a) and all enthalpies (ΔH) for the formation of the two products. Use the lowest calculated energy as the point of reference for the energy diagram (zero) . The Spartan program calculates energies in the unit called hartrees (1 hartree = 2625.5 kJ/mol). Calculate the differences of each appropriate intermediate in units of hartrees, then convert to kJ/mol.

The total energy of the starting materials is simply the sum of the energies for both starting materials – add the values in hartrees, then compare by difference with TS and D-A product energies, and convert to kJ/mol.

Finally, estimate the expected ratio of *endo* to *exo* products at room temperature (25 C) by comparing the ratio of activation energies (see discussion of this in lecture). Compare this ratio to the GC results obtained during the laboratory experiment.