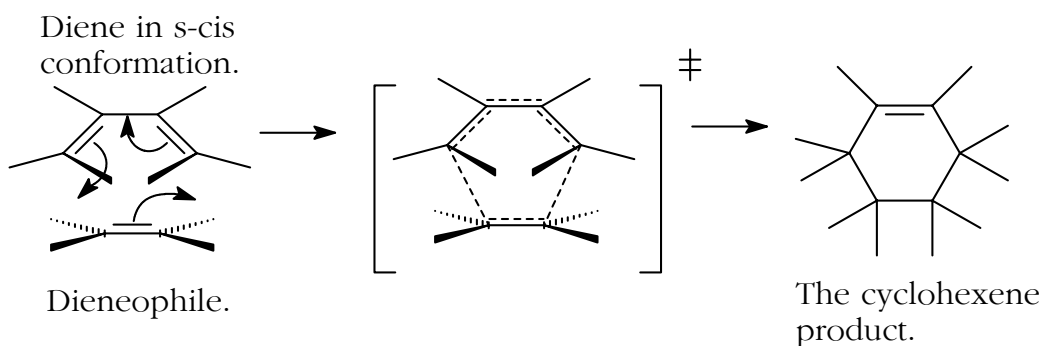Name_____

Chem 322 - Organic Chemistry II
Laboratory Exercise – Molecular Modeling – Part 3

This time we are going to examine the Diels-Alder reaction[1] and some related reactions. As you may recall, the Diels-Alder reaction produces a cyclohexene ring when a conjugated diene in the s-cis conformation reacts with a compound that contains a double bond (the "dieneophile"). This reaction is one of a class of reactions that are known as *electrocyclic* reactions. In electrocyclic reactions – unlike typical polar or free radical reactions – there are no intermediates. The reactants get together and the electrons rearrange themselves in "concerted" fashion to break and make bonds giving the product as a result. In the figure below you can see the reactants aligned ready to react, the transition state, and the final product.

Diene in s-cis
conformation.

‡

Dieneophile.

The cyclohexene
product.

[1,3-Butadiene is a mediocre diene and ethylene is a very poor dieneophile, so reaction does not ordinarily take place between them. However, we use them as examples to simplify the discussion. A Diels-Alder reaction that does work well is the one between 1,3-cyclopentadiene and maleic anhydride, a reaction you carried out in the Chem 221 laboratory.]

The Diels-Alder and related reactions are a subclass of electrocyclic reactions known as *cycloaddition* reactions. The genesis of the term cycloaddition is fairly obvious in relation to the Diels-Alder reaction – the product is cyclic and results from the addition of the dieneophile to the diene.

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[1]The Diels-Alder reaction is discussed in Chapter 14 of the fifth edition of "Organic Chemistry" by John McMurry. It is also discussed in Chapter 30 and it is the material in that chapter that is more relevant to the work in this exercise.

You may have noticed in the figure on the previous page that it is the four π electrons in the conjugated diene that interact with the two π electrons in the dieneophile to form the product. Now, in the product we have one new π bond and two new σ bonds. We might imagine that in the reaction process one of the π orbitals in the diene rearranges itself to hold the two π electrons in the product. On the other hand, the two new σ bonds that join the formerly separate pieces together in the product, must have been formed by the diene donating two electrons toward the dieneophile to form one of the bonds and the dieneophile donating two electrons toward the diene to form the other one.

Well, if the dieneophile is to donate two π electrons toward the diene, the diene will have to accept them and they will endeavor to interact with the lowest energy unoccupied molecular orbital (LUMO) in the diene. The π electrons that the dieneophile is donating are in the highest energy occupied molecular orbital (HOMO) in the dieneophile. *So, for reaction to take place the LUMO of the diene and the HOMO of the dieneophile had better not be orthogonal.*

Likewise, if the diene is to donate two π electrons toward the dieneophile, the dieneophile will have to accept them and they will endeavor to interact with the lowest energy unoccupied molecular orbital (LUMO) in the dieneophile. The π electrons that the diene is donating are in the highest energy occupied molecular orbital (HOMO) in the diene. *So, for reaction to take place the LUMO of the dieneophile and the HOMO of the diene had better not be orthogonal.*
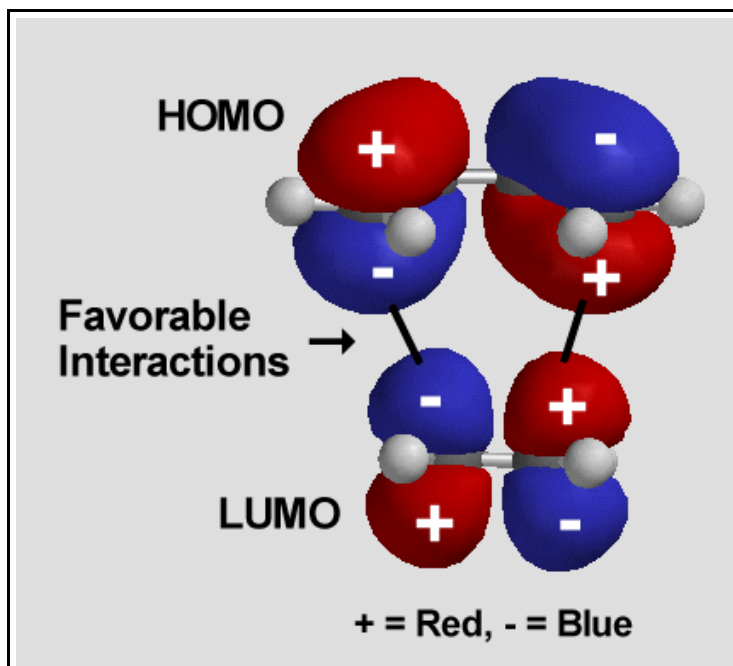
"Hey, doc! Dat all makes sense 'cept the part about da diene donatin' π electrons from the HOMO. Da diene has four π electrons – that means two π orbitals. From our previous endeavors in molecular modeling I'm guessin' that these orbitals are the HOMO and a lower energy HOMO(-1) orbital. Why can't da donated electrons come from the HOMO(-1) orbital?"

"Yet another excellent point, Rooster. The assumption here is that the less energetic HOMO(-1) π electrons will try to remain less energetic and not try to cross an energy (of activation) barrier. They can do this by relocating themselves in a π bond in the part of the product that came from the diene. On the other hand the higher energy HOMO π electrons will cross the energy barrier to become σ bond electrons. If this assumption leads to predictable results, we'll keep it; if not, we'll scrap it."
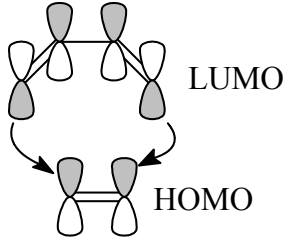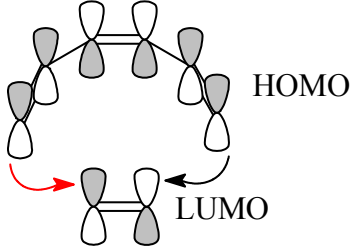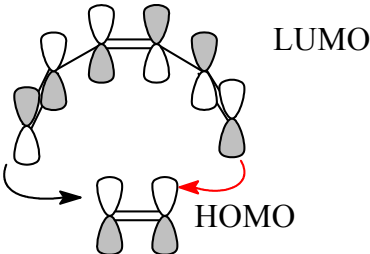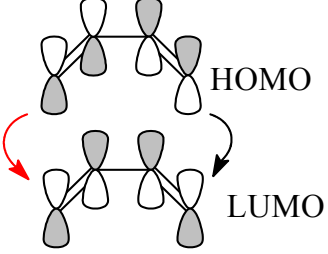
"O.K., doc. Guess it's kinda like when I go to da dance club. I'm th' most energetic guy there. I get out there on th' floor an' impress the chicks. Hip hop, break dancin', the Lindy – I do 'em all. Dose utter guys – no energy – they hold up da wall, if ya know what I mean. Hey, doc, ya should see me at da club."
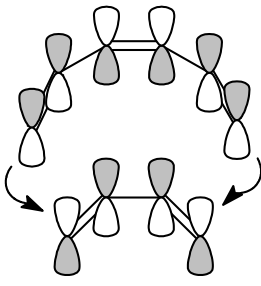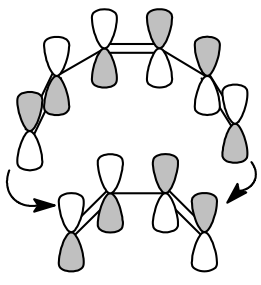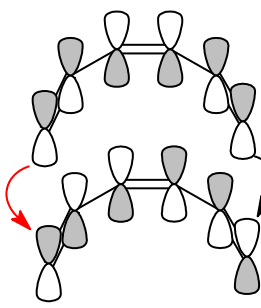
"Just as soon as I activate that accidental death and dismemberment policy, Rooster."

O.K. What we're going to do is look at the HOMO/LUMO interactions between several pairs of molecules all of which have π molecular orbitals. One such pair, of course, will be a 1,3-diene and an alkene – the Diels-Alder reaction. When we bring the pairs of molecules onto the screen we will align them as shown in the figure to the right (for the Diels-Alder reaction). As we do this fill in the table below. In the first column fill in the orbital interactions at the ends of the π orbitals in the reactants. As an example, this has been done for the situation shown to the right. In the second column indicate either that the two compounds would have orthogonal π systems or that they would react. In the third column indicate the total number of π electrons in both reactants.

Molecule Pairs	Orthogonal or Interactive	Total Number of π-Electrons
	Orthogonal	4
	Interactive	6

LUMO HOMO	Interactive	6
HOMO LUMO	Orthogonal	8
LUMO HOMO	Orthogonal	8
HOMO LUMO	Orthogonal	8

HOMO LUMO	Interactive	10
LUMO HOMO	Interactive	10
HOMO LUMO	Orthogonal	12

Click on Titan in the Start menu. When it boots, click on the ⬛ icon in the upper right corner to make the window full-screen. This time you will not have to construct all the molecules and carry out the calculations; that has already been done.

Click on the Open File icon, 📂, and open the **diels-alder-ethylene1.spartan** file. Again click on the Open File icon, 📂, and open the **diels-alder-ethylene2.spartan** file. [These files are identical but Titan will not let you open the same file twice.] You should have two molecules of ethylene in the work area, one above the other. Click on the top molecule to select it. Click on Display|Surfaces. When the Surfaces List dialog box opens place a check mark in the yellow box next to HOMO. The top ethylene should now be adorned with its HOMO. Double click the bottom ethylene molecule [one click deselects the top molecule; the second click selects the bottom one]. The Surfaces List box now refers to this molecule. [Move the molecule if you need more space between the molecules – right click and drag.] Click on the yellow box next to LUMO. The bottom ethylene should now be adorned with its LUMO. Fill in the first line of the table. Double click on the top molecule to select it. Then click on the Close File icon to banish this molecule. (If you are asked if you want to save changes, click on no.)

Click on the Open File icon, 📂, and open the **diels-alder-butadiene1.spartan** file. This should be the selected molecule, so place a check mark in the yellow box next to HOMO. Butadiene should now be adorned with its HOMO. Double click on the ethylene molecule to select it and place a check mark in the yellow box next to LUMO. Ethylene should now be adorned with its LUMO. Fill in the second row of the table. Uncheck the yellow box next to LUMO and check the one next to HOMO. Double click on butadiene, unchck the yellow box next to HOMO and check the one next to LUMO. Fill in row three of the table.

"Hey, doc! I'll betcha you wan' us ta continue on in this fashion 'til we fill in all the rows in da table."

"Hey, Rooster, yer smarter than ya sound, but read on."

Write down the total number of π electrons for the *interactive cases*, in order, below:

_6_, _6_, _10_, _10_, ____.

Have you seen this series of numbers elsewhere in this course? If so, where?

4n+2 rule for aromatic conjugated monocyclic π-systems.

Close down Titan.