Name_____

Chem 322 - Organic Chemistry II
Laboratory Exercise – Molecular Modeling – Part 2

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.

Click on the New 🗋 icon (or File|New *via* menu). The Entry Molecule Builder will appear on the right. If you click on an atom type shown on the builder and then click on the green work area, an atom of that type will appear.
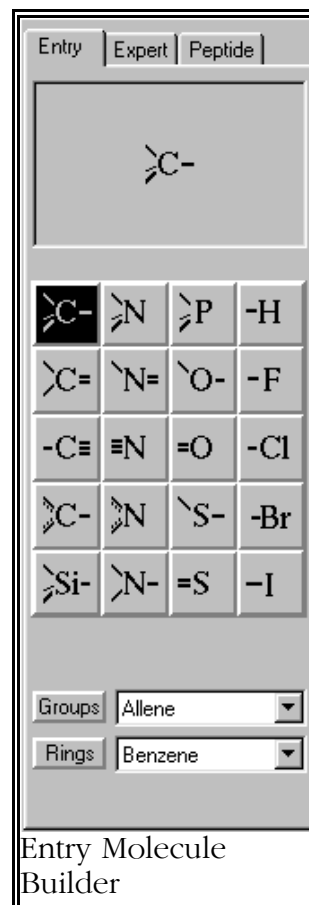
Click on the linear carbon with three free valences on one side and one on the other side -C≡ in the Builder Menu; then click on the green work area and a carbon with one (yellow) free valence on one side and three (yellow) free valences on the other side will appear in wire form. Click on the triple free valence and a second linear carbon is joined to the first through a triple bond. You now have acetylene minus its hydrogens. Click on the Minimize icon ⬇E which will cause hydrogens to become attached at the yellow free valences and will do a molecular mechanics calculation (using an algorithm based on the "MMFF94" force field) to find an energy minimized conformation for the molecule. (This is similar to the "beautify" function in Cache.)

Click on Setup|Calculations.... In the resulting dialog box the top line should have appropriate selections made so it reads – Calculate: Equilibrium Geometry with Hartree-Fock 3-21G(*). The second line should have appropriate selections made so it reads, Start From: MMFF geometry. In other words we are going to calculate the lowest energy (equilibrium) geometry using the Hartree-Fock molecular orbital method employing the so called 3-21G(*) "basis functions." [Basis functions are essentially atomic orbitals. The molecular orbitals will be calculated from these basis functions just as we might form a π and a π^* orbital from two p_z atomic orbitals on adjacent carbon atoms.]

On the Compute: line, check Elect. Charges. On the Print: line, check Orbitals & Energies and Atomic Charges. Click on the OK button to close the dialog box.

Click on Setup|Surfaces. Click on the Add button and select Surface: density and Property: potential; click on the OK button.

We are going to look at all the occupied molecular orbitals in this molecule and the two

Entry	Expert	Peptide

>C-

>C-	>N	>P	-H
>C=	`N=	`O-	-F
-C≡	≡N	=O	-Cl
>C-	>N	`S-	-Br
>Si-	>N-	=S	-I

Groups | Allene
Rings | Benzene

Entry Molecule Builder

unoccupied molecular orbitals of lowest energy. There are 14 electrons in this molecule: each carbon contributes 6 and each hydrogen contributes one. Consequently, there will be 7 occupied molecular orbitals – the seven lowest energy orbitals will each hold two electrons. [This assumes that the two highest energy electrons are not held in a pair of degenerate orbitals, in which case each degenerate orbital would take one electron, by Hund's rule. This would require 8 molecular orbitals.] The seven occupied orbitals are HOMO, the highest (energy) occupied molecular orbital, and HOMO-1 through HOMO-6. Select these options, in turn, from the Surfaces List dialog box by clicking on the Add... button and making the appropriate selections from the menu list using HOMO and HOMO{-}. Then add LUMO and LUMO+1 to the list of surfaces you want Titan to calculate.

Check to be sure all the surfaces you want Titan to calculate are listed in the Surfaces List dialog box. Click on Setup|Submit. A dialog box will ask you for a name for the file; call it acetylene_hf3-21g.spartan. Click on OK and when Titan tells you the calculation has started click on OK. This calculation should not take too long – probably a minute or two depending on the speed of your computer. It is an *ab initio* molecular orbital calculation, which could mean a long calculation time. However, Hartree-Fock is a simple *ab initio* method, the 3-21G(*) basis set is not unduly complex and, most importantly, the molecule is very small, consisting of only four nuclei and 14 electrons.

When Titan tells you the calculation is complete, click on the OK button then on Display|Surfaces if this dialog box is not already open. Click to place a check mark in the yellow box to the left of density ... potential.   You should see a rainbow Easter egg. Click on the red part of the egg and then on Display|Properties. Notice that the potential is negative in the red region. This means that a point positive charge would be attracted to this region of the molecule (energy would decrease; hence the negative sign). Make the potential surface transparent.

What part of the acetylene molecule corresponds to the red region of the potential surface?

Does this make sense?

A hydrogen ion, H^+ is essentially a point positive charge. Draw the structure of the ion that would result if H^+ approached the middle of the acetylene molecule and then became bonded to one of the carbon atoms.

Now click on the blue part of the potential surface (twice).

What part of the acetylene molecule does this correspond to?

What is the sign of the potential now?

What does this mean in terms of the interaction of a point positive charge with this part of the acetylene molecule?

If one looks at the potential surface of ethane, the change in potential along a carbon-hydrogen bond is not nearly so great. Why is the potential difference greater in the case of acetylene? Hint: What is the hybridization of the carbon in acetylene and the carbon in ethane and how does the fraction of s-orbital in the hybrid orbital affect how much the atom attracts electrons?

What can you say about the interaction between a negatively charged species and the hydrogens on acetylene?

Draw the structures of the products of the following reaction:

$$H-C\equiv C-H \; + \; \overset{\oplus}{Na} \quad \overset{\ominus}{:}NH_2 \quad \longrightarrow$$

Remove the checkmark from density ... potential in the Surfaces List dialog box and look at the acetylene molecule. It is quite symmetrical. It contains or has associated with it several *symmetry elements.* One of these symmetry elements is the plane of symmetry that is perpendicular to the triple bond and lies half way between the two carbons, bisecting the molecule. Another symmetry element would be a plane of symmetry that contains all four of the atoms in acetylene – this plane passes through the centers of all four nuclei. Actually there are an infinite number of these planes since all four nuclei lie in a straight line and an infinite number of planes can pass through the same straight line, which is the place where they mutually intersect. There are also

Plane of symmetry bisects triple bond.
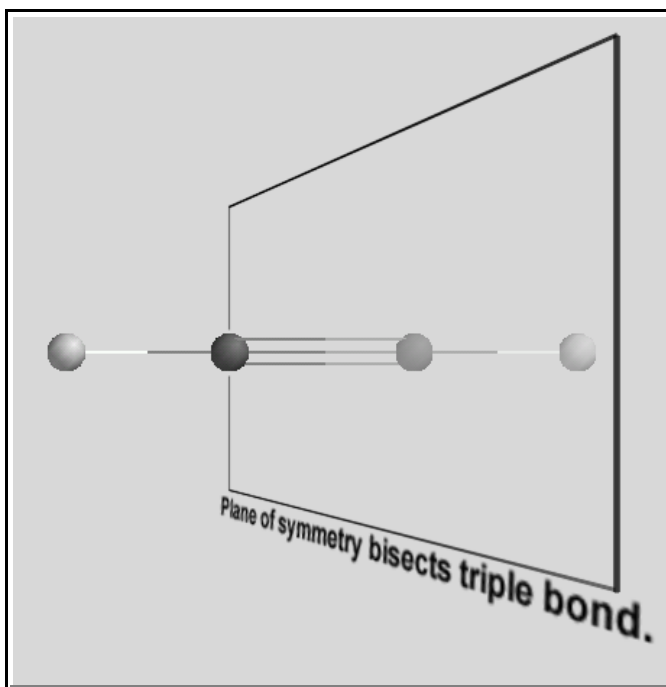
axes of symmetry and a center of symmetry. We will have occasion to consider the planes in a bit because it turns out that if a molecule is symmetrical in some way, the molecular orbitals in that molecule must also reflect that symmetry.

You are aware that molecular orbitals are like waves in that they have amplitudes. And these amplitudes may be positive or negative. If two orbitals are positioned in space in such a way that a positive part of one overlaps a positive part of another, the result will be that they will combine constructively to produce an orbital that is bigger and positive in that region of space. (This is like two hills adding together to make a bigger hill.) The same if true if negative parts overlap except that the resulting orbital will be negative in that region of space. (This is like two valleys adding together to make a bigger valley.) On the other hand, if two orbitals are positioned in space in such a way that a positive part of one overlaps a negative part of another, the result will be that they will interact in a destructive way. (This is like adding a hill to a valley – they wipe each other out.) When Titan shows molecular orbitals places of positive amplitude are red and places of negative amplitude are blue.

Click on the yellow box next to HOMO(-6) in the Surfaces List box. Look at the orbital. Remove the check next to HOMO(-6) and place one next to HOMO(-5).

> With regard to the plane of symmetry that bisects the molecule, what can you say about HOMO(-6)? Is it symmetric (blue reflects onto blue, or red reflects onto red)? Or is it anti-symmetric (blue reflects onto red, or red reflects onto blue)?

> With regard to the plane of symmetry that bisects the molecule, what can you say about HOMO(-5)? Is it symmetric (blue reflects onto blue, or red reflects onto red)? Or is it anti-symmetric (blue reflects onto red, or red reflects onto blue)?

HOMO(-6) and HOMO(-5) look quite similar. They are the same size and shape, but one is symmetric and the other antisymmetric with respect to the bisecting plane. We know that they are the two lowest energy molecular orbitals in the molecule, and since they have the same location, size, and shape, they probably have similar energies. Let's look up their energies. (Remember when you did Setup|Calculations you checked Orbitals & Energies on the "Print" line. Now, we're going to make use of that.) Click on Display|Output. Scroll down until you reach a line that says, "Closed-Shell Molecular Orbital Coefficients." The next line down lists five molecular orbitals (1 through 5) and their "eigenvalues". The eigenvalues are the energies of the orbitals and they are given in atomic units (au) [I know – it doesn't tell you what the units are and it should. You wouldn't make this mistake, right?] and, on the next line, electron volts (ev). MO #1 is HOMO(-6), MO #2 is HOMO(-5), *etc.* While you're here, fill in the table below. You'll have to scroll down to get the molecular orbital energies for #6 through #9.

MO:	1 [HOMO(-6)]	2 [HOMO(-5)]	3 [HOMO(-4)]	4 [HOMO(-3)]	5 [HOMO(-2)]
Eigenvalues [energies, au]					
MO:	6 [HOMO(-1)]	7 [HOMO]	8 [LUMO]	9 [LUMO(+1)]	
Eigenvalues [energies, au]					

Are the energies of HOMO(-5) and HOMO(-6) similar?

Are the energies of these two orbitals similar to the energy of HOMO(-4) or much lower?

Given the size and shape of these *molecular* orbitals and their energy, do you think they might correspond to what we usually think of as the 1s *atomic* orbitals of the carbons (of which there are two, one for each carbon)?

So, what appears to have happened here is that the Titan molecular orbital program has combined the 1s orbital of carbon-1 with the 1s orbital of carbon-2 and come up with two molecular orbitals that occupy the same region of space as the 1s atomic orbitals. If two atomic orbitals are combined to form molecular orbitals, two molecular orbitals must result. [This is the same situation as when two parallel atomic p orbitals on adjacent carbons combine to form π and π* molecular orbitals.]

"But, doc, when ya think of the 1s electrons on the carbons ya got yer two 1s electrons on this carbon and then ya got yer two 1s electrons on that carbon. And the electrons are definitely in two different orbitals 'cause they're on different atoms. But in this picture, all four electrons are located in the same region of space. Now, I know orbitals max out at two electrons and ya say there are two orbitals here, each with two electrons in it. But I don't unnerstand – like don't the orbitals get in each other's way. Like, aren't all four electrons really in the same orbital?"

"Another good point, Rooster. But note that one of these orbitals, HOMO(-6), is symmetric with respect to the plane that bisects the triple bond and the other, HOMO(-5), is anti-symmetric with respect to this symmetry element."

"Uhh, yeah, doc. One of 'em got two blue balls an' the other got one red ball and one blue ball."

"Ummm, that's the idea. Now where the two orbitals are in phase – where the blue ball of HOMO(-6) overlaps that of HOMO(-5) – there is a favorable interaction between the molecular orbitals. However, where the orbitals are out of phase – where the blue ball of HOMO(-6) overlaps the red ball of HOMO(-5) – there is an equal, *but unfavorable*, interaction between the two molecular orbitals. So, the unfavorable interaction exactly cancels out the favorable interaction and the orbitals ignore each other even though they occupy the same region of space. We say that the orbitals are *orthogonal*."

"Orthogonal! Hey, if I work that into a conversation, ya think it'll impress chicks?"

"Never worked for me."

Uncheck the yellow box next to HOMO(-5) in the Surfaces List dialog box and check the one next to HOMO(-4).

> Sketch or describe this orbital.
>
> Is it symmetric or anti-symmetric with respect to the symmetry plane that bisects the triple bond?
>
> Is it symmetric or anti-symmetric with respect to a symmetry plane that passes through the four nuclei?
>
> Is this orbital of the σ-type or π-type?
>
> Is it a bonding orbital and which atoms does it bond together?

Uncheck the yellow box next to HOMO(-4) in the Surfaces List dialog box and check the one next to HOMO(-3).

> Sketch or describe this orbital?
>
> Is it symmetric or anti-symmetric with respect to the symmetry plane that bisects the triple bond?
>
> Is it symmetric or anti-symmetric with respect to a symmetry plane that passes through the four nuclei?
>
> Is this orbital of the σ-type or π-type?
>
> Is it a bonding orbital and which atoms does it bond together?

Click on the surface of this MO and convert it into the mesh format by using the drop-down menu at the bottom right of the screen. Check the yellow box next to HOMO(-4) *without* unchecking the one next to HOMO(-3). Click on the surface of HOMO(-4) and convert it into the transparent format by using the drop-down menu at the bottom right of the screen.

Are HOMO(-4) and HOMO(-3) orthogonal?

Uncheck HOMO(-3) and (-4) in the Surfaces List box and check the yellow box next to HOMO(-2).

Sketch or describe this orbital.

Is it symmetric or anti-symmetric with respect to the symmetry plane that bisects the triple bond?

Is it symmetric or anti-symmetric with respect to a symmetry plane that passes through the four nuclei?

Is this orbital of the σ-type or π-type?

Is it a bonding orbital and which atoms does it bond together?

What is the energy of HOMO(-1)?
What is the energy of HOMO?
Are these orbitals actually degenerate, even though Titan seems to imply that one is of higher energy than the other by calling them HOMO and HOMO(-1)?

Uncheck the yellow box next to HOMO(-2) and check the one next to HOMO(-1).

Sketch or describe this orbital.

Is it symmetric or anti-symmetric with respect to the symmetry plane that bisects the triple bond?

Is it symmetric or anti-symmetric with respect to the symmetry plane that passes through the four nuclei and coincides with the node in this orbital?

Is this orbital of the σ-type or π-type?

Is it a bonding orbital and which atoms does it bond together?

Uncheck the yellow box next to HOMO(-1) and check the one next to HOMO.

Sketch or describe this orbital.

Is it symmetric or anti-symmetric with respect to the symmetry plane that bisects the triple bond?

Is it symmetric or anti-symmetric with respect to the symmetry plane that passes through the four nuclei and coincides with the node in this orbital?

Is this orbital of the σ-type or π-type?

Is it a bonding orbital and which atoms does it bond together?

Do what you need to do to view HOMO(-1) and HOMO at the same time.

Are these two degenerate orbitals orthogonal?

Ignoring HOMO(-6) and (-5), which do not describe valence electrons, how many σ-bonds does Titan say acetylene has?
How many σ-bonds are there in a Lewis structure of acetylene?

Again ignoring HOMO(-6) and (-5), how many π-bonds does Titan say acetylene has?
How many π-bonds are there in a Lewis structure of acetylene?

Optional — Examine the degenerate LUMOs.

Close Titan.