**Chemistry 14CL**

**Worksheet for the Molecular Modeling Workshop**

**(Revised FULL Version 2012 – J.W. Pang)**

**(Modified – A. A. Russell)**

*Structure of the Molecular Modeling Assignment*

The molecular modeling assignment is divided into two sections. The first section is a simple exercise to familiarize you with the Spartan PC software. The second section deals with the dibenzalacetone molecule that you synthesized in the laboratory during the aldol condensation reaction assignment. You will have a chance to examine the three different isomers of dibenzalacetone and investigate their structures and stabilities.

**Note:** You may need to click the "Enable Editing" button before you start typing your responses.

**Question 1**

Write the names of the students in the group. *Put an asterisk beside the name of the student who logged on to the computer*.

***Response:***

****IMPORTANT INSTRUCTIONS – FILE SAVING****

*You cannot save any files constructed on PC Spartan or this worksheet directly on a local computer hard drive. You will need to save all the work on the SLC server in the folder belonging to the group member who logged onto the computer.*

***Instructions for saving the WORD file***

*Use the following filename format when saving the file. Save the file as "MMW_2A_jbruin" where "2A" indicates the lab section and "jbruin" indicates the name (**use only first initial & last name**) of the student who logged on to the SLC computer. "MMW" stands for the "Molecular Modeling Workshop".*

***Instructions for opening Spartan PC 14***

Click on the **START** button at the bottom left-hand corner of the screen. Go to "**PROGRAMS"** and select "**SPARTAN 14"**.

***Resizing Windows***

Resize the PC Spartan window and this document window so you can see both windows at the same time.

***** SECTION 1 (Questions #2 – 8): Practice Example - Study of Acetic Acid ($CH_3COOH$ ) *****

**Question 2**

*Using Spartan PC 14*

In the Spartan window, you should see a blank screen with a series of menu items at the top. Select the **FILE** item with the mouse and then **NEW**. This should bring up a smaller boxed area with a collection of molecular "fragments" on the right side of the screen. You will use this molecular "Tool Box" of pre-drawn elements to draw your structures in this workshop.

*In this question, you will learn how to rotate, move or resize a molecule or molecular fragment in SPARTAN PC.*

**Directions:** Click on the $sp^3$ carbon (four bonds) in the upper left hand corner of the fragment menu. You should now see it in your work area. Move the mouse while holding down the left button of the mouse. Record what happened to the molecular fragment as you move the mouse while holding down the left button of the mouse in the space provided below.

Repeat the similar procedure except now hold down the right button and move the mouse at the same time. Record what happened to the molecular fragment as you move the mouse while holding down the right button of the mouse in the space provided below.

***Response:***

**Question 3**

Now select the $sp^2$ carbon fragment (represented by two single bonds and one double bond) by clicking on it from the Molecular Fragments Tools Menu. Click on one of the yellow lines on the $sp^3$ carbon you selected earlier. You have now connected both the $sp^3$ and the $sp^2$ fragments together. Next, select the double bonded oxygen from the menu and put it on to the double bond on the $sp^2$ carbon that you just added. Now put a single bonded O on to the SAME carbon to form carboxylate group. Finally, select the H atom and add them on to the remaining available bonds. You should now see the molecular model of acetic acid on your screen. Rotate the molecule to look at it in various directions. *Briefly describe the shape of the molecule.*

***Response:***

**Question 4**

From the TOP tools bar, select the button that contains the letter "**E**" with a *DOWN* arrow to minimize the structure. This is a "Molecular Mechanics" procedure that minimizes the strain energy in all the bonds of the molecule. The strain energy should show up at the lower right corner of the screen.

Record the strain energy. If any atoms moved during the minimization process, describe how they moved.

*Note:* During the energy minimization process, the molecule will adjust to the nearest local minimum on a potential energy surface. It also provides an estimate of the strain energy of the molecule in kcal/mole. In most cases, it is necessary to redo the minimization process several times in order to reach a *true minimum*. This is why you may need to minimize the energy more than once. A global minimum (or true minimum) on a potential energy surface corresponds to the most stable form of molecular configuration of the molecule. However, potential energy surface can contain multiple local minimum points before reaching the true minimum or global minimum.

In Spartan PC, the "Strain Energy" refers to the difference in energy between the molecule and its "strain free" analog.

***Response:***

**Question 5**

Return to the upper menu in Spartan and select **FILE** then **SAVE AS**. Use the same procedure as described in question #1 to save the file.

Save the molecule by using the following file name format. For example, if Joe Bruin in Lab 1E is the one who log on to the SLC computer, the file name will be "jbruin_1E_acid". The word "acid" indicates that this is the file for the acetic acid.

Once you save the file, click the **V** button (this closes the builder) and bring you to the **VIEW** mode. At this point your acetic acid molecule should be on the green background. Select **MODEL** from the upper menu and look at the various representations that are possible for this molecule. By using the ball and wire model and the **GEOMETRY** menu item, measure the distance between the acid proton and the carbonyl oxygen.

To Measure Distance:

1. Select **MEASURE DISTANCE** under the **GEOMETRY** menu.

2. Click on the two atoms you wish to measure the distance between. Each atom will turn gold when you select it. Read the distance from the yellow bar at the lower right of the Spartan window. You may need to enlarge this window to make the bar visible. Record the value below.

***Response:***

**Question 6**

Measure one of the bond angles on the methyl carbon.

To Measure Bond Angles:

1. Select **MEASURE ANGLE** under the **GEOMETRY** menu.

2. Click on the three atoms making up the angle you wish to measure. For example, if you want to measure the F-C-H bond angle, click the atoms in this order: F, C, H or H, C, F. Read the bond angle from the yellow bar at the top of the Spartan window.

3. This angle measurement is now completed.

Record this value.

***Response:***

**Question 7**

Measure the bond angle on the carboxylic acid carbon. There are three different choices for this bond angle. Your group should make a note of which angle was being measured based on the atoms that you select to measure the angle. Record this value. Compare this value with the ideal bond angle for $sp^2$ carbons. Explain any differences.

*Please be very careful with the order that you select the atoms to measure the bond angle. When selecting atoms to measure a bond angle, you should always remember to use the standard convention in trigonometry.*

***Response:***

**Question 8**

*Dihedral Angle Measurement*

Dihedral angle refers to the angle between TWO planes. In the case of molecular geometry, you will need to select FOUR atoms (or THREE BONDS VECTORS) in order to define the dihedral angle.

If ALL the atoms in the molecule lie on the same plane, all the dihedral angles should be zero.

To Measure Dihedral Angles:

1. Select **MEASURE DIHEDRAL** under the **GEOMETRY** menu.

2. In the exact order, click on one of the methyl hydrogen atoms, the methyl carbon, the carbonyl carbon, then the carbonyl oxygen. Record the dihedral angle.

3. Record this value. REPEAT the same measurement two more times for the other two methyl hydrogen atoms that you did not select in step 2.

Compare ALL three dihedral angles and explain whether acetic acid is a planar molecule (refer to the definition above). We are now done with acetic acid. Select **CLOSE** under the **FILE** menu.

***Response:***

******** Section 2 (Questions #9-43): Practical Consideration - Study of Dibenzalacetone ********

**Question 9**

*Before your group continues further, your group should SAVE this word file at this point. Close the file and re-open it to make sure that all the contents are saved properly in the file.*

*In this section, you will use molecular modeling to investigate the molecular geometry and the stability of the three different stereo-isomers of dibenzalacetone (one of the isomers is the product that you obtained in the aldol condensation assignment)*

Select **FILE** and **NEW** and build the (trans, trans) isomer of dibenzalacetone. If you don't know how the structure looks like, refer to the lab manual. You may find it easiest to start from the center carbonyl carbon and oxygen and work toward each side. The benzene rings are most easily added as a single group. In the Spartan builder, select BENZENE in the Rings box. Click on the "Rings" button. A benzene ring will appear in the box above the atom buttons. Click on an open valence (yellow bond) in the molecule where you want the benzene to be attached. Continue to built the structure until you complete the molecular model for the (*trans*, *trans*) dibenzalacetone isomer.

*Bond rotation (only work in BUILD mode):*

If you need to carry out a bond rotation when building the molecule in the ***BUILD*** mode, select the bond you want to rotate by placing the cursor on it and click the left button of the mouse. The bond should have a RED ROTATION ARROW symbol on it. Continue with the following step to complete the rotation of the bond. If your computer has a three-button mouse follow direction **(a)**; if your computer has a two-button mouse follow direction **(b)**.

**(a)** Hold down the space bar and the middle mouse button. A RED ROTATION ARROW should appear on the bond. Now move the mouse to 'rotate' the selected bond.

**(b)** Hold down the '**ALT**' key and the left mouse button at the same time. Now move the mouse to 'rotate' the selected bond.

After you have successfully constructed the (trans, trans) isomer of dibenzalacetone, click on the **UPWARD ARROW** button located on the bottom of the screen. The IUPAC name of the isomer should be next to it. A small window will show up. Check the option to see whether "**3-21G**" is selected. If not, change the option to "**3-21G**" and click "**REPLACE**". Close the small window that contains all the options. "3-21G" or "6-31G*" are different basis sets (i.e. mathematical functions) that chemists use to perform molecular computation.

**Note:** If necessary, you can zoom in or zoom out the structure by holding the "SHIFT" key and press the RIGHT button of the mouse at the same time. Move the mouse to enlarge or reduce the size of the molecular structure.

Save the molecule and name the file by using the following format. For example, if Joe Bruin in Lab 1E is the one who log on to the SLC computer, the file name will be "jbruin_1E_isomer0". The word "isomer0" indicates that this is the file for the original isomer **BEFORE** the minimization process. Now, examine the isomer carefully BEFORE you continue the following

steps. Pay special attention to the molecular geometry of the isomer BEFORE the minimization. You should enlarge the molecule (see above) before you continue the following steps.

**MINIMIZE** the molecule (as described in question #4). Click the strain energy button again UNTIL the value stays constant. Record the strain energy. Describe what happened to the molecule as the minimization occurred. If nothing happen to the structure during the minimization process, simply write "No structural change during minimization".

*Please keep in mind that if you rotate ANY bond in the molecule AFTER minimization, you will have to redo the minimization process again.*

*Note:* During the energy minimization process, the molecule will adjust to the nearest local minimum on a potential energy surface. It also provides an estimate of the strain energy of the molecule in kcal/mole. In most cases, it is necessary to redo the minimization process several times in order to reach a *true minimum*. This is why you may need to minimize the energy more than once. A global minimum (or true minimum) on a potential energy surface corresponds to the most stable form of molecular configuration of the molecule. However, potential energy surface can contain multiple local minimum points before reaching the true minimum or global minimum.

Save the molecule and name the file by using the following format. For example, if Joe Bruin in Lab 1E is the one who log on to the SLC computer, the file name will be "jbruin_1E_isomer1". The word "isomer1" indicates that this is the file for the first isomer after the minimization.

***Response:***

**Question 10**

*Now sketch the molecule in your LAB NOTEBOOK as it appears on the screen.*

***IMPORTANT: During the workshop, you will be asked to measure bond distance & angles for the isomer. Make sure one of your group members record all the bond distances & bond angles in the lab notebook as well.***

Click on the **V** button to exit the build mode and examine the shape of the molecule. What is the C-C-C bond angle on *the carbonyl carbon*?

*Please be very careful with the order of the carbons that you select to measure the bond angle.*

***Response:***

**Question 11**

Select **SPACE-FILLING** under the **MODEL** menu. Based on this view of the molecule, explain what interactions may cause the C-C-C angle you measured previously to differ from the ideal bond angle for $sp^2$ carbons.

***Response:***

**Question 12**

Select **BALL AND SPOKE** under the **MODEL** menu. What is the bond angle on the olefin carbon (sometimes also refer to as the alkene carbons) atom *adjacent to the carbonyl carbon*?

*Note: You may measure the olefin carbon bond angle by choosing an olefin carbon located adjacent to either side of the carbonyl carbon.*

***Response:***

**Question 13**

Again, examine the space-filling model and discuss what interactions may cause the previously measured angle to differ from the ideal bond angle for $sp^2$ carbons.

***Response:***

**Question 14**

What is the bond angle on the olefin carbon *adjacent to the phenyl ring*?

*Note: You may measure the olefin carbon bond angle by choosing an olefin carbon located adjacent to either side of the phenyl ring.*

***Response:***

**Question 15**

Explain why the previously measured angle differs from the ideal bond angle for $sp^2$ carbons.

***Response:***

**Question 16**

Now examine bond distances. What is the length of the carbonyl (C=O) bond?

***Response:***

**Question 17**

What are the lengths of the two olefin (C=C) bonds located adjacent to the carbonyl carbon?

***Response:***

**Question 18**

What is the average length of the C=C bonds in the phenyl ring? You will need to examine all of the C=C bonds in the phenyl ring in order to answer this question. Again, make sure one of your group members recorded all these information in the lab notebook.

*Note: You only need to examine the C=C bonds for ONE of the phenyl rings.*

***Response:***

**Question 19**

Explain why the carbonyl bond length differs from the olefin bond lengths.

***Response:***

**Question 20**

Explain why the carbon-carbon double bond lengths in the phenyl ring differ from the carbon-carbon double bond lengths (i.e., olefin carbons) outside of the ring.

***Response:***

**Question 21**

What is the length of the single bond between the carbonyl carbon and the adjacent olefin carbon?

Note: You may measure the carbon single bond located adjacent to either side of the carbonyl carbon.

***Response:***

**Question 22**

The average length of a carbon-carbon single bond is 1.54 Å. Explain why the bond length that you measured in the previous question differs from this value?

***Response:***

**Question 23**

What is the average carbon-hydrogen bond length on the phenyl ring? You will need to examine all the C-H bonds distance in the phenyl ring before you can answer this question.

*Note: You only need to examine the C-H bonds for ONE of the phenyl rings.*

***Response:***

**Question 24**

What is the CLOSEST distance between a hydrogen atom in the molecule and the carbonyl oxygen? *You may need to check a few measurement before you can find the closest distance.*

***Response:***

**Question 25**

Is this hydrogen atom bonded to an olefinic or phenyl carbon atom?

***Response:***

**Question 26**

The average O-H alcohol bond length is 0.96 Å, and the oxygen-hydrogen bond distance when hydrogen bonding occurs is 2.07 Å. Discuss whether intra-molecular hydrogen bonding is likely to occur in your molecule.

***Response:***

**Question 27**

Examine the molecule. Is your isomer a planar molecule (i.e. *ALL atoms in the molecule MUST position on the same plane*)? You will need to rotate the molecule and examine the positions of all the atoms in the molecule.

Use the same instructions outlined in question #8 and check for the dihedral angles to confirm whether the molecule is in fact planar. For the two sets of olefin carbons and phenyl rings in the molecule, measure the dihedral angle by selecting the C=C (olefin) atoms and the C=C (phenyl)

atoms located on one side of the molecule. The FOUR atoms that you select MUST BE CONNECTED in a continuous order in the molecule. Record this value. Repeat the same procedure and record the dihedral angle on the other side of the molecule. Do the dihedral angles confirm the "observation" that you did earlier in this question about the molecular geometry (i.e. planar to not planar)?

***Response:***

**Question 28**

If the previous answer is "YES", discuss *why* this is the most stable configuration for this question.

If the previous answer is "NO", type "Not Planar" as your response for this question and proceed to question #29.

***Response:***

**Question 29**

*If your answer for question #27 is "YES", type "PLANAR" and continue to the next question.*

Using *only* the knowledge of basic molecular geometry, explain whether the non-planar structure a reasonable molecular representation for the (trans, trans) dibenzalacetone in its most stable configuration? Explain your reasoning.

***Response:***

**Question 30**

You will now calculate various energies for the molecule. Under the **SETUP** menu select **CALCULATION**. The title of the molecule can be anything you want. Under **CALCULATE** select **ENERGY** (GROUND STATE) with Semi-Empirical and PM3. The other options, which are the default conditions, should not need to be changed. Check that the following conditions are set and then select **OK**.

**Total Charge: 0 (or Neutral); Multiplicity: Singlet**

***Note:*** Multiplicity refers to the spin multiplicity (2S+1) and is related to spin quantum number (S). For a molecule with NO UNPAIRED electrons, the value of "S" is zero. Therefore, the multiplicity is equal to one (or singlet). Semi-empirical method is a quantum mechanical computational method. PM3 is a method that is commonly used within the semi-empirical computational model.

None of the other boxed areas should have check marks (**except** for the "SYMMETRY" option). The **OPTIONS** box should be empty. Return to the **SET-UP** menu and click **SUBMIT**. In about 15 seconds (may be longer depending on the speed of the computer processor and the molecular geometry) another box should appear saying the job has been completed. Go to the **DISPLAY** menu choice. Select **OUTPUT** to obtain the heat of formation (or standard enthalpy of formation) for this particular isomer of dibenzalacetone (i.e. $\Delta H_f°$ product).

**Note:** This is NOT to be confused with the standard enthalpy of reaction ($\Delta H°$).

$\Delta H° = \Sigma(c \times \Delta H_f°)$ (products) - $\Sigma(c \times \Delta H_f°)$ (reactants) where "c" corresponds to the stoichiometric coefficient used in the standard enthalpy of reaction.

You may have to scroll down the screen in order to find it since the output file contains a lot of information in addition to the heat of formation value. Record this value including its unit.

Keep a record of this value in your lab notebook as well.

***Response:***

**Question 31**

Congratulations. You are now ready for the next molecule.

Close the current file. Open the "isomer0" file that your group saved earlier. You will modify the original isomer before minimization to create the (cis, trans) dibenzalacetone isomer.

**Before** you modify the original structure to a different isomer, click on the **UPWARD ARROW** button located on the bottom of the screen. The IUPAC name of the isomer should be next to it. A small window will show up. Check the option to see whether "**3-21G**" is selected. If not, change the option to "**3-21G**" and click "**REPLACE**". Close the small window that contains all the options.

Select **BUILD** from the top menu, and then **ADD FRAGMENT**. Since the next isomer you will now draw involves a change of groups around one of your double bonds, the easiest procedure is to rotate around the double bond. (This is not physically possible but we can do this on the computer!) To carry out this rotation (ONLY WORK IN BUILD MODE), select the appropriate double bond that you want to rotate and click the left button of the mouse. A small red arrow should show up around the bond you just clicked. If your computer has a three-button mouse follow direction **(a)**; if your computer has a two-button mouse follow direction **(b)**.

**(a)** Hold down the space bar and the middle mouse button. A rotation arrow should appear on the bond. Now move the mouse to 'rotate' the phenyl group from one side of the double bond to the other side.

**(b)** Hold down the '**ALT**' key and the left mouse button at the same time. Make sure that the selected bond has a rotation arrow surrounding the bond; otherwise, Spartan PC won't allow you to rotate the bond. This should give you the new isomer. Now move the mouse to 'rotate' the phenyl group from one side of the double bond to the other side.

Now, examine the isomer carefully BEFORE you continue the following steps. Pay special attention to the molecular geometry of the isomer BEFORE the minimization. You should enlarge the molecule (see above) before you continue the following steps.

As before, **MINIMIZE** the molecule and record the strain energy. Describe what happened to the molecule during the minimization process. If nothing happen to the structure during the minimization process, simply write "No structural change during minimization".

Save the molecule and use the word "isomer2" in the file name to indicate this file is for isomer#2 after the minimization process.

***Response:***

**Question 32**

Click on the **V** button to exit the builder. Describe the geometry of this molecule and its energy. In your report, record the bond angles for the C-C-C carbonyl and olefin carbons and the bond distances for the carbonyl and olefin bonds. Again, all the numerical information (i.e. the heat of formation, bond distances and angles) that you obtained so far should also be recorded in the lab notebook.

***Response:***

**Question 33**

We will now investigate the planarity of the molecule by measuring two sets of dihedral angles in the molecule. For the two sets of olefin carbons and phenyl rings in the molecule, measure the dihedral angle by selecting the C=C (olefin) atoms and the C=C(phenyl) atoms located on one side of the molecule. The FOUR atoms that you select MUST BE CONNECTED in a continuous order in the molecule. Record this value. Repeat the same procedure and record the dihedral angle on the other side of the molecule.

*Note: Dihedral angle refers to the angle between TWO planes. This is the reason why you need to select FOUR atoms in order to define the orientation of the two planes. If all the atoms in the molecule lie on the same plane, the dihedral angle is zero. Please be careful with the order of the carbon atoms that you click to find the dihedral angle.*

***Response:***

**Question 34**

Discuss the cause of the dihedral angles in (cis, trans) dibenzalacetone.

***Response:***

**Question 35**

Calculate the Heat of Formation for this molecule as described in Question #30? Record this value in your lab notebook as well. You should also notice the correct IUPAC name is now listed on the bottom of the screen.

***Response:***

**Question 36**

Close the current file. Open the "isomer0" file that your group saved earlier. You will now modify the original isomer before minimization to create the (cis, cis) dibenzalacetone isomer.

**Before** you modify the original structure to a different isomer, click on the **UPWARD ARROW** button located on the bottom of the screen. The IUPAC name of the isomer should be next to it. A small window will show up. Check the option to see whether "**3-21G**" is selected. If not, change the option to "**3-21G**" and click "**REPLACE**". Close the small window that contains all the options.

Do not minimize the (cis, cis) dibenzalacetone isomer yet. Save the molecule and use the word "isomer3" in the file name to indicate this file is for isomer#3.

Click on the **V** button to exit the builder. Select **SPACE FILLING** under **MODEL**. Describe the shape of the space-filling model of this un-minimized structure.

***Response:***

**Question 37**

Measure the distance between the two hydrogens (*within the SAME phenyl ring*) in the ortho (i.e. the 1,2 position) position on *each* of the phenyl ring in the molecule.

Repeat the same measurements for the two hydrogen atoms (*within the SAME phenyl ring*) in the meta (i.e. the 1,3 position) positions on *each* of the phenyl ring.

***Response:***

**Question 38**

Examine the isomer very carefully BEFORE you continue the following steps. Pay special attention to the molecular geometry of the isomer BEFORE the minimization. You should enlarge the molecular structure before you continue the following steps.

Minimize the molecule. Record the strain energy for this isomer and describe what happened to the molecule during the minimization process.

If nothing happen to the structure during the minimization process, simply write “No structural change during minimization”.

Re-save the molecule and use the word "isomer3" in the file name to indicate this file is for isomer#3.

***Response:***

**Question 39**

Follow the same direction as in question #37, measure the distance between the two hydrogen atoms in the ortho positions, and the two hydrogens in the meta positions on each of the phenyl ring.

***Response:***

**Question 40**

Compare the two intramolecular distances before and after minimizing the structure (questions 37 & 39). Explain the differences.

***Response:***

**Question 41**

Explain the shape of isomer3 (i.e. why did the minimization cause the molecule to have this particular geometry?).

***Response:***

**Question 42**

Calculate the Heat of Formation for this molecule as described in Question #30? Record this value in your lab notebook as well. You should also notice the correct IUPAC name is now listed on the bottom of the screen.

***Response:***

**Question 43**

Compare and explain why the heat of formation (questions#30, 35 and 42) and the strain energy (questions #9, 31and 38) differ in the three isomers.

***Response:***

Congratulations: You have completed the molecular modeling assignment activity. Send a copy of this report to your TA for grading.. You should also send a copy to yourself and your partner for use in studying for your exams. You do not need to print the **report**; you may submit it electronically.

Before exiting PC Spartan, **you DO NEED to print copies of each of your dibenzalacetone isomers** to include with your written notebook report.