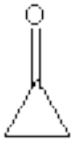
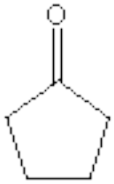
AROMATIC RESONANCE EFFECTS IN CYCLIC KETONES

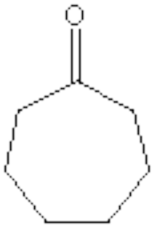
Goal: In this experiment, you will use computational chemistry to probe the effects of aromaticity upon bond strengths and lengths. The vibrational spectral frequencies for a variety of cyclic ketones will be predicted using molecular orbital methods, and the trends in bond length and C=O stretching frequency will be compared to expectations based on resonance theory and aromaticity models. If you wish you may work in groups of two or three, and share the results of your computations (for example you may do calculations for two or three of the molecules and then share the results with three or two other people. Discuss the results amongst yourselves, but each person must write up and submit his or her own report, written in his or her own words.

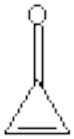
For the calculations, use the SPARTAN computer program (Wavefunction Inc.) on the PCs in the CRC. If you need a refresher on the use of SPARTAN, refer to the tutorials from the previous modeling experiments, alkenes and nitration.

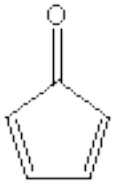
Procedure: log in and launch Spartan. The main Spartan menu will appear, with a set of menu choices and a blank screen. For every structure shown, carry out the following set of steps:

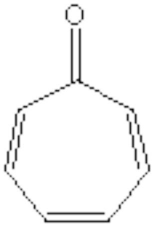












- Click on "File"-"New" to get the Builder Menu

- Build the desired molecule using appropriate molecular fragments. Note that for some molecules, before connecting the next fragment or closing a ring, you may have to rotate a bond to get the atoms in the approximately correct positions. Otherwise, undesired, strange-looking geometries may result (e.g., for rings, cis-, not trans- double bonds are desired). Also as you are building a ring, some atoms may overlap and make building difficult. Rotating a bond will help here as well. To rotate a bond, select the bond by clicking once on it with the left mouse button, then, holding down the alt key and the left mouse button, move the mouse to obtain the desired rotation.

Example: to make cyclopropenone, first make the C=O (under groups, choose carbonyl, then click in the builder window). Attach an sp2 carbon to each side of the carbonyl. If necessary, rotate the sp2 carbons so both double bonds are facing away from the oxygen. Connect the ends of the double bonds to make the ring (Build, make bond, click on each end of the double bond fragments). Minimize (under Build). This should result in an approximately correct geometry. With all of the structures always apply the test of reasonability - see if what you made after minimization looks like a reasonable geometry. If not, try rebuilding the molecule, connecting atoms in a slightly different order or with bonds rotated slightly differently.

- Click on "File"-"Save" and give the file a name by clicking in the file box section.

- Click on "Setup"-“Calculations” and choose "Semiempirical - AM1”. Start from: MMFF. On “Compute” click on IR and under Print, Vibrational Modes and Atomic Charge. (Other values that should be the default settings are Ground State and Symmetry.

- Click on "Submit" to begin the job run. Most of these calculations will take less than a minute or so.

Data to Record. For each molecule, after the calculation has finished, record the following data:

- Click on "Geometry"-"Measure Distance" in the Main Menu, then click on the middle of the C=O bond for each molecule and record the bond length r(C=O) in angstroms (Lower right). Click on Geometry, Measure Distance again to turn this off.

- Click on "Display"-"Properties" and record the dipole in Debyes. Keep this window open.

- Click on the O atom of the C=O bond and record the Mulliken charge. Click on the O again then on the C of the C=O bond and record that charge.

- Click on "Display"-"Spectra". (If necessary, move the window away from the molecule so the molecule is visible.) Find the carbonyl stretching frequency by alternately selecting a number in the menu that appears. This will visualize the vibration for that frequency. Check out different models (ball and spoke, space-filling, etc). Record the C=O stretch frequency in wavenumbers. Note that frequencies calculated with this method are at least 15% larger than experimental values.

When finished with each molecule, select file, close, then file open to build the next molecule.

Analysis. Recall the Hückel rule concerning the number of electrons that yield aromatic or pseudoaromatic properties in a cyclic, conjugated system. This rule holds both for neutral and charged cyclic systems. Some of the molecules on which you have carried out calculations can be drawn with resonance structures that conform to the Hückel rule. Some resonance structures that you draw may not correspond to simple expectations for stable Lewis structures, but they will be appropriate for the Hückel rule.

For each molecule, draw charge separated and/or neutral resonance structures (as appropriate) that you think best realistically represent the electronic structure as computed. Note that it is very unusual to get a full (+) or (-) charge in the Mulliken analysis, but you may see trends in the charge density which support resonance structures that have more charge separation in some cases.

Based upon the best resonance structure which you choose for each molecule, decide whether the computed C=O stretching frequency is consistent with that resonance structure, by comparing it to the analogous frequency for the corresponding saturated molecule. For example, if you think that any of the molecules favor a C-O (single-bond) containing resonance structure, what do you expect would happen to the computed C=O frequency, by comparison to a molecule with a strong C=O double bond?

Briefly discuss whether you feel the computed results support the Hückel model of pi-electron structure, or contradict it, or show no definite trend.

Some background. In addition to Hückel effects, carbonyl stretching frequencies are sensitive to several other factors, one of which is ring strain. For the cycloalkEnones it is therefore most useful to make comparisons between molecules having the same ring size. For the cycloalkAnones, with the

Hückel effect removed, one can observe the effect of ring size on frequency. The carbonyl stretch of acetone and cyclohexanone occurs at about 1715 cm-1. Because these are unstrained, non-conjugated molecules, this is considered to be the "normal" stretching frequency of a ketone. Comparisons can therefore be made to this "standard" value.

Experimental frequencies for some cyclic alkenones are as follows:

Cyclopropenone -- 1840 cm-1
Cyclopentadienone -- 1870 cm-1
Cycloheptatrienone -- 1651 cm-1

For comparison, find the exp'l C=O stretching frequencies of the saturated structures from the library. One good source is the Aldrich Library of Infrared Spectra. A web search may also produce useful data. Note though that frequencies are also sensitive to other factors such as physical state (e.g., gas phase vs solution vs pure), so comparisons must be made carefully.

Briefly discuss how these experimental results compare with your computed results (absolute numbers and relative trends), and how they compare with expectations from the Hückel model. For such calculations consider trends to be more important than close agreement of the actual values. How do the dipoles, charges and bond lengths fit into the story?

Things to consider: How is energy related to frequency? All else being equal, how should bond order (single/double) affect length and strength of a bond?

This exercise was written by Paul Lahti and tweaked a bit by Peter Samal.

<u>Hints</u>: See Wade, Problem 16-15. What does the Huckel rule tell you? What are the two major resonance structures (RSs) for a carbonyl group? For the compounds examined, in which cases does one of the RSs contribute more than normally and why? How can these ideas be tested with calculations? If a bond has more or less single bond or double bond character how will this affect the bond length? - the charges on the C and O? - the dipole moment? - the C=O stretching frequency (is it easier to stretch a C=O or C-O and how would this relate to stretching frequency?) How do these trends go along with the idea of the Huckel rule and RSs? How well do the calculations agree?

(revised 3/08)