

Announcements

- 1) Next Week's Lab: Experiment #10 Molecular Modeling
Go directly to 111C for lab next week.
New Due Date: Mon./Tues. Sept. 20/21
- 2) Always come to the lab dressed appropriately
- 3) Class website: Announcements, Lecture Notes, Schedule (revised),...
Department of Chemistry: <http://www.uiowa.edu/%7ec004141a/>
- 4) No lab on Monday, September 6th and Tuesday, September 7th

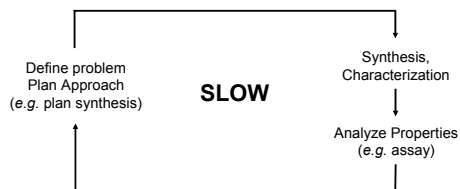
Experiment #10:

Molecular Modeling: Aromatic Resonance Effects in Cyclic Ketones

- Purpose: use computational chemistry to probe the effects of strain and aromaticity upon bond strength and length of the C=O group in cyclic ketones
- you will:
 - 1) predict vibrational spectral frequencies for a variety of cyclic ketones
 - 2) compare the trends in bond length and C=O stretching frequency to expectations based on resonance theory and aromaticity
- Note: Experiment #10 is conducted using PCs in 111C CB. You will work in pairs and can work at any computer and any time outside laboratory hours.

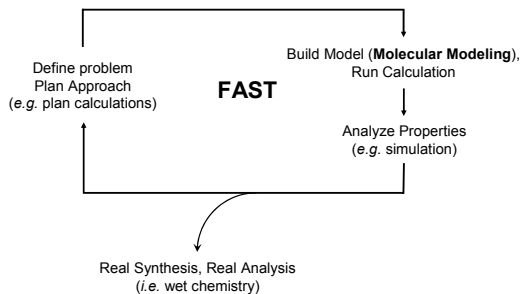
Wet Chemistry

Wet Chemistry



Computational Chemistry

Computational Chemistry



Why Do Molecular Modeling?

Reasons:

- 1) Can be faster
- 2) Environmentally-friendly
- 3) Lower cost
- 4) Safer
- 5) Can study unstable molecules and transition state
- 6) Provides detailed analyses

.... what is molecular modeling useful for.....?

Common Tasks of Molecular Modeling

- 1) Calculate the energy of a particular geometry (single point energy)
- 2) Find LOWEST ENERGY geometry (geometry optimization) *
- 3) Calculate properties (e.g. bond lengths, bond angles, charges) *
- 4) Find transition state in reactions (mechanisms)
- 5) Determine product distributions in reactions
- 6) Determine intermolecular interactions (e.g. drug-enzyme)

The ENERGY of a molecule depends upon its GEOMETRY!

....what is the basis of the calculation?....

The Calculation

Largely Based on Quantum Mechanics (Molecular Orbital Methods):

Ab Initio:

- * accurate but relatively slow, computationally 'expensive'
- * solves the energy of the Schrodinger Equation

$$E\Psi = H\Psi$$

E = energy, Ψ = position, mass, velocity, H = Hamiltonian function

Semi-Empirical:

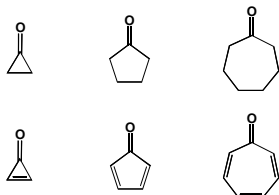
- * solves Schrodinger Equation but uses experimental data (parameters)

Molecular Mechanics:

- * 'ball-and-spring' calculation, very fast and cheap

Our Calculations

Cyclic Ketones

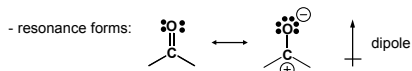


Study C=O functionality in terms of: 1) vibrational frequency and 2) bond length

Why? C=O group is sensitive to environment (neighboring bonds), so systematic changes to environment should provide insight into nature of C=O bond

The Carbonyl Group

- C=O \rightarrow C atom (sp^2 hybridized) and O atom (sp^2 hybridized)
- typical C=O and C-O bond distances are 1.21 Å and 1.43 Å, respectively



- C=O vibrational frequency (IR spectroscopy): 1710 – 1740 cm^{-1}

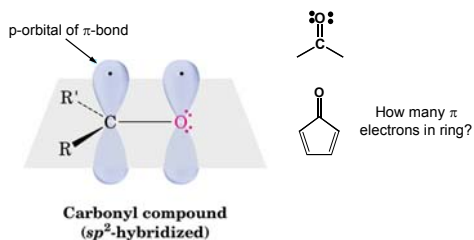
$$\nu = \frac{1}{2\pi c} \sqrt{\frac{f(m_1+m_2)}{m_1 \times m_2}}$$

ν = frequency (cm^{-1})
 f = force constant (stiffness) (dyne/cm)
 c = velocity of light (cm/s)

- f is approximately 5×10^5 dyne/cm for single bonds, and approximately two and three times this value for double and triple bonds, respectively

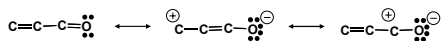
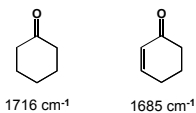
(i.e. f is directly proportional to bond strength)

Orbital Picture of C=O Group



What Factors Influence Stretching Frequency of C=O Group?

1) Conjugation (i.e. alternating single and double bonds) with a double bond or aromatic ring lowers stretching frequency



Aromaticity

- a molecule is aromatic only if it has a planar, monocyclic system of conjugation with a total of $4n+2$ π electrons, where n is an integer ($n = 0, 1, 2, 3, \dots$) (Hückel $4n + 2$ rule)

- aromatic: 2, 6, 10, 14, 18... π electrons
- antiaromatic: 4, 8, 12, 16... $4n$ π electrons, planar
- not aromatic: 4, 8, 12, 16... $4n$ π electrons, not planar

Examples:

1) cyclobutadiene two double bonds, planar
four π electrons antiaromatic

2) benzene three double bonds, planar
six π electrons aromatic

- **NOTE:** presence of aromaticity lowers C=O stretching frequency -

2) Incorporation of C=O group into a small ring (3-, 4-, or 5-membered) raises the stretching frequency



1715 cm^{-1}

120°



1748 cm^{-1}

108°



1783 cm^{-1}

90°



1850 cm^{-1}

60°

(sp^2 hybridized;
33% s-character)

atoms of C=O sigma bond exhibit greater s-character (more sp-like) \longrightarrow
(C=O is therefore shorter and stronger)

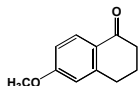
- Recall: for C-C=C-C, atoms C2 and C3 are sp hybridized (50% s-character) -

3) Changing an alkyl substituent of a ketone for an electron donating or withdrawing group lowers and raises frequency, respectively

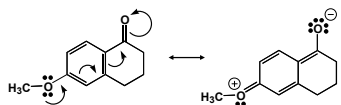
- particularly important when an alkyl substituent is replaced by a hetero atom such as N, O, or X (halogen)



1683 cm^{-1}



1674 cm^{-1}



Procedures and Precautions

General

1) Build molecule using the model builder of Spartan

Note: will have to learn the basics of building

Note: geometry must be minimized for each molecule

2) Calculate geometry using semi-empirical (AM1) methods

3) Record data from calculated structure

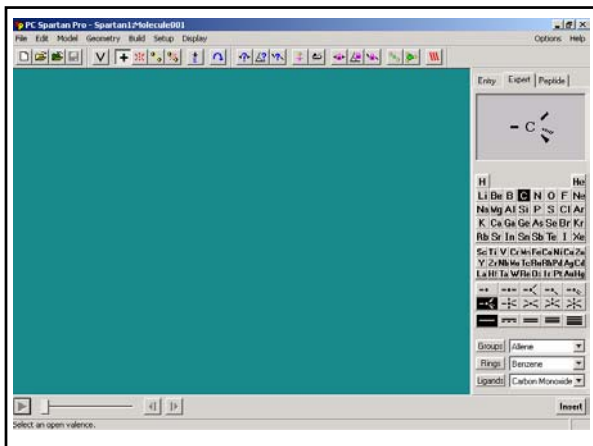
- required data: i) energy of molecule

ii) C=O stretching vibration

iii) C=O bond length (angstroms)

iv) direction of dipole moment (negative end)

v) charges (Mulliken) for C and O atoms of C=O group



Results and Discussion

Present Data in Table Format:

Molecule	Energy (kcal/mol)	Bond Length (Å)	Direction of Dipole	Charges	
				Carbon	Oxygen

(example of Table given on website)
