XNH_2 + (aniline, NH_3^+) → XNH_3^+ + (aniline, NH_2)

Molecular Modeling
for Organic Chemistry

R— (allyl) →[NBS] R—(Br) + R—(Br)
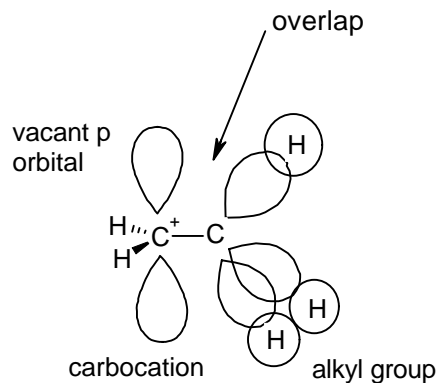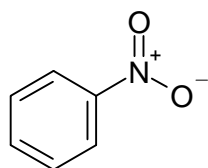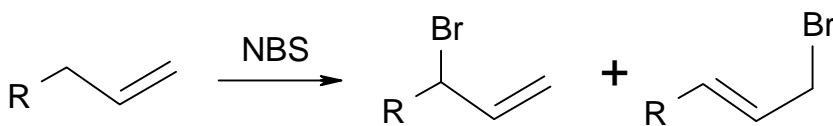
Thomas K. Green
Department of Chemistry
University of Alaska Fairbanks

overlap

vacant p orbital

H

$H\cdots C^+ — C$

H

carbocation

H

H

alkyl group
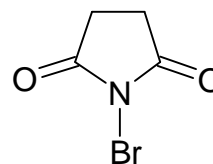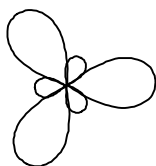
Many of the experiments in this manual were adapted from Warren Hehre's excellent book "Experiments in Computational Organic Chemistry" and from the HyperChem manual "Getting Started".

HyperChem Experiments

Introduction

Welcome.

This manual is an introduction to the HyperChem computer program, a simulation software that will allow you to build models for different organic compounds. From these compounds you will be able to measure different molecular attributes, such as bond angles and heats of formation, that will allow you to make inferences about molecular stability and reactivity. Using HyperChem can be a welcomed supplement to the sometimes arduous laboratory work inherent to chemistry. In fact, building and manipulating molecules can actually be fun.

As foreshadowed by the introductory quote, most of the skills necessary for successful completion of the experiments included in this manual will be obtained on your own. You will learn how to build, manipulate, and make calculated inferences about assigned organic molecules mainly from trial and error. This manual has been designed to allow for flexibility in the assignment of experiments in an attempt to coordinate lab assignments with material covered in lecture, and the experiments will be assigned in such a way that skills learned in early assignments will be used in later ones.

Energy minimization

HyperChem is a powerful computational software package that is capable of examining potential energy surfaces of molecules. HyperChem can perform an energy minimization (or geometry optimization) of a molecule using a variety of computational methods. Both molecular mechanics and semi-empirical methods are available. Energy minimization alters the geometry or shape of a molecule to lower the potential energy of the molecule and to yield a more stable conformation. As the minimization progresses, it searches for a structure in which the energy does not decrease with infinitesimal changes in geometry. At this point, the conformation is relatively stable, and is referred to as a *minimum* (Points A and C on the potential energy contour map below). If the energy lowers by small changes in one or more dimensions, but not in all dimensions, it is a *saddle point* (Point B). A molecular system can have many minima. The one with the lowest energy is called the *global minimum* (Point C) and the rest are referred to as *local minima* (Points A and B).

Other important terms:

gradient

The derivative of the energy with respect to all Cartesian coordinates. You will see the gradient on the bottom of the HyperChem screen as calculations are being carried out. As a default, the program must achieve a gradient of 0.1 kcal/Å mol or less before calculations will stop. This gradient can be changed by the user.

convergence

This means that the default convergence criterion (or the criterion that you set) has been met. If the calculation has converged, it will read CONV=YES at the bottom of the screen. If it says CONV=NO at the end of the calculation, the molecule has not been minimized.

single point calculation

This is a calculation to obtain the total energy of the unoptimized structure (without geometry optimization).

Getting Started

Preliminary Assignment: It is strongly advised that you obtain the HyperChem manual called "Getting Started" and work through at least Lessons 1- 5, pp 17-75. This work should be done before you actually work formal assignments in order to save you a lot of frustration.

Opening HyperChem: Getting into the HyperChem executive file is straightforward. It can be accessed from any computer in the Chemistry Department Computer Lab 172.
.

Caution: The Chemistry Department has a 10-user license and you will be locked out of the program if you are the eleventh user!

Gas Phase versus Liquid Phase

Molecules created using HyperChem are present in the gas phase (under default conditions). In the laboratory, such as those encountered in organic chemistry, most reactions are carried out in the liquid state. While the difference in phase may seem like a trivial fact, it has great significance in many of the deductions you can make, since solvents can affect the energy, conformation, and the reactivity of a molecule.

Equilibrium Constants

In some of the experiments that follow you will be ask to calculate the enthalpy changes, $)$H, for a reaction or a conformational change. Organic chemists often assume that enthalpy changes for a reaction are approximately equal to the free energy changes ($)$G. $)$H). This approximation assumes that the entropy change, $)$S, for a reaction is small or zero or that the temperature is low enough that the T$)$S is small. We must be cautious in making this assumption since some reactions have large changes in entropy.

During some of the experiments, you will be expected to use some simple thermodynamic equations. It may be helpful if you are reminded of the equation relating free energy (ΔG) to the equilibrium constant, K_{eq}

$$DG=-RT\ lnK_{eq}.$$

R is the gas constant with a value of 1.987 cal K^{-1} mol^{-1} and T is the temperature in Kelvin. HyperChem cannot calculate $)$G but it can calculate $)$H for a reaction. Again, if we assume that $)$G . $)$H, we can then calculate the K_{eq} for the process or reaction.

HyperChem Input Files

Once you have built a structure in HyperChem, you can save it for later use. This is a good idea since it saves you time if you want to re-examine your structure at a later date. Why build it twice?! You can do this by going to File and Save. You must give it a name like cyclo.hin. The file can be recalled for visualizaiton and manipulation at a later time.

Log Files

On some experiments you will ask to keep a log file. A log file records the results of your calculations in the form of a text file. It contains the heat of formation of your molecule, among other parameters. There are two approaches to the log file.

Saving Manually: To start a log file, go to File and then Start Log. You will given a choice as to where to place your log file. Choose to put it in C:/Hyper directory. It can be retrieved for later use. Also, you will need to give your file an appropriate name, such cyclo.log or whatever. After Start Log, go ahead and perform the geometry optimization on your molecule. After the calculation is complete, choose File and then Stop Log. You can then go to any text editor such as Word or Word Perfect and retrieve the log file. Usually, you will want to scroll down and find the Heat of Formation. Your *.log file can be saved on a floppy just like the *.hin file.

Butane Analysis

Goal: To minimize the energy of butane's conformations using the MM+ force field.

Background: Energy minimization alters the geometry of a molecule to lower the energy of the system and to yield a more stable conformation. As the minimization progresses, it searches for a molecular structure in which the energy does not change with infinitesimal changes in geometry. This means that the derivative of the energy with respect to all Cartesian coordinates, called the ***gradient***, is near zero.
This is known as a ***stationary point*** on the potential energy surface.

If small changes in geometric parameters raise the energy of the molecule, the conformation is relatively stable, and is referred to as a ***minimum***. If the energy lowers by small changes in one or more dimensions, but not in all dimensions, it is a ***saddle point***. A molecular system can have many minima. The one with the lowest energy is called the ***global minimum*** and the rest are referred to as ***local minima***. By calculating the energies for six stationary points of butane, one can compare the values to determine the global minimum energy conformation.

Procedures

Choosing the Force Field

Before you build butane and perform a molecular mechanics optimization, you should choose a molecular mechanics force field provided with HyperChem.

A force field contains atom types and parameters that must be assigned to the molecule before you perform a molecular mechanics calculation. For this exercise, you use the MM+ force field.

To choose the force field:

1. Choose Molecular Mechanics on the Setup menu
2. When the dialog box appears, choose MM+.

Building Butane

The first form of Butane you build is an eclipsed form where the CCCC dihedral angle is $O^{0.}$

To build this eclipsed form:

1. Set the Default Element to carbon and get into drawing mode.

2. Set the select level to Atoms.
3. Choose Labels on the Display menu and label the atoms by number.
4. Make sure Explicit Hydrogens is turned off on the Build menu.
5. Draw the 2D structure by clicking and dragging so that four carbons are connected together.

6. Choose Add H & Model Build on the Build menu.
   The Model Builder builds the anti conformation of butane as the default structure, where the CCCC dihedral angle is 180^0. You want to change this angle to O^0. To do so;
7. Get into selection mode.
8. Make sure Multiple Selections is turned on.
9. Select the four-carbon torsion angle by selecting 1-2, 2-3, and 3-4 bonds in that order.
10. Choose constrain Bond Torsion on the Build menu, and set the constraint to 0 degrees, and then choose OK.
11. R- click on an empty area of the work space.
12. Double-click on the Selection tool to invoke the Model Builder. HyperChem rebuilds the structure with the torsional constraint.

Optimizing the Structure

The next step is to minimize the structure by performing a molecular mechanics optimization. To do this;

14. Choose Compute.
15. Choose Single Point.
16. L-click on OK to close the dialog box and start the calculation.

The calculation begins and information about the run appears on the status line. After a few moments, the run finishes. Record the energy of the single point structure below on the answer sheet. This calculation gives the energy of the molecule without optimization with the exact dihedral bond angle constraint. Measure the CCCC dihedral angle and record it.

17. Now optimize the structure by choosing Compute and then Geometry Optimization.
18. L-click on OK to start the calculation. Record the optimized energy and the CCCC dihedral bond angle. Print the structure and attach to the report sheet.
19. Now go back to Step 9 and repeat the process for 60, 120, 180, 240 and 300 degree bond constraints. Complete the answer sheet.

HyperChem #1

Butane Analysis

Results:

Butane Conformations				
Constrained Dihedral Angle (E)	**Single Point MM+ Energy (kcal/mol)**	**Single Point MM+ Dihedral Angle (E)**	**Optimized MM+ Energy (kcal/mol)**	**Optimized MM+ Dihedral Angle (E)**
0E				
60E				
120E				
180E				
240E				
300E				

Analysis:

1. How do the single point energies compare with the geometry optimization energies in each case? Is this what you would expect? Explain.

2. How do the single point dihedral angles compare with the geometry optimization angles in each case? Is there a significant difference in any case? Give a possible explanation for the differences in dihedral angles in terms of steric interactions.

3. Draw a Newman projection for each conformation and summarize the energies for the six forms of butane after geometry optimization. Calculate the relative energies, where the most stable conformation has a relative energy of 0 kcal/mol. Compare these with the experimental energies given in the text. (McMurry, p 117).

| Dihedral Angle (E)	Newman Projection	Optimized Energy (kcal/mol)	McMurry Energy (kcal/mol)

4. How do the MM+ optimized energies compare with those found in the text (McMurry)? For which conformations are there significant differences?

5. Draw an energy diagram for the rotation from one conformer to another as a function of the dihedral angle. Use the relative MM+ energy values. See McMurry Figure 4.5 for comparison.

CCCC Dihedral Angle
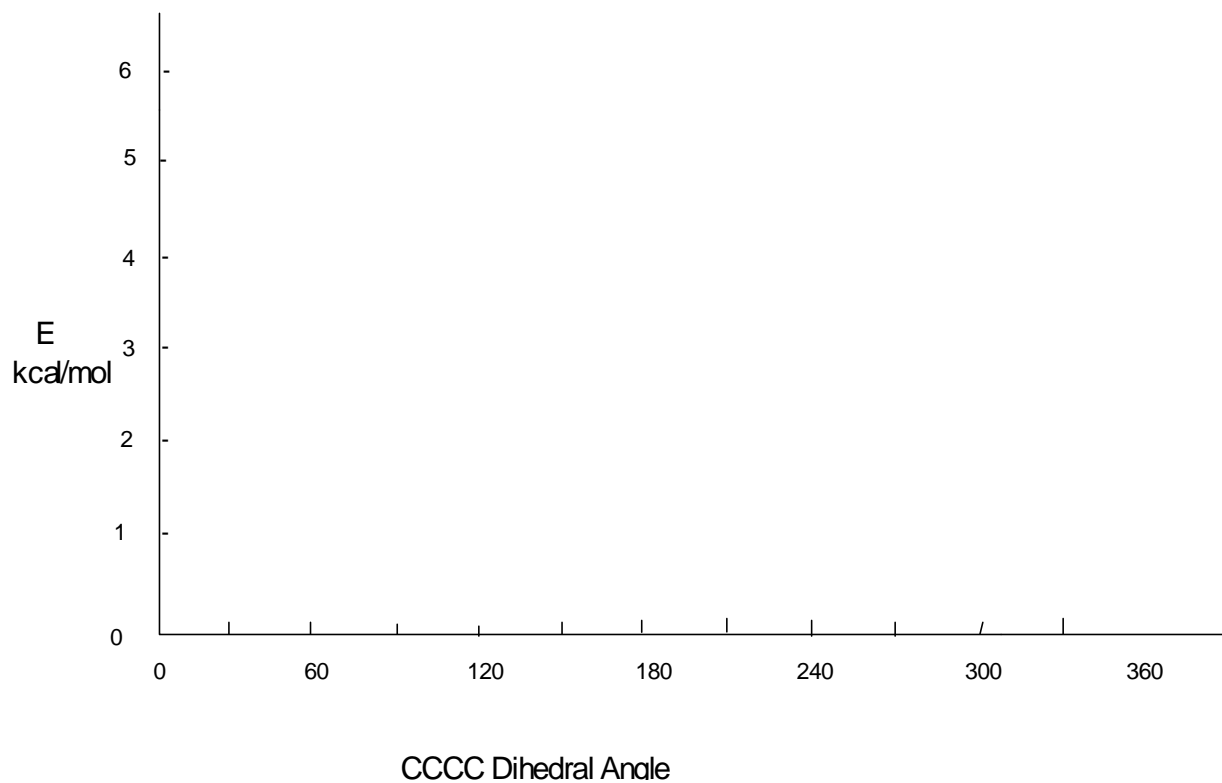
6. Which conformations represent energy minima? Which conformations represent energy maxima?

7. Briefly discuss the types of strain (steric and torsional) associated with each conformation of butane. Are there any conformations which are totally free of strain? Which one(s)? See McMurry, Table 4.1.

8. Sketch the expected energy diagram for 2-methylbutane as it rotates about the C_2-C_3 bond. Be quantitative in terms of the relative energies of the conformations.

E
kcal/mol

6

5

4

3

2

1

0

0   60   120   180   240   300   360

CCCC Dihedral Angle

11
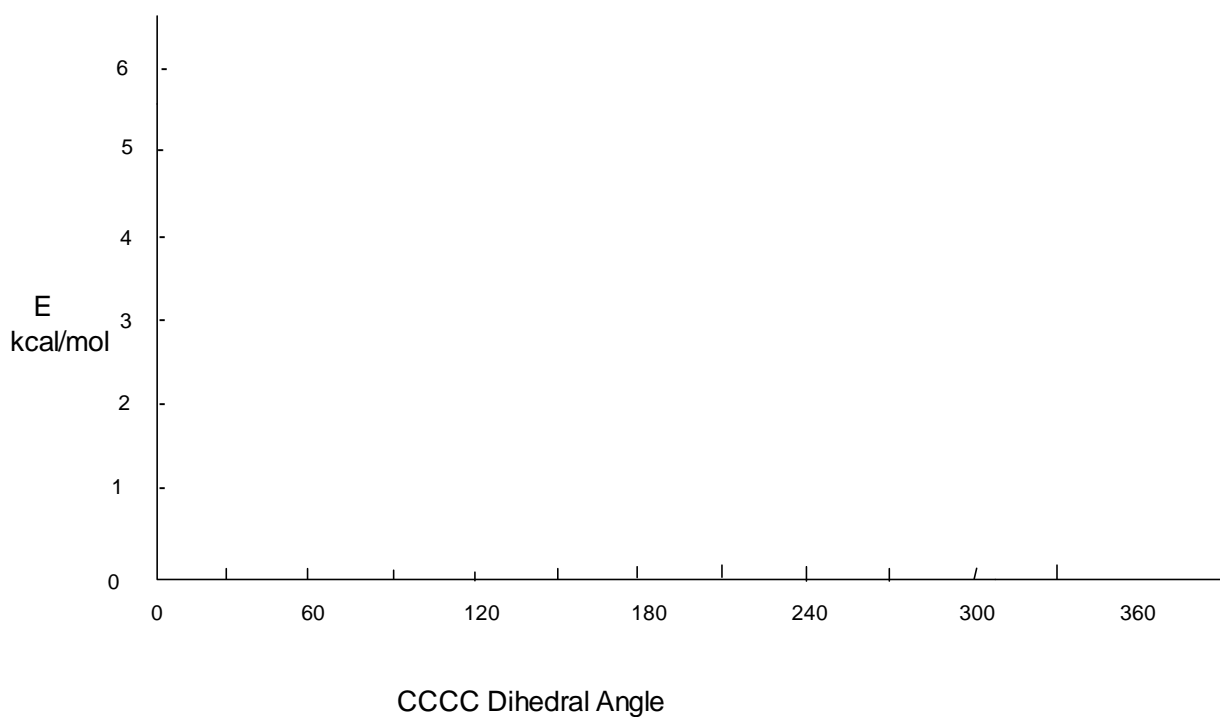
Cyclohexane Analysis

Goal: To determine the most stable conformation of cyclohexane using the AMBER force field calculations.

Background: At room temperature, cyclohexane rapidly undergoes changes in conformation by rotating along each of the CC bonds. As cyclohexane changes conformation, the hydrogens change position, and the molecule assumes a new three-dimensional shape. The change from one chair conformation to another (changing axial hydrogens to equatorial and visa versa) is called a ***chair-chair interconversion***. By determining the heat of formation of the chair conformation and the intermediates of the chair interconversion, you can determine the relative stabilities of each conformation.

Procedures

Choosing the Force Field

Before you build the chair structure of cyclohexane and perform a molecular mechanics optimization, you should choose a molecular mechanics force field provided with HyperChem.

A force field contains atom types and parameters that must be assigned to the molecule before you perform a molecular mechanics calculation. For this exercise, you use the AMBER force field.

To choose the force field:

1. Choose Molecular Mechanics on the Setup menu.
2. When the dialog box appears, choose AMBER.

Building Chair Cyclohexane

The first form of cyclohexane you build is the chair form.

To build the chair conformation:

1. Set the Default Element to carbon and get into drawing mode.
2. Set the select level to Atoms.
3. Choose Labels on the Display menu and label the atoms by number.
4. Make sure Explicit Hydrogens is turned off on the Build menu.
5. Draw the 2D structure by clicking and dragging.
6. Choose Add H & Model Build on the Build menu.
7. Turn off Show Hydrogens on the Display menu.
8. Rotate and translate the structure until it look like this:
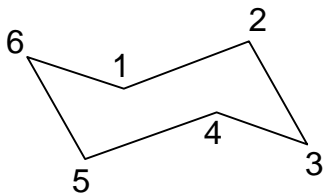
The Model Builder builds the chair form of cyclohexane as the default structure. The structure is not optimized, but it has a standard set of bond lengths, angles, and torsions. Print the structure and attach to the report sheet.

Measuring Structural Properties of Chair Cyclohexane

Now measure the structural properties of the model-built structure. Later, you compare this with geometry measurements from the optimized structure.

To measure the geometry of the molecule:
1. Get into selection mode.
2. Set the select level to Atoms and turn Multiple Selection off.
3. Select a few bonds, angles, and torsion angles to explore the geometry of the structure. Record these values on the report sheet.
4. R-click in an empty area of the workspace to make sure nothing is selected.

Optimizing the Structure

The next step is to minimize the chair structure by performing a molecular mechanics optimization.   .

1. Choose Compute.
2. Choose Geometry Optimization.
3. L-click on OK to close the dialog box and start the calculation.
   The geometry optimization begins and information about the run appears on the status line. After a few moments, the run finishes. Record the energy of the optimized structure on the report sheet.

Measuring Properties of the Minimized System

Now compare the structural properties of the minimized system with those of the model-built structure.

1. Select various bonds, angles, and torsion angles. Values appear on the status line when you make your selections. Record these values.
2. Compare these values with the previous values from the unminimized structure.
3. Print the structure and attach to the report sheet.

Transforming from Chair to Boat Cyclohexane

In this exercise, you reflect one end of the molecule to produce the boat form of cyclohexane.

To define a reflection plane:
1. Turn on Multiple Selections. (under Select)
2. If you are not in selection mode, L-click on the Selection tool.
3. Double-click on the Selection tool to return to the model-built structure.
4. L-click on bonds 1-2 and 4-5 to select the reflection plane.:
5. Choose Name Selection on the Select menu.
6. Choose PLANE, and then choose OK.

To reflect one end of the molecule:
1. If necessary, Choose Show Hydrogens and use the Zoom tool to scale the molecule so that the entire molecule is in view.
2. LR-drag to extend the selection to include all atoms on one side of the initially selected bonds, including hydrogens.
3. Choose Reflect on the Edit menu.
   The selected atoms are reflected through PLANE, producing the boat transformation of cyclohexane. The structure should now look like this:
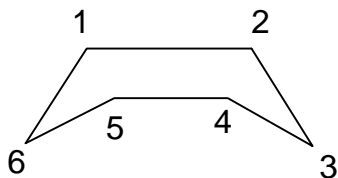
4. R-click in an empty area of the workspace to deselect the atoms.

Measuring the Axial Hydrogens

Two axial hydrogens are fairly close together in the boat structure. These are sometimes referred to as the "flagpole" hydrogens.

To measure the distance:
1. L-click on these two atoms:
2. Record the through-space distance between these two atoms on the report sheet.
   This value is quite close for atoms that are nonbonded. Optimizing the structure moves these atoms further apart to lower the energy.

Optimizing the Boat Cyclohexane

To minimize the boat structure:
1. R-click in an empty area of the workspace to deselect the atoms.
2. Choose Geometry Optimization on the Compute menu.
   As each conformation appears in the workspace, values for the energy and gradient appear on the status line. After the minimization finishes, record the energy and remeasure bond lengths, angles, and torsion angles.

Remeasuring the Axial Hydrogens

1. L-click on the two axial hydrogens.
   Record the new H-H distance.
   The optimized boat structure is a saddle point. The plane of symmetry in the starting structure balances all forces perpendicular to that plane. The optimizer search directions are based on these forces, and therefore, all search directions have the same symmetry plane. HyperChem finds a saddle point that is a minimum with respect to all dimensions except the symmetry plane.
2. Print the structure and attach to the report sheet.

Creating Twist Boat Cyclohexane

A third form of cyclohexane, the twist boat form, is a true local minimum. A simple way to obtain this is to modify the boat from slightly by imposing a bond torsion constraint, rebuilding, and optimizing the structure.

To set torsion bond constraint:
1. R-click in an empty area of the workspace to clear the selection.
2. Turn off Show Hydrogens.
3. Select a four-carbon atom torsion angle by selecting 6-1, 1-2, and 2-3 bonds in that order. You must select the bonds in this order so that the correct angle is constrained. The Model Builder calculates geometries according to the order of selection; specifying a constraint for this particular torsion only changes the position of carbon 6.
4. Choose constrain Bond Torsion on the Build menu, and set the constrain to **30** degrees, and then choose OK.
5. R-click in an empty area of the workspace.
   The torsion is deselected, but the constraint remains set.

To rebuild the molecule with the bond torsion constraint:
1. Double-click on the Selection tool to invoke the Model Builder.
   HyperChem rebuilds the structure with the torsional constraint to create a canonical twist boat form of cyclohexane.

Optimizing Twist Boat cyclohexane

Optimize this geometry using the minimization variables from the previous optimization.

To minimize the twist boat structure:
1. Choose Geometry Optimization on the Compute menu.
2. Choose OK to begin the minimization using the previous options.
   After the minimization finishes, record the energy and measure bond lengths, angles, and torsion angles.
3. Print the structure and attach to the report sheet.
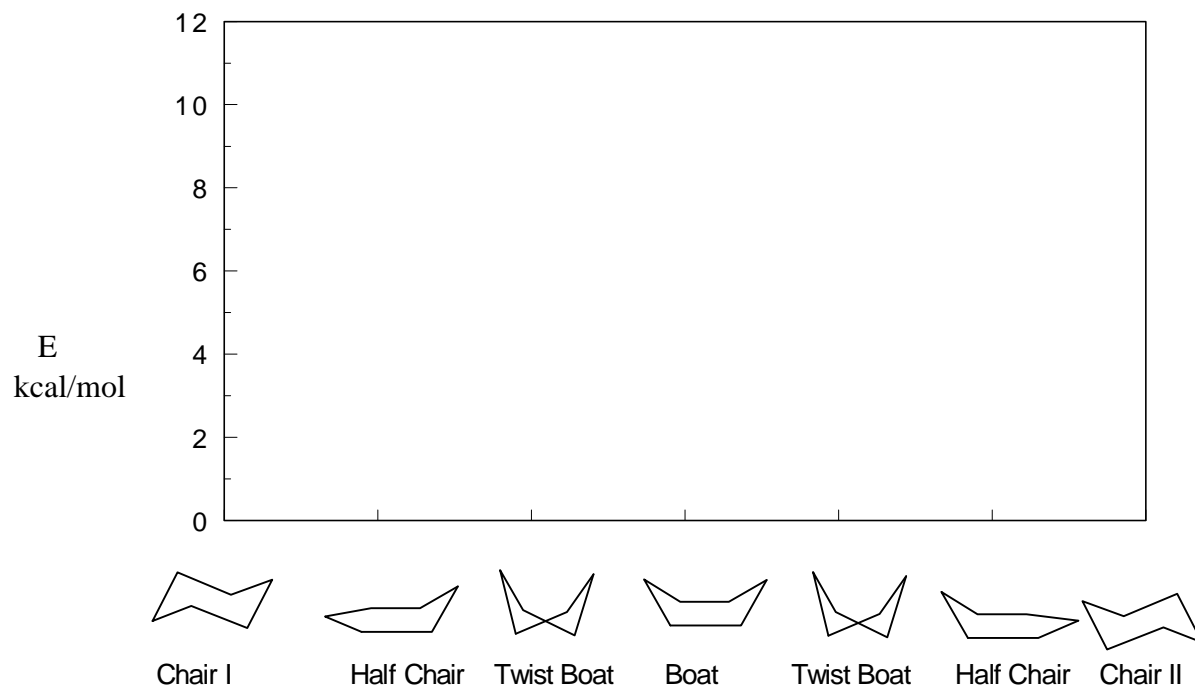
HyperChem #2
Cyclohexane Analysis

Results:

Conformation	CC bond Distance (**D**)	CCC bond angle (**E**)	CCCC Torsion (**E**)	Energy (kcal/mol)
Chair				---
Chair (optimized)				
Boat				---
Boat (optimized)				
Twist-Boat				---
Twist Boat (optimized)				

1. Compare the H_{axial} - H_{axial} distance of both the original and optimized cyclohexane structures. What happened to the distance once the structure was optimized? Is this expected? Explain.

2. Determine the relative energies of each conformation.

	Chair	Boat	Twist Boat
Absolute Amber Energy (kcal/mol)			
Relative Amber Energy (kcal/mol)	0.0		
Wade Energy (kcal/mol)	0.0		

3. Draw an energy diagram for the interconversion of chair cyclohexane to another chair cyclohexane. Use the Amber energy values. Use a value of 10 kcal/mol for the energy of the half-chair.

E
kcal/mol

12

10

8

6

4

2

0

Chair I   Half Chair   Twist Boat   Boat   Twist Boat   Half Chair   Chair II

Ring Strain in Cycloalkanes and Cycloalkenes

Goal: To determine ring strain in cycloalkanes and cycloalkenes using Semi-empirical AM1 calculations.

Background: Small-ring cycloalkanes are thermodynamically less stable than the corresponding *n*-alkanes. While each of the C atoms in the ring is sp^3 hybridized, the ring structure compresses the CCC bond angles from the tetrahedral bond angles found in the *n*-alkane. ***Eclipsing interactions*** between CH bonds, which may be unable to assume fully ***staggered*** arrangements, also adds to the relative instability of the small-ring structures. A simple way of determining ring strain for cycloalkanes is to find the heat of reaction for the hydrogenation of each cycloalkane.
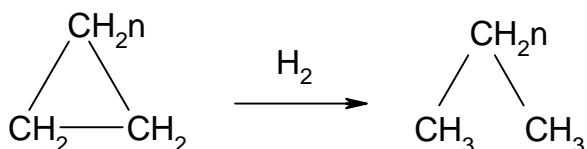
Small-ring cycloalkenes are more strained than the corresponding cycloalkanes. In these molecules, sp^2 hybridized carbons (which want to adopt 120^E bond angles) are compressed even more so than are the sp^3 hybridized carbons. This is particularly evident in small-ring cycloalkenes which possess a *trans* double bond. The difference in strain energy between a cycloalkene and the corresponding cycloalkane may be estimated from the reaction below:
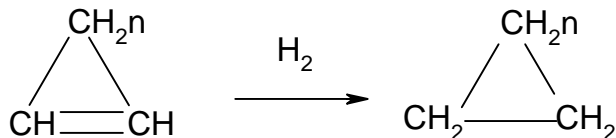
Procedure for Cycloalkanes.

1. Construct cyclopropane and then Add H and Model build (under the Build menu).
2. Choose Setup, AM1 and then OK.
3. Choose Script, Open Script, and then optimize.scr. This will start the calculation.
4. After the calculation is complete, record the heat of formation.
5. Now measure and record these values on the answer sheet.
   a. C-C bond length
   b. C-C-C bond angle
   c. HCCH dihedral angle (include H which are cis to each other in the ring).
6. Go to Step 1 and repeat for cyclobutane, cyclopentane, cyclohexane, and then cycloheptane.

Procedure for Alkanes.

Repeat the procedures above for propane, butane, pentane, hexane, and heptane. For Step 5, do only part (a) and (b).

Procedure for Cycloalkenes.

Repeat the procedures above for cyclopropene to cycloheptene. Do not do Step 5. To obtain a double bond, left-click on the single bond while in the Draw mode (right-click to go back to the single bond.) There are two distinct stereoisomers for cycloheptene corresponding to a *cis* and a *trans* arrangement about the double bond. (There are also *trans* stereoisomers for the smaller ring cycloalkenes. These are, however, very high in energy and need not be considered here). Construct both isomers for cycloheptene. After optimizing each structure, examine it and note any deviations from planarity about the double bond, e.g. twisting of the double bond. Pay special attention to *cis*- and *trans*-cycloheptene.

Name:_____

Date:_____

HyperChem #3
Ring Strain in Cycloalkanes and Cycloalkenes

Results:

Cycloalkane	$\rangle HE_{formation}$ (kcal/mol)	CC Bond Length (D)	CCC Bond Angle (E)	HCCH Dihedral (E)
cyclopropane				
cyclobutane				
cyclopentane				
cyclohexane				
cycloheptane				
propane				
butane				
pentane				
hexane				
heptane				
cyclopropene				
cyclobutene				
cyclopentene				
cyclohexene				
cis-cycloheptene				
trans-cycloheptene				

Analysis:

1. Calculate the energies of reaction for the hydrogenation of each of the cycloalkanes to the corresponding alkane given the heat of formation of H_2 is -5.2 kcal/mol.

$$) H^E_{reaction} \ = \ E) H^E_{f,products} \ - \ E) H^E_{f,reactants}$$

Cycloalkane	$) H^E_{reaction}$ (kcal/mol)	Wade Strain Energy (kcal/mol)
cyclopropane		
cyclobutane		
cyclopentane		
cyclohexane		
cycloheptane		

2. How do these values compare with those given in the text (Wade, Chapter 3, Table 3-4). Do you uncover any significant deviations?

3. Discuss the ring strain present in the cycloalkanes in terms of angle and torsional strain.

4. Consider cyclopropane. How many eclipsed CH bonds are there in this molecule? Given this, what is the amount of torsional strain in cyclopropane and what is the amount of angle strain? Use your $) H^E_{reaction}$ as an estimate of the total ring strain.

5. Calculate $\Delta H^E_{reaction}$ for the hydrogenation reaction of each cycloalkene.

Cycloalkene	$\Delta H^E_{reaction}$ (kcal/mol)	$\Delta HE_{relative}$ (kcal/mol)
cyclopropene		
cyclobutene		
cyclopentene		
cyclohexene		
cis-cycloheptene		
trans-cycloheptene		
cis-2-butene		0.0

6. The calculated $\Delta HE_{reaction}$ values above give the amount of heat released upon hydrogenating the double bond. It is useful, however, to have an acyclic "standard" with which to compare your hydrogenation results. The reaction of cis-2-butene to n-butane is suitable for this purpose. You already have the data on n-butane; the AM1 heat of formation of cis-2-butene is -2.28 kcal/mol. Calculate the hydrogenation of this alkene.

7. The values you calculate must now be compared relative to that of cis-2-butene in order to estimate the additional ring strain in the cycloalkene due to the double bond. Calculate this relative value for each cycloalkene. Which cycloalkenes are most highly strained as a result of the double bond in the ring? Which are least strained? Give an explanation of these results in terms of twisting of the double bond and/or deviation from normal bond angles.

8. Finally, calculate the total strain energy in each cycloalkene. This is the sum of $\Delta H^E_{relative}$ (conversion to cycloalkane) and $\Delta H^E_{reaction}$ (conversion to alkane). Calculate these values and compare these to the Experimental values in the table. For which cycloalkenes is there significant deviation?

Cycloalkene	Total Ring Strain (kcal/mol)	Experimental Ring Strain (kcal/mol)
cyclopropene		-54
cyclobutene		-34
cyclopentene		-7
cyclohexene		-2
cis-cycloheptene		-7
trans-cycloheptene		-27

Infrared Spectra of Organic Molecules

Goal: To compute and assign the vibrational spectra of various organic molecules using the Semi-empirical PM3 calculations.

Background: Absorption of light in the infrared region of the electromagnetic spectrum excites vibrational motions. Both the absorption frequencies and intensities are sensitive to detailed molecular geometry. Because of this, vibrational spectroscopy, i.e. infrared and Ramen spectroscopy, is used to search for evidence that a particular functional group is present. The ***fingerprint region*** of the spectrum (below 1400 cm^{-1}) may be surveyed to compare an unknown with an authentic sample. If the infrared spectra in this region are identical, then the two compounds are almost certainly the same. Finally, vibrational spectra also provide a sensitive barometer to changes to both geometry and to electronic structure due to association, e.g. hydrogen bonding or to solvation.

In this experiment, we will apply the PM3 Semi-emperical method to compute and assign the infrared spectra of various types of organic compounds. This will illustrate the general approach to computing spectra, as well as provide a measure of the utility of the PM3 method for this task.

Procedure

1. Construct the molecule using the Draw tool and click and drag to build the structure without the hydrogens (see next page for special instructions on *cis*-2-butene). To place O and N atoms into the structure, double click on the Draw tool on the left. You will see a Periodic Table. Double click on the atom of choice and then add your atom in the usual manner. To make double and triple bonds, left-click on the single bond when in the Draw mode. This yields a double bond. Left-click again to obtain a triple bond. Finally, if you right-click you can remove the extra bond. Once you have the right carbons, oxygens, and nitrogens in your structure, choose Build and Add H and Model Build.
2. Choose Setup, Semi-empirical and PM3. Click OK.
3. Choose Compute and then Geometry Optimization.
4. After the calculation is complete, choose Compute and then Vibrations.
5. After the calculation is complete, choose Vibrational Spectrum. The spectrum of frequencies corresponding to each normal mode is displayed. The vertical lines at the top represent all the vibrational fundamental frequencies. Not all of these are IR-active. The spectrum at the bottom correspond to IR-active vibrations. The height of the bottom row of lines corresponds to their IR intensities.
6. Click on Animate Vibrations and set Frames 10 and Amplitude 1.
7. L-click on an IR-active vibrations. The highlighted line is violet. Information on this line is shown beneath the spectrum at the bottom of the dialog box.
8. To visualize the vibrational motion for the selected line, choose OK. The dialog box disappears and the vibration is observed. To stop the vibration, choose Cancel. Then choose Compute and Vibrational Spectrum to return to the dialog box.
9. For each molecule, try to find the vibrational mode corresponding to the indicated bond in the Table. After finding the vibration, describe the motion in words and then record the frequency and compare it to the accepted value for this vibration.

Constructing *cis*-2-butene.

When you model build 2-butene, you will get the *trans* isomer. You need to convert it to the *cis*. Click on the Select Tool on the left and click and drag from C-1 to C-4. All four carbons should be highlighted in green. Now, go to the Build menu and choose Constrain Bond Torsion and then cis and then OK. Now deselect the carbons by right-clicking. Finally, double click on the Select Tool. The *trans* will convert to the *cis*.

HyperChem #4
Infrared Spectra of Organic Molecules

Results:

| Molecule	Bond	Experimental Wavenumber (cm⁻¹)	Calculated Wavenumber (cm⁻¹)	Description of Vibrational Motion (stretch or bend)
butane	C-H of CH_3	2800-3000		
	C-H of CH_2	2800-3000		
	C-H of CH_3	1450		
cis-2-butene	C=C	1640		
	C_{sp3}-H	2800-3000		
	C_{sp2}-H	3000-3100		
1-butyne	C≡C	2200		
	C_{sp}-H	3300		
benzene	C=C	1600, 1500		
	C_{sp2}-H	3000-3100		
methanol	O-H	3300		
	C-O	1050		
acetaldehyde	C=O	1710		
	O=C-H	2700, 2800		
acetonitrile	C≡N	2200		
acetic acid	C=O	1710		
	O-H	3000		
	C-O	1100		

# Carbocation Stability and Hyperconjugation

Goal: To investigate the stabilities of various carbocations and the effect hyperconjugation has on bond length and charge density using Semi-empirical AM1 calculations.

Background: Carbocations represent one of the most important and common type of intermediates in organic chemistry. The relative stability of a carbocation is indicative of its likelihood to undergo reaction. Many means of stabilization exist; a common one is hyperconjugation.

Hyperconjugation involves the overlap of the filled F bond with the empty p orbital on the positively charged carbon atom (see figure below). Even though the attached alkyl group rotates, one of its sigma bonds is always aligned with the empty p orbital on the carbocation. The pair of electrons in this sigma bond spread out into the empty p orbital, stabilizing the electron-deficient carbon atom.
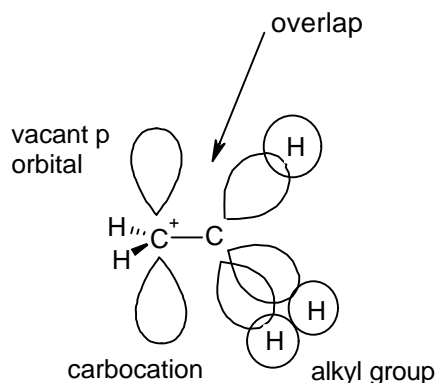
We can think of hyperconjugation in terms of classical forms. Consider, for example, that the isopropyl cation is stabilized by hyperconjugation, creating several resonance forms as shown below.
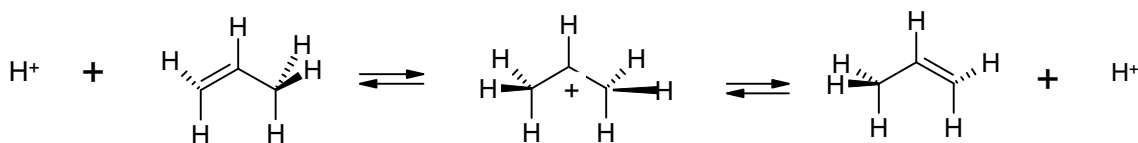
Hyperconjugation should therefore increase the bond order of the CC bond (more double bond character) and thereby shorten the CC bond. It should also weaken and lengthen the CH bond that donates electron density to the empty p orbital. Finally, a significant positive charge should be transferred to the H atom involved in hyperconjugation.

Procedure

The first step will be to build and minimize, in turn, the *t*-butyl, *sec*-butyl, and *n*-butyl carbocations. You will begin by building the parent hydrocarbon of the carbocation and then removing a hydrogen atom from the appropriate carbon.

Isobutane = *t*-butyl carbocation carbocation.

Butane = *n*-butyl or *sec*-butyl carbocation.

1. Use the Draw tool to construct isobutane.
2. Click on Build and then Add H and Model Build
3. Use the Select tool and delete the appropriate H to yield the carbocation.
4. Click on Setup and then Semi-empirical.
6. Click on AM1 and then options.
7. Set the Total Charge at 1 and the Spin Multiplicity at 1 (all spins paired).
8. Compute and then Geometry Optimization.
9. After computations are complete, be sure to record the heat of formation.

Recording Data

1. Record the C-C bond lengths, all C_{sp3}-H bond lengths (where the C_{sp3} carbon is adjacent to the C_{sp2} carbon), and all angles about the central C_{sp2} carbon.
2. Click on Display and then Labels.
3. Click on Charges and then OK. The atom charges should be display. Record the charges on H atoms which might be involved in Hyperconjugation (on C_{sp3} adjacent to C_{sp2}). Note any differences. The H atoms with the greater charges are more involved in hyperconjugation. Print the structure with the charges and attach to the report.

HyperChem #5
Carbocation Stability and Hyperconjugation

Results:

1. Record the C-C bond lengths, all C_{sp3}-H bond lengths (where the C_{sp3} carbon is adjacent to the C_{sp2} carbon), and all angles about the central C_{sp2} carbon.

Carbocation	C-C bond length (**D**)	C_{sp3}-H bond length (**D**)	Angle about C_{sp2} (**E**)
t-butyl	C2-C1=	C1-H=	CCC=
	C2-C3=	C1-H=	
	C2-C4=	C1-H=	
sec-butyl	C1-C2=	C1-H=	CCC=
	C2-C3=	C1-H=	CCH=
	C3-C4=	C1-H=	
n-butyl	C1-C2=	C2-H=	CCH=
	C2-C3=	C2-H=	HCH=
	C3-C4=		

2. Record the charge density of each carbocation.

t-butyl	*sec*-butyl	*n*-butyl
C1-H=	C1-H=	C2-H=
C1-H=	C1-H=	C2-H=
C1-H=	C1-H=	
	C3-H	
	C3-H	

3. Record the heat of formation for each carbocation below.

Carbocation	Heat of Formation (kcal/mol)
t-butyl	
sec-butyl	
n-butyl	

Analysis:

1. Examine the C-H bond lengths for each carbocation. Do you notice a difference in bond lengths for a given carbocation? What does bond length indicate about the extent of participation in hyperconjugation?

2. Examine the C-C bond lengths. What type of C-C bonds possess the shortest bond lengths in each carbocation? What does C-C bond length indicate about the degree of hyperconjugation?

3. Examine the bond angles in each carbocation. What is the expected bond angle for the carbocation (i.e. the expected hybridization)? Is there deviation from this bond angle in any of the carbocations? Give a possible explanation for this deviation.

4. Examine the charges on the H atoms. Are any of the H atoms highly charged? What does a positive charge on the H atoms indicate about the degree of participation in hyperconjugation of the C-H bond?

5. Examine the heats of formation for the carbocations. Are the results what you expect based on your knowledge of carbocation stability? Explain.

HyperChem #6

Stabilities and Structures of Benzyl and Allyl Carbocations

Goal: To determine the stability of benzyl and allyl carbocations using Semi-empirical AM1 calculations.

Background: Allyl and benzyl carbocations are unusual in that they possess very high stabilities. They are often seen as ***thermodynamic sinks*** in mass spectral fragmentation patterns. Also, these carbocations and their derivatives have been characterized extensively by NMR spectroscopy in super acids. Their high stability is attributed to the donation of B electrons into the vacant p orbital at the carbocation center, i.e. resonance stabilization. This implies that the B electrons (also the positive charge) of the allyl and benzyl cations are significantly delocalized. In order for this to occur, the cations must adopt planar geometries to allow overlap of the vacant p orbital with the conjugated B electron system.

allyl cation   benzyl cation
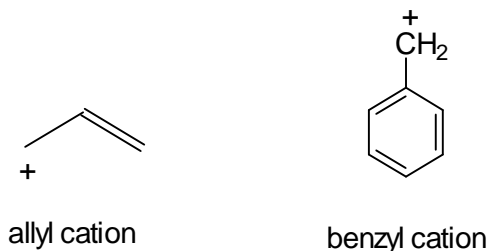
In this experiment, Semi-empirical AM1 calculations are used to examine the geometries and charge distributions of these carbocations. After calculating the heat of formation $(\rangle H_f)$ for each cation, the difference in the planar and perpendicular form of each will be examined. The difference of these $\rangle H_f$ values should provide a measure of the additional stabilization afforded by delocalization of the B electrons.

Procedure

The first step is to construct both the planar and perpendicular cations and calculate their heats of formation. After minimizing their energies, it will be useful to examine the atom charges associated with each C atom in order to determine where the positive charge is distributed.

1. Click on Build and make sure that Explicit Hydrogens is turned on.
2. Use the Draw tool and construct allyl cation. Do not Add H and Model Build yet.
3. Use the Draw tool to add the Hydrogen atoms to your structure.
4. Once you have drawn the structure, double click on both C-C bonds so that dotted lines appear . This

33

indicates that the bonds are conjugated.

5. Click on Build and then Model Build. You should get a totally planar structure. (Note that no Hydrogens are added).
6. Now use the Select tool and click and drag from C1 to one of the H atoms on C3. You should have four atoms selected.
7. Click on Build and then Constrain Bond Torsion. Choose other and set the angle at 90^0 and then OK.

8. Deselect the four atoms and the click on Build and then Model Build. The structure you now have should be the perpendicular allyl cation, where the terminal CH_2 is twisted perpendicular to the double bond.
9. Choose Setup, AM1 and then Options.
10. Set the Total Charge and Spin Multiplicity both to a value of 1. Choose OK and then OK.
11. Go to compute and click geometry optimization.
12. Once calculations are complete, record the heat of formation by going to Compute, Properties and Details. For Atom Charges, go to Display, Labels and then Charge. Print the structure with the charges and attach to your report.

The general procedure above can be used to construct the perpendicular benzyl carbocation. Be sure to double click on the aromatic ring so that a dotted line appears in the ring, indicating conjugated bonds in the ring. For constructing the planar allyl and benzyl carbocations, you may skip steps 6-8. Be sure to print each structure with the charges and attach to your report.

Name:_____

Date:_____

HyperChem #6

Stabilities and Structures of Benzyl and Allyl Carbocations

Results:

1. Record the CC Bond Length and C atom charges for both the perpendicular and planar **allyl carbocation.**

	CC Bond Length (D)	**C Atom Charges**
Perpendicular Allyl	C1-C2=	C1=
	C2-C3=	C2=
		C3=
Planar Allyl	C1-C2=	C1=
	C2-C3=	C2=
		C3=

2. Record the heat of formation for each carbocation.

Carbocation	**Heat of Formation (kcal/mol)**
Planar Allyl	
Perpendicular Allyl	
Planar Benzyl	
Perpendicular Benzyl	

Analysis:

1. Examine the CC bond lengths of both forms of the allyl carbocation. In which structure are they different and in which are they the same? Is this result what you expected?

2. Examine the C atom charges on both forms of the allyl. Where is most of the positive charge located? Is this what you expect for these structures? Draw both resonance forms of the planar allyl carbocation.

3. Examine the C atom charges of both forms of the benzyl carbocation.
     For the planar benzyl form, is the charge shared by the ring carbons? Draw all resonance forms of the planar benzyl carbocation. Are these resonance forms consistent with the results of your calculations?

4. The **difference** in the H_f values of the planar and perpendicular forms is an estimate of the amount of stabilization provided by delocalization of the pi electrons. Calculate these differences. Are the magnitudes of these differences consistent with the number of resonance forms possible for each carbocation? Explain.

CH_3OH

Br

Br

CH_3OH
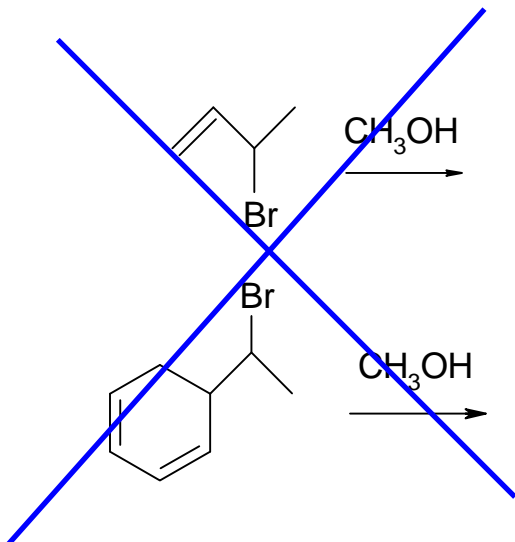
Aromaticity of Thiophene

Goal: To investigate the energy of stepwise hydrogenation of benzene and thiophene using Semi-empirical AM1 calculations and to interpret these results in terms of aromatic stabilization.

Background: Benzene possesses unusual thermodynamic stability relative to what might be expected for "1,3,5-cyclohexatriene," an imaginary molecule. In this experiment, you are to calculate the *aromatic stabilization* of benzene. This energy is calculated by determining the heat of reaction for the hydrogenation of one double bond in benzene, and then comparing this to the heat of reaction to an average heat of the second and third double bonds as shown below.
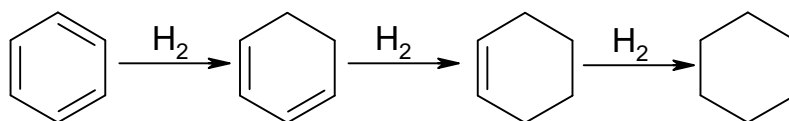
The difference in the heats of hydrogenation of benzene and that of 1,3-cyclohexadiene corresponds to the aromatic stabilization of benzene.

Far less is known about the *aromaticity* of heterocycles. For example, there is still controversy as to whether or not thiophene is aromatic. In this experiment, you will calculate the aromatic stabilization of thiophene in an analogous fashion to that of benzene--by determining the heat of reaction for the stepwise conversion of thiophene to dihydrothiophene.
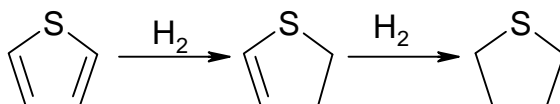
Procedures: Build benzene, 1,3-cyclohexadiene, cyclohexene, and cyclohexane and optimize their structures using Semi-empirical AM1 calculations. Determine the heat of formation for each structure. Do this by choosing Setup, Semiempirical, AM1, and then Compute, Geometry Optimization. Build thiophene, dihydrothiophene, and tetrahydrothiophene. Optimize these structures and record their heats of formation. (Note: Ensure that benzene and thiophene are aromatic by double clicking on the built structure. A dashed line indicates that the double bonds of the structure are conjugated and that your structure is indeed aromatic.)

HyperChem #7
Aromaticity of Thiophene

Results:

Molecule	Heat of Formation (kcal/mol)
benzene	
1,3-cyclohexadiene	
cyclohexene	
cyclohexane	
thiophene	
dihydrothiophene	
tetrahydrothiophene	

Analysis:

1. Calculate the heat of reaction for each hydrogenation reaction. Note: The heat of formation of molecular hydrogen is -5.2 kcal/mol. Show calculations.

2. Are any of the hydrogenation reactions endothermic? Which one(s)? Why?

3. Determine the aromatic stabilization of both benzene and thiophene. Which is more aromatic according to your results? Explain.

Conformations of 1,3-Butadiene

Goal: To establish the geometry of each minimum energy conformer of 1,3-butadiene using Semi-empirical AM1 calculations.

Background: The conformation of conjugated dienes is governed by a combination of electronic and steric interactions. The preferred *s-trans* conformation minimizes steric interactions while maximizing conjucation by allowing the two pi bonds to be coplanar. The geometry of the higher-energy *s-cis* conformer is somewhat unclear. Is the carbon backbone planar in order to maximize conjugation, or is it slightly twisted in order to relieve steric interactions?
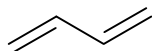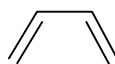
trans-1,3-butadiene   *cis*-1,3-butadiene

1. Choose the Draw tool and make sure Carbon is the default element.
2. Choose Select and then Atoms.
3. Make sure Explicit Hydrogens is turned off on the Build menu.
4. Draw a four-carbon chain and then double click on C1-C2 and C3-C4 bonds. This should convert them to double bonds.
5. Go to the Build menu and choose Add H and Model Build. You should now have the s-trans conformation of 1,3-butadiene.
6. You need to restrain the bond angles in the molecule before computing so that you can obtain the heat of formation as a function of dihedral (torsion) angle. To do this, first click on the Select Tool and click and drag from C-1 to C-4.
7. Go to the Build menu and choose Constrain Bond Torsion. Choose Other and then type in the bond angle (180, in this first case). Choose OK.
8. Now choose the Select menu and Name Selection. Choose Other and type in the word Angle. Choose OK.
9. Go the Setup menu and choose Restraints... Click on Add. Click on Other under Restrained Value and then type in the desired angle (again, 180 in this first case). Choose OK.
10. Deselect the atoms by right clicking. Now double click on the Select tool. The molecule will be built with the proper angle. You are now ready to compute the heat of formation.
11. Go the Setup and choose Semi-empirical and then choose AM1.
12. Go to Script, choose Open Script, and then optimize.scr
13. Once the computation has converged, record the heat of formation.

14. Measured the final bond torsion angle on your optimized structure and record it. It may have change somewhat from the original restrained angle.
15. Now you will want to build the molecule with a different torsion angle and again compute the heat of formation. Go back and repeat Steps 6-14. You may omit Step 8.

HyperChem #8
Conformations of 1,3-Butadiene

Results:

Original Dihedral Angle (E)	Optimized Dihedral Angle (E)	Heat of Formation (kcal/mol)
180E		
150E		
120E		
90E		
60E		
45E		
30E		
15E		
0E		

1.   Plot the heat of formation (y-axis) as a function of the measured dihedral angle (x-axis) using a graphing software (Excel, Lotus 1-2-3, etc). Draw a smooth curve through the points. Identify on the graph the planar *s-trans* and *s-cis* conformations. Also identify the transition state for the interconversion of the two conformations.

Analysis:

1.   Which conformation is more stable, *s-trans* or *s-cis*? Which conformation is least stable? Explain.

3. From your graph, determine the approximate Energy of Activation for the conversion of the *s-trans* into the *s-cis*. Record the energy below.

4. According to your data, are there other conformations close in energy to the *s-cis* conformation? Which one(s)? Give a possible explanation of why these other nonplanar conformations might be as stable as the planar *s-cis* conformation.

HyperChem #9
Electrophilic Aromatic Substitution

Goal: To compare the stabilities of sigma complexes resulting from nitration of substituted benzene, and to compare the directing and activating effects of substituents using Semi-empirical AM1 calculations.

Background: Electrophilic aromatic substitution is the most important chemical reaction of aromatic compounds. The reaction occurs in two steps: initial electrophilic addition of give a sigma complex, followed by deprotonation and formation of a substituted benzene.
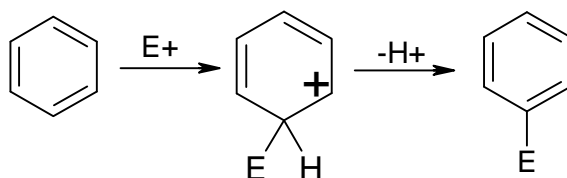

The first step is usually rate-determining. Substituents can influence both the orientation of the reaction (*ortho, meta, para*) as well as the rate of the reaction. In this experiment, semi-empirical AM1 calculations are used to determine the preferred site of nitration on aniline and nitrobenzene and to compare the relative rates of reaction.


nitrobenzene   aniline
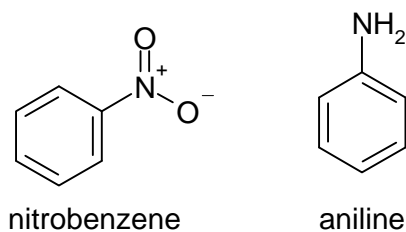
Procedures:

1. Build benzene and optimize the structure using the AM1 method. Be sure to make the ring aromatic by double-clicking on the ring while in the Drawing Mode. You should get a structure like this for Benzene.
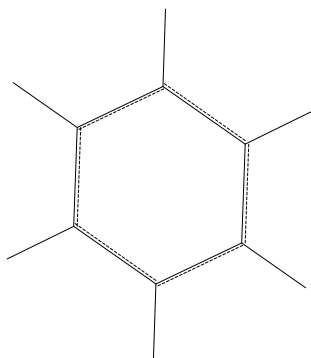
2. Build the sigma complex resulting from nitration of benzene. To do this, modify the benzene ring by replacing a hydrogen with a NO_2 group to one of the carbon atoms. Be sure to L-click on both N=O bonds to convert them to double bonds. Then convert the substituted carbon to sp^3 hybridization by right clicking on the two CC bonds bonded to the substituted carbon. Finally, Add H and Model Build the structure to arrive at the sigma complex. It should look like this.
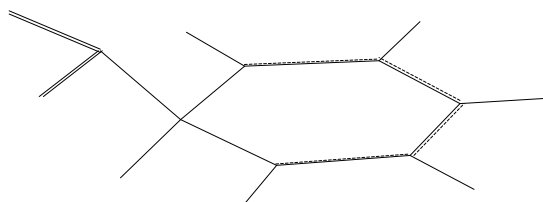
3. Optimize and record its heat of formation. To do this, you go to Setup menu and choose Semiempirical and AM1 and then Options. Enter a value of 1 for both the Charge and Spin Multiplicity. Choose OK and OK. Now choose Script, Open script and then optimize.scr. Record the heat of formation when the calculation is complete.

4. Repeat the process for aniline. Optimize and record the heat of formation.

5. Build the sigma complexes resulting from nitration of aniline in the *meta* position and the *para* position. Optimize and record the heats of formation for each species.

6. Finally, do the same for nitrobenzene, again for both the parent compound and the signal complexes resulting nitration in the *meta* and *para* positions of nitrobenzene.

7. Finally, you will need to build NO_2^+ in order to calculate the heat of reaction for the first step in nitration of each species. Optimize and record its heat of formation of this species. Again, be sure to make double bonds to both oxygen atoms.

HyperChem #9
Electrophillic Aromatic Substitution

Results:

Molecule	Parent Molecule (kcal/mol)	Meta Sigma Complex (kcal/mol)	Para Sigma Complex (kcal/mol)
Benzene			
Aniline			
Nitrobenzene			
Nitronium Ion		--	--

Analysis:

1. Which sigma complex is most stable for aniline? Is this result consistent with the known directing effect of the amino group? Explain.

2. Which sigma complex is more stable for nitrobenzene? Is this result consistent with the known directing effect of the nitro group? Explain.

3. Using the most stable sigma complex only, calculate the heat of reaction for its formation (first step in EAS) for each molecule. Write each reaction below and give the heat of reaction.

4. Assuming the relative heats of reactions reflect the relative activation energies for sigma complex formation, order the aromatic molecules according to their reactivity toward the nitronium ion. Are your results consistent with the known activating and deactivating effects of the amino and nitro groups in EAS reactions?

Keto-Enol Equilibria

Goal: To establish keto-enol equilibrium constants for two carbonyl compounds using Semi-empirical AM1 calculations and to investigate the impact of intramolecular hydrogen bonding on this equilibrium.

Background: A ketone or aldehyde is always in equilibrium with some amount of its enol form.
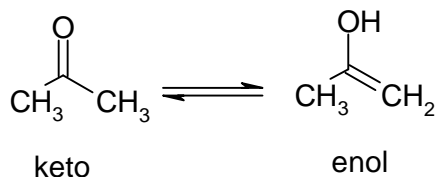

The amount of enol present at equilibrium depends on the structure of the ketone or aldehyde, the solvent and the temperature, and other factors such as conjugation and hydrogen bonding. In this experiment, you will evaluate the equilibrium constants for three carbonyl compounds.

Procedures:

1. Build the carbonyl compound acetone and its corresponding enol form. Calculate their heats of formation using the AM1 method and record these in the report sheet.

   Hint: Build the ketone form and then minimize the structure. Then delete a hydrogen atom on the alpha carbon (use the Select Tool) and, using the Draw tool, build the enol form by converting the C=O to a single bond and the C-C to a double bond. Go to the Build menu and Add H and Model Build. You should have the enol form. Minimize and record heat of formation.

2. Build the diketone 2,4-pentadione, minimize the structure and record the heat of formation. For the enol form, you will build two structures which are shown.
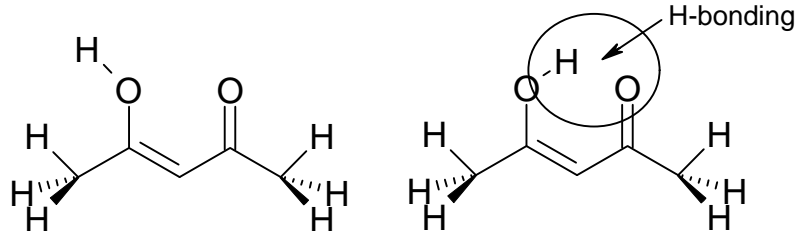
In the form on the left, the OH is pointing away from the C=O so that it cannot H-bond to the carbonyl group. If the compound is not already like this, go to the Select mode and click and drag from the H of the OH to the C_{sp2} bearing the H (four atoms selected). Go to Build and set Constrain Bond Torsion to *Trans*. Model Build the structure. Optimize the structure and record the heat of formation.

3. Now build the other enol form by setting the Constrain Bond Torsion to *Cis*. Again, optimize the structure and record the heat of formation.

HyperChem #10
Keto-Enol Equilibria

Results:

1. Record the heat of formation for each structure below. Calculate the K_{eq} for each keto-enol pair. From K_{eq} calculate the percent of each form at equilibrium.

Molecule	H_f Keto Form (kcal/mol)	H_f Enol Form (kcal/mol)	K_{eq} Equilibrium Constant
Acetone			
2,4-pentadione Non-H-Bonded			
2,4-pentadione H-Bonded			

Analysis:

1. Which form, the keto or enol, is favored for the non-H-bonded dicarbonyl molecule? How does the magnitude of the equilibrium constant compare to that of acetone. Suggest a reason for the difference observed in K_{eq} for these two molecules.

2. Which form, the keto or enol, is favored for the H-bonded 2,4-pentadione? How does this compare to non-H-bonded molecule? Based on your results, what is the principle factor responsible for stabilization of the enol form of 2,4-pentadione?   Explain in detail.

3. As discussed in the Introduction, we can calculate an equilibrium constant if we assume that $\Delta G \approx \Delta H$. This is a reasonable assumption for the keto-enol equilibria of acetone and the non-hydrogen bonded diketone, but not for the hydrogen bonded diketone. Why not? (Hint: what other factor is important in determining ΔG?) Explain in detail.

HyperChem #11
Basicities of Amines

Goal: To compare the basicities of amines in the gas phase using Semi-empirical AM1 calculations.

Background: Consider the following proton transfer reaction:
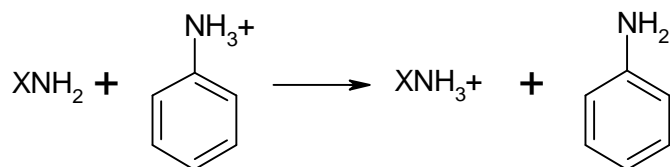
The heat of reaction for this process provides a measure of base strength relative to aniline. In this experiment, you will determine the heat of reaction for the above reaction for each of the following amines.

4-nitroaniline   3-nitroaniline   aniline   4-methoxyaniline   cyclohexylamine
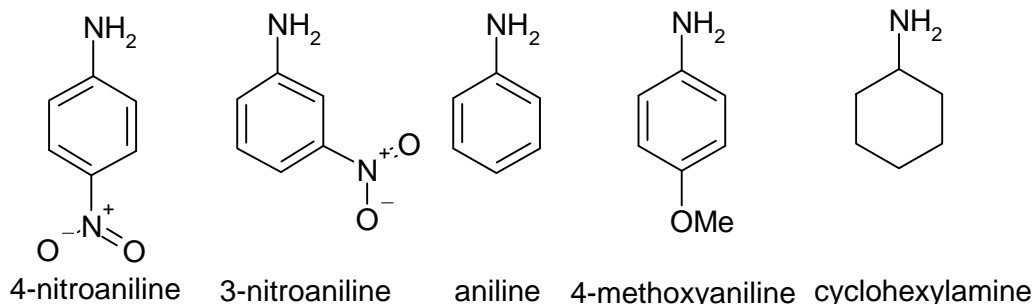
Procedures

Build each amine and its corresponding protonated form. Determine the heat of formation for each molecule using the AM1 method. Go to Setup and choose AM1 and then Script, Open script, optimize.scr.

Hints: After building each amine and minimizing, do not delete the structures. Instead, build the protonated form of the amine by choosing Explicit Hydrogens in the Build menu and adding a hydrogen atom to the nitrogen atom. Model Build the protonated structure. Check under Options in the Semi-empirical Method box to assure that the Charge and Spin Multiplicity values are set to **1**. Finally, optimize and determine the heat of formations in the usual manner.

HyperChem #11
Basicities of Amines

Results:

Amine	Known pK_b	Protonated Amine (kcal/mol)	Heat of Proton Transfer (kcal/mol)
4-nitroaniline	13.00		
3-nitroaniline	11.53		
aniline	9.37		
4-methoxyaniline	8.66		
cyclohexylamine	3.34		

Analysis:

1. Calculate the heat of reaction for each proton transfer reaction with aniline. According to the known pK_b this, which is the strongest base? Are your values consistent with the known pK_b's in terms of basicities?

2. Which is a stronger base, aniline or 4-nitroaniline? Explain. Draw appropriate resonance structures to justify your answer.

3.   Which is a stronger base, aniline, or 4-methoxyaniline? Explain.

4.   Which is the strongest base? Why is this base much stronger than the others?

Free Radical Reactions of Alkenes

Goal: To rationalize the observed regioselectivity in free-radical substitutions in terms of stabilities of intermediate free radicals by examining the distribution of spin density in free radicals.

Background: Alkenes containing allylic hydrogens undergo reactions with N-bromosuccinimide (NBS) in which an allylic hydrogen is replaced with bromine, leaving the double bond intact.
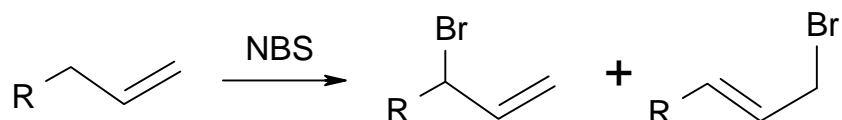
The reaction is known to proceed via abstraction of a hydrogen atom from the alkene, followed by rapid combination with a bromine radical. There are five possible sites for hydrogen abstraction from 1-butene, yielding five possible free radical intermediates, **1-5**.
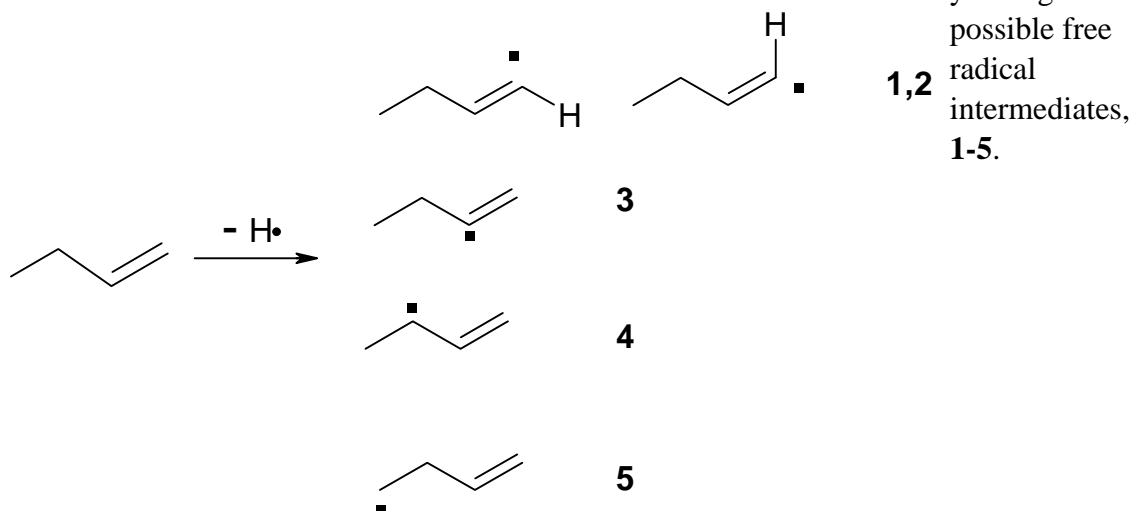
Note that radicals **1** and **2** are stereoisomers, unless the radical assumes a linear geometry. Two different products are known to result from the reaction, both seeming to arise via the intermediary, free radical **4**.

In this experiment, we examine the radical intermediate involved in NBS bromination of alkenes in order to explain the observed regioselectivity. Specifically, we consider the bromination of 1-butene and examine radical stabilities to identify the radical first formed, and spin densities to examine the fate of this radical.

Procedure

1. Build 1-butene in the normal fashion and, after model building, rotate the molecule so it looks like   the structure below.
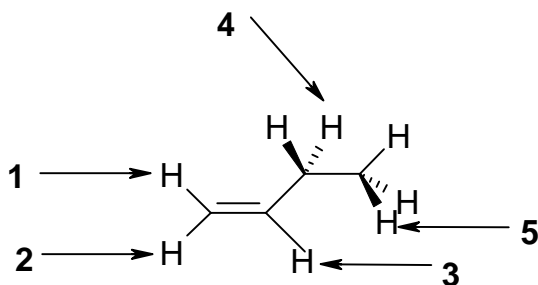
2. Using the Select Tool, select H-1 and then hit the Delete key.
3. Choose Setup, AM1, and then Options. Set the Total Charge to 0 and the Spin Multiplicity to 2 (one unpaired electron).
4. Choose Script, Open script and optimize.scr. If a Warning appears, choose Continue.
5. After the calculation is complete (if it does not converge, repeat Step 4), record the heat of formation.
6. Choose Compute, Contour Plot, and Total Spin Density. Click OK. A spin density map, showing the concentration of unpaired electrons, will appear on your molecule. It should look like a p orbital in shape. You may want to rotate the molecule and then replot to see this effect.
7. Print the stucture with the contour map and attach to your report.
8. Rebuild the original molecule by choosing Build and Add H and Model Build.
9. Repeat Steps 2-9 for the other radicals, removing H-2, H-3, H-4 and H-5 in turn.

HyperChem #12
Free Radical Substitution Reactions of Alkenes
Results:

Free Radical	Heat of Formation (kcal/mol)	Approximate Bond Dissociation Energy (kcal/mol)
1		
2		
3		
4		
5		

Analysis:

1. Do you obtain five distinct radicals? Are radicals **1** and **2** distinguishable?

2. Which of the possible structures is energetically most favorable? Is your result consistent with experimental observations? Identify other structure(s) of comparable energy.

3. Using Table 4-2 on page 142, Wade, try to estimate the approximate C-H bond dissociation energies (BDE)for each C-H bond above. Complete the table above with these energies. Do the radical stabilites as measured by H_f correlate with the approxmiate bond disscociation energies? Is this what you expect?

4. The bromine radical produced in the initiation step will attack the site of highest spin density. Would bromine radical attack at the high spin density carbons of radical **4** result in the observed isomeric mixture? Explain.

5. Draw resonance forms of the intermediate radical **4**. Are these forms consistent with your spin density map that you observe for this radical? Explain.