

An isodesmic reaction is one in which the total number of each type of chemical bond is the same in both reactants and products. Because of this equality in bond type, results of calculations using such a reaction should benefit from cancellation of errors.

Build a molecule of acetone.

Click on the “Minimization” icon (10th across top). This does a simple MM minimization.

Choose Setup / Calculations.

Choose Equilibrium Geometry at Ground State with Semi-Empirical AM1.

Click Submit. Save as acetone.spartan in an appropriate folder.

Click “OK” to started message and “OK” to completed message.

Choose Display / Properties to find the heat of formation. Place the value in the table below.

Choose Setup / Calculations.

Choose Equilibrium Geometry at Ground State with Semi-Empirical PM3.

Click Submit. Click “OK” to started message and “OK” to completed message.

Choose Display / Properties to find the heat of formation. Place the value in the table below.

Choose Setup / Calculations.

Choose Equilibrium Geometry at Ground State with Hartree-Fock 6-31G*.

Click Submit. Click “OK” to started message and “OK” to completed message.

Choose Display / Properties to find the energy. Place the value in the table below.

Choose Setup / Calculations.

Choose Equilibrium Geometry at Ground State with Density Functional B3LYP 6-31G*.

Click Submit. Click “OK” to started message and “OK” to completed message.

Choose Display / Properties to find the energy. Place the value in the table below.

Save and Close the file.

Repeat the above steps for molecules of methane, acetaldehyde, and ethane. Fill in the table.

For each method calculate the $\Delta_r H = \sum H(\text{products}) - \sum H(\text{reactants})$. Sum the first two columns in the table (Acetone + Methane) and subtract the sum of the last two columns (Acetaldehyde + Ethane). *The difference calculated in the case of the HF and DFT methods will be in atomic units (hartrees). Multiply the difference by 627.51 to convert the difference into kcal mol⁻¹.*

Compare your results with the experimental value (-9.9 ± 0.3 kcal mol⁻¹).

Results

Method	Acetone	Methane	Acetaldehyde	Ethane	$\Delta_r H$ (kcal mol ⁻¹)
AM1 (kcal/mol ⁻¹)					
PM3 (kcal/mol ⁻¹)					
HF 6-31G* (au)					
B3LYP 6-31G* (au)					

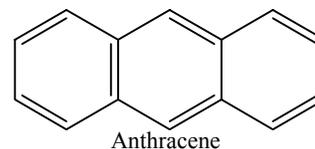
Experimental Value = -9.9 ± 0.3 kcal mol⁻¹

Exercise 3 Electronic Transitions in Aromatic Compounds

NOTE: The calculations described below will take several minutes, even on “fast” machines.

UV-Vis Spectrum of Anthracene

Use the Entry builder and in the “Rings” pull-down menu near the bottom, choose “Anthracene”. Click once in the work area to draw the ring.



Click on the “View” icon (5th across the top) to display the hydrogens.

Choose Setup / Calculations.

Choose Equilibrium Geometry at Ground State with Density Functional B3LYP 6-31G*.

Check the ‘UV/vis’ box, then click “Submit”.

Save the file as anthraceneUV.spartan in an appropriate location.

Click “OK” to started message and “OK” to completed message. (Completion takes some time).

Choose Display / Spectra, and click on the UV-vis tab, if necessary. A list of wavelengths and intensities is displayed.

Click on the “Draw UV Spectrum” button to see the traditional plot.

The wavelength axis is in nm. Record the λ_{\max} values here: _____ nm & _____ nm.

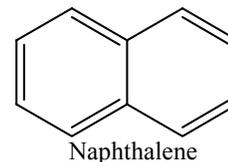
Save and Close the file.

UV-Vis Spectrum of Naphthalene

Repeat the above procedure for naphthalene.

Record the the λ_{\max} value here: _____ nm.

Save and Close the file.



Based on the results of the above calculations, what effect does the number of condensed rings have on the position of the longest wavelength absorption?

To compare the calculated λ_{\max} values obtained for anthracene and naphthalene, go to the NIST Chemistry WebBook available at: <http://webbook.nist.gov/chemistry/> and search by name or formula for the two compounds.

Exercise 4 NMR Chemical Shift Calculations

Build a molecule of benzene.

Choose Setup / Calculations.

Choose Equilibrium Geometry at Ground State with Hartree-Fock 3-21G(*).

Check the “NMR” box and click “Submit”.

Save the file as benzeneNMR.spartan in an appropriate location.

Click Submit. Click “OK” to started message and “OK” to completed message.

Choose Display / Spectra.

Click on the “Draw ^1H Spectrum” and record the calculated chemical shift in the table below.

Click on the “Draw ^{13}C Spectrum”. To separate the two spectra on the screen, carefully click on the x-axis until the highlighted spectrum changes color. The highlighted spectrum can now be moved using right click / drag. Record the calculated chemical shift in the table.

Save and Close the file.

Repeat the above process for chloroethane and for ethanol. Record the chemical shifts below.

Compare your results with the experimental values given.

Benzene	Calc.	Exp.	CH₃CH₂OH	Calc.	Exp.
H's		7.16	Methyl H's		1.16
C's		128.4	Methylene H's		3.59
			Hydroxyl H		4.00
CH₃CH₂Cl			Methyl C		17.6
Methyl H's		1.48	Other C		57.0
Methylene H's		3.57			
Methyl C		18.7			
Other C		39.9			