

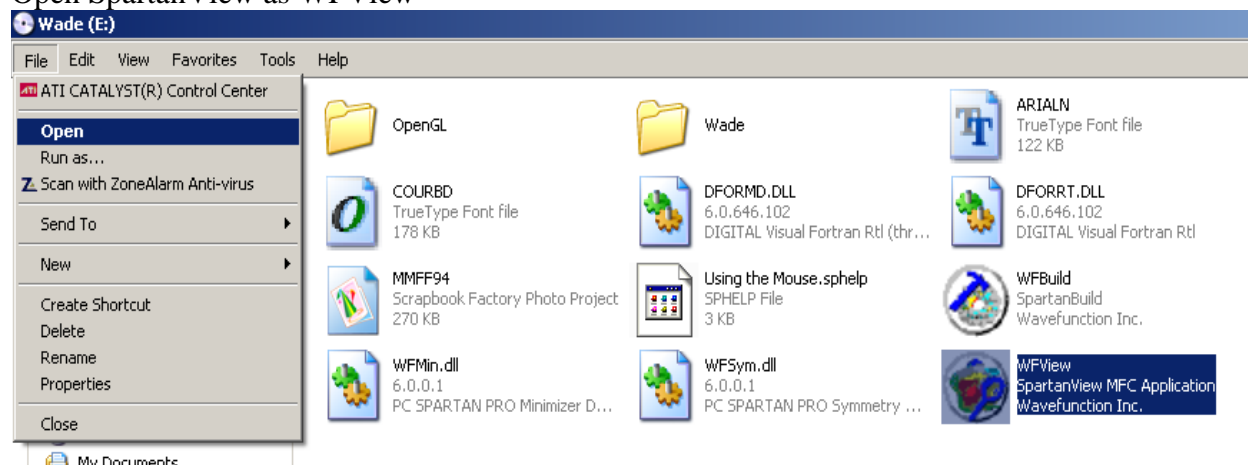
Exp. 3: Computational Chemistry -- Modeling Diels Alder Reactions

This week we will be looking at models of the energy requirements for Aromaticity and for Diels Alder reactions. In order to help you understand the two topics we will start with some simple models of compounds that you already know about. Based on your knowledge of polarity and electronegativity you will discover how electronic distributions are displayed in the Spartan Modeling Program. The data is archived on the L.G. Wade Jr. *Molecular Modeling Workbook's* CD.

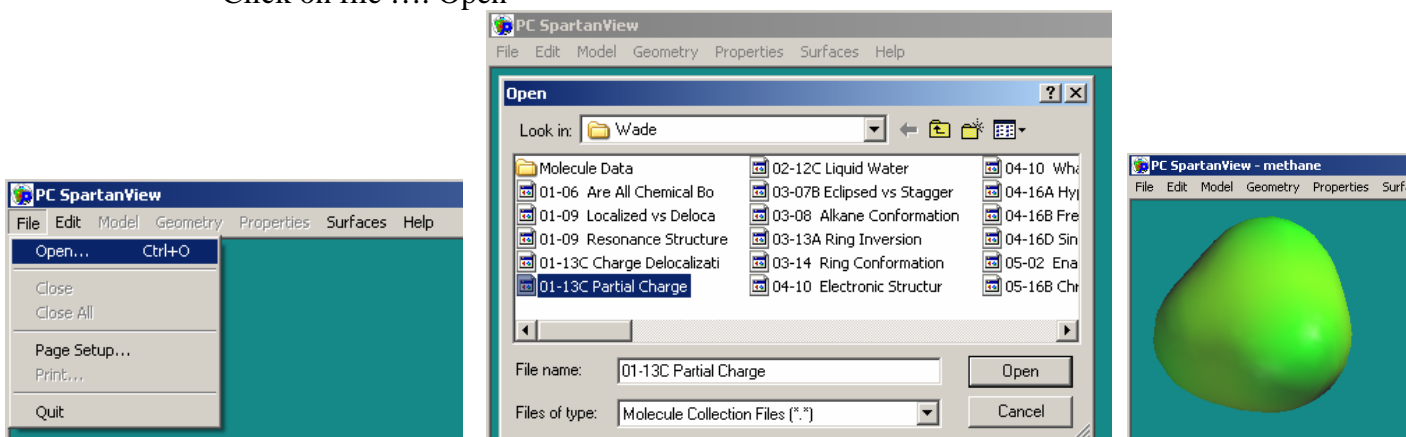
Obtain a *Molecular Modeling Workbook* CD. We will be working in the computer lab this week.

Put the disc in your CD or DVD player.

Open SpartanView as WFView



Open 01-13C Partial Charge
Click on file Open



When the box opens choose: 01-13C partial charge.

To see how the colored surfaces represent the charge distribution in various compounds Click on each of the models then click on surfaces and check solid. They all should look similar to the green model above.

From your knowledge of the polarity of these models (names are provided in the title) answer the following:

A) The red color represents a _____ charge.

B) The green color represents a _____ charge.

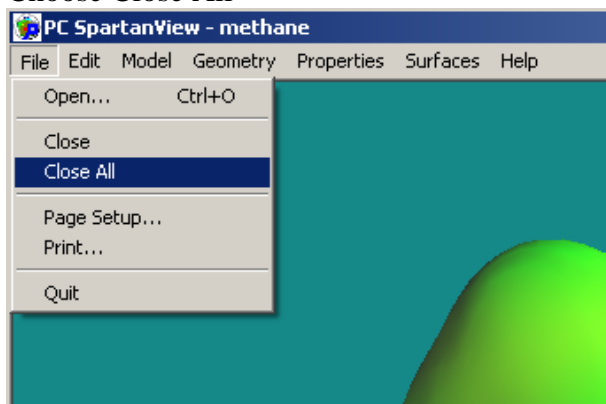
C) The blue color represents a _____ charge.

If you prefer you may use the transparent surface so that you can see the model below. Rotate the models to see how they look from different viewpoints. To rotate a molecule hold the left mouse key down and move the mouse. To move a molecule hold the right mouse button while moving the mouse.

When you are done close all of the files.

Go to File

Choose Close All



Let's look at how charges can be delocalized and how that can affect acidity and basicity.

Open 01-13C Delocalization

Click on the three top structures they are anions and show the solid surface electron distribution. The names are in the titles. The structures below them are the conjugate acids. As the anion is more delocalized, the base becomes more stable (and therefore less basic).

How would you rank these anions in terms of basicity?

_____ > _____ > _____

The strength of the acid is determined by the stability of the conjugate base. A more acidic compound will have a more stable conjugate base. How would you rank the conjugate acids in this set?

_____ > _____ > _____

The K_a is related to the acidity of the acid. How would you rank the K_a 's of these acids?

_____ > _____ > _____

What are the actual K_a 's of these neutral compounds?

How would you rank these compounds based on their experimental K_a 's?

_____ > _____ > _____

Does your model help you to see the relationship between charge distribution and acid strength (or K_a)?

Now let's look at some carbocations.

Open the file 06-13A Phenyl vs Benzyl

Observe the electronic distribution for each of the cation models (bottom row).

Observe the difference in charge distribution for each of the cations.

Which is the most delocalized?

Which is the least delocalized?

How would you rank these carbocations in terms of stability?

_____ > _____ > _____

How would you rank these carbocations in terms of acidity?

_____ > _____ > _____

How would you rank the associated neutral compound in terms of acidity?

_____ > _____ > _____

Aromaticity is another interesting topic that can be looked at through modeling. In lecture we have discussed a variety of molecules that are aromatic. Here we will look at the electronic distribution of two of these compounds.

Open the file 16-10 Polar Hydrocarbons

Observe the electronic distribution for each of the fulvalenes (bottom row).

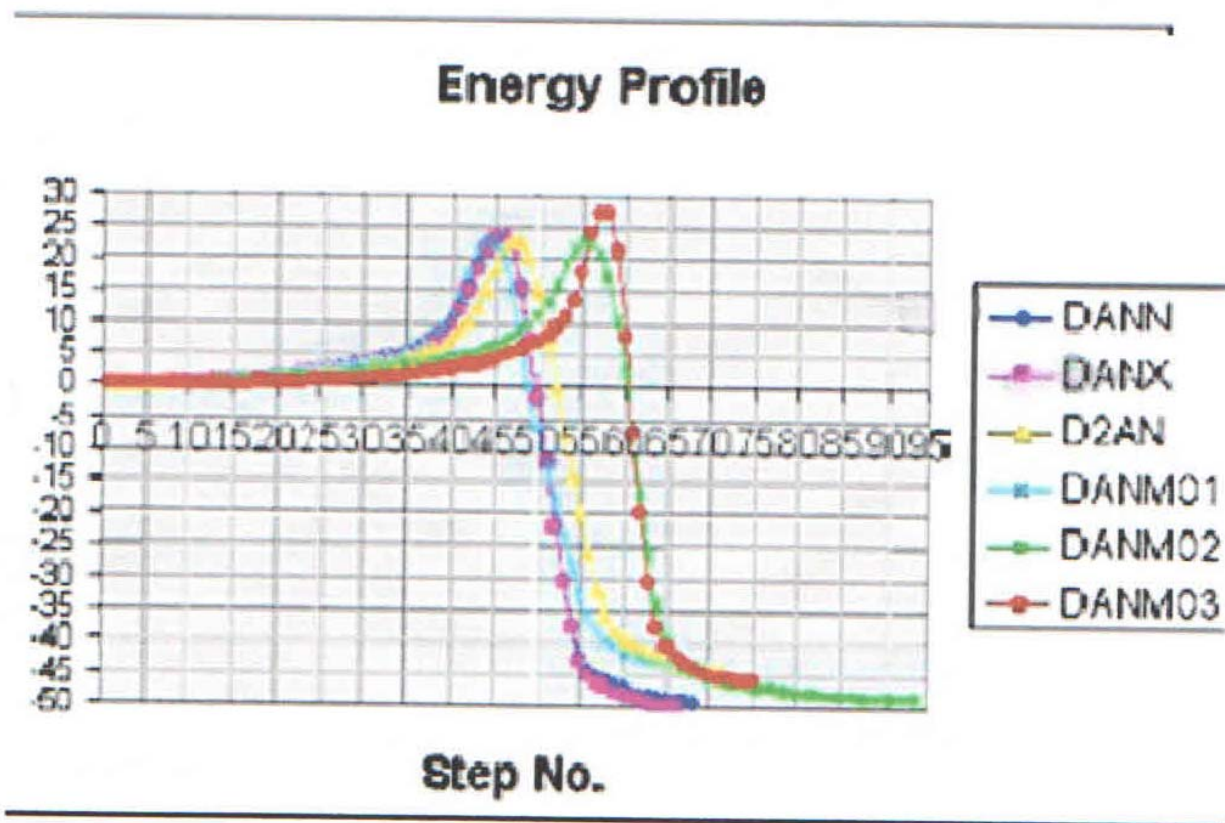
Which structure is more delocalized and more stable? It has more resonance structures in this configuration.

What is the structural difference between them?

Why does the structural difference affect the stability?

Molecular Modeling: Diels Alder Reactions

The following molecular modeling simulations were constructed as part of an undergraduate thesis: *A Computational Study of Molecular Vibrations and Reaction Pathways*, Barry McCarthy (1996) Brunel University, West London, U.K. The graph below shows the energy profiles of the reactions that have been normalized with the starting points set to zero. The curves approximate relative vibrational energies of the reactions, but do not directly provide measurable energies of activation or free energies (ΔG) of reaction. However, it allows a direct comparison between the reactions that would not otherwise be possible. From the graph it can be seen that all of the reaction profiles are very similar yet subtly different. We will interpret Barry McCarthy's simulations and compare them to modeling data generated using Spartan's computational engines.

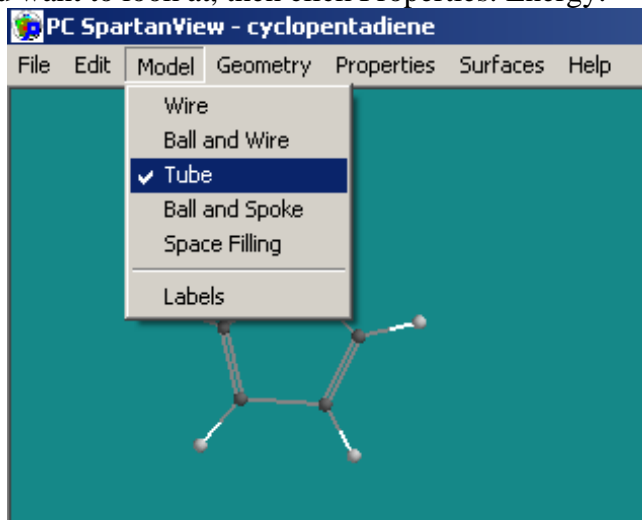
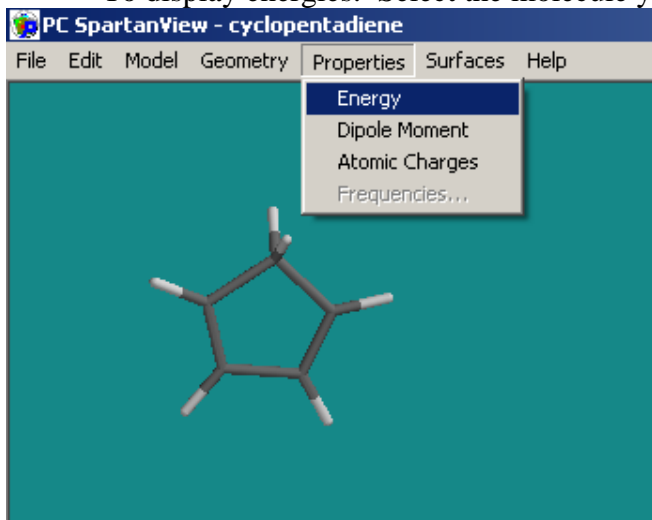


Meaning of the code on the above Energy Profile:

Code	Reaction
DANN	Butadiene and acrylonitrile (endo)
DANX	Butadiene and acrylonitrile (exo)
D2AN	Butadiene and acrylodinitrile
DANMO1	1-methoxybutadiene and acrylonitrile
DANMO2	1-methoxy-2-cyanobutadiene and ethene
DANMO3	Butadiene and 1-methoxyacrylonitrile

Open the file 15-11 electron flow in di.

To display energies: Select the molecule you want to look at, then click Properties: Energy.



All of the other molecules will disappear.

To select another molecule you must get out of the energy mode.

Select Model: Tube (any model will work – this just returns it to the original.)

Complete the following table (use four decimal places for *au* values) and answer the following questions. T.S. = transitional state.

Reactant	Energy(<i>au</i>)	T.S. Energy(<i>au</i>)	$\Delta E(\text{T.S.}-\text{Reactants})(\text{au})$	$\Delta E(\text{T.S.}-\text{Reactants})(\text{kJ})$
A) cyclopentadiene				
B) ethene				
[A---B]	-----			
C) cyanoethene (acryloni				
[A---C]	-----			
D) tetracyanoethene				
[A---D]	-----			

Hint: $\Delta E(\text{T.S.}-\text{Reactants})(\text{au})$ for [A---B] = Energy (T.S.) – [energy (A) + energy (B)]

1. Using different colors of ink, plot the three reactions (A with B, A with C, and A with D) on a same energy diagram (a diagram similar to the “Energy Profile” provided in the lab), showing ΔG^\ddagger for each and assuming that the reactions are exergonic while the relative energy states of the products are (A-D) > (A-C) > (A-B). Assume that all of the reactions begin at the same relative energy state (set to zero) for the reactants (A, B, C, and D) and that $\Delta E(\text{T.S.}-\text{Reactants})(\text{kJ})$ equals ΔG^\ddagger (1 *au* = 2625.5 kJ/mol). Label on the diagram the energy of all the T.S. (transitional states).

2. Rank the reactions (A with B, A with C, and A with D) in increasing order of rate. (*hint: what is the relationship between energy and rate?*)

_____ < _____ < _____

3. Observe the energy surfaces for the reactants from the CD. Circle the respective blue and red regions and label them in the structures you draw.

4. Consider Barry McCarthy's data for D2AN (see the code reference in the table at the bottom of page 4), referring to the "Energy Profile." Where would it fit in the relative rates of reaction? Rerank them.

_____ < _____ < _____ < _____

Predict D2AN's energy surface by drawing its structure and labeling its surface as in question 3.

5. Briefly explain what feature of the dieneophile is thought to account for the increase in rate and why.