Names: _____ Section_____

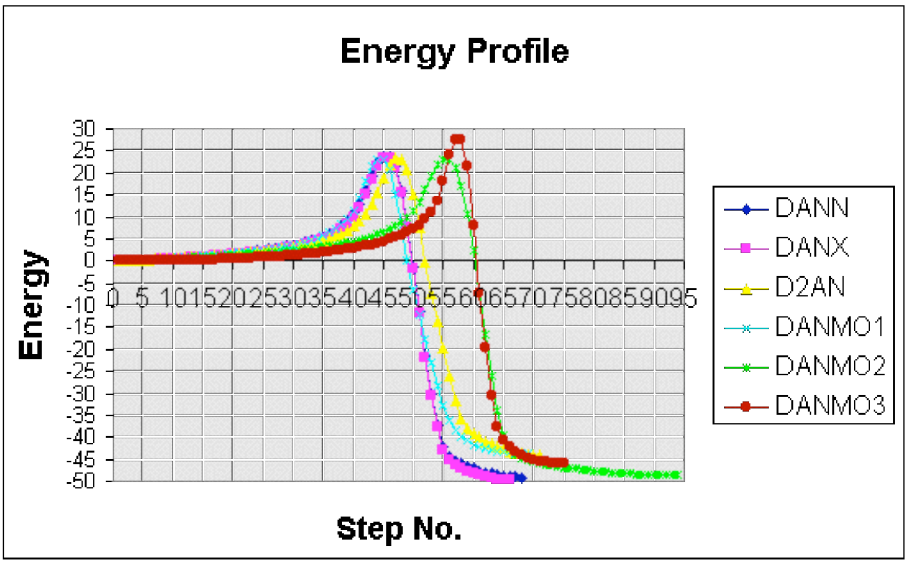
Chem 226/ Fall 2005 Dr. Rusay

Molecular Modeling: Diels Alder Reactions (I)

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.

Reaction:	**Code:**
Butadiene + Acrylonitrile (endo)	DANN
Butadiene + Acrylonitrile (exo)	DANX
Butadiene + Acrylodinitrile	DA2N
1-methoxybutadiene + Acrylonitrile	DANMO1
1-methoxy-2-cyanobutadiene + Ethene	DANMO2
Butadiene + 1-methoxyacrylonitrile	DANMO3

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 measureable energies of activation or free energies (ΔG) of reaction. However, it allows a direct comparison between the reactions which would not otherwise be possible. From the graph it can be seen that all of the reaction profiles are very similar yet subtly different.



The modeling/synthesis experiment was intended to have each of you use WebMO to build structures of reactants, intermediates and products to use in the construction of similar simulations. However, the necessary WebMO computational engine, Gaussian, is not yet available for DVC use, so instead we will interpret Barry McCarthy's simulations and compare them to modeling data generated using Spartan's computational engines. The data is archived on the L.G. Wade Jr. *Molecular Modeling Workbook's* CD that is available from the chemistry stockroom or from Dr. R..

Working with a partner obtain a *Molecular Modeling Workbook* CD; using either a PC or Mac open Spartan View and folder 15-11. Complete the following table (use four decimal places for *au* values) and answer the questions before the next lab. Also, before leaving today begin the Diels Alder reaction of maleic anhydride and furan following the procedure found in, *Lehman*, Minilab #27, pp. 504-505 or the University of Saskatchewan publication (handout). Prepare a pre-lab in your lab notebook before mixing the reactants and have it initialed. One per group with both names on the pages is acceptable.

Reactant	Energy (*au*)	T.S.	Energy (*au*)	$\Delta E_{(T.S.-Reactants)}$ (*au*)	$\Delta E_{(T.S.-Reactants)}$ (kJ)
A) cyclopentadiene					
B) ethene		[A---B]			
C) cyanoethene (acrylonitrile)		[A---C]			
D) tetracyanoethene		[A---D]			

1. Assume that all of the reactions begin at the same relative energy state for the reactants and that $\Delta E_{(T.S.-Reactants)}$(kJ) equals $\Delta G^{\ddagger}$ (1 *au* = 2625.5 kJ/mol). Plot the reactions on the same energy diagram showing $\Delta G^{\ddagger}$ for each and assuming that the reactions are exergonic where the relative energy state of the products are A-D > A-C > A-B.

Rank the reactions in increasing order of rate.

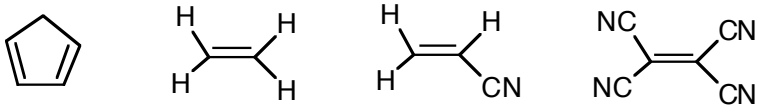
_____ < _____ < _____

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

2. Consider Barry McCarthy's data for D2AN. Where would it fit in the relative rates of reaction? Re-rank them.

_____ < _____ < _____ < _____

3. Observe the energy surfaces for the reactants from the CD. Red is more negative; blue more positive and green intermediate. Circle the respective blue and red regions and label them in the following structures.



4. Consider D2AN; predict its energy surface by drawing its structure and labeling its surface as above.

5. For the DANN and DANX reactions draw the respective structures of the Diels Alder products, label them endo- and exo- and identify which would have the lower $\Delta G^{\ddagger}$. Which is thermodynamically more stable? Does the T.S. on the CD correspond to DANN or DANX? _____

DANN: DANX: