Names: _____ Section_____

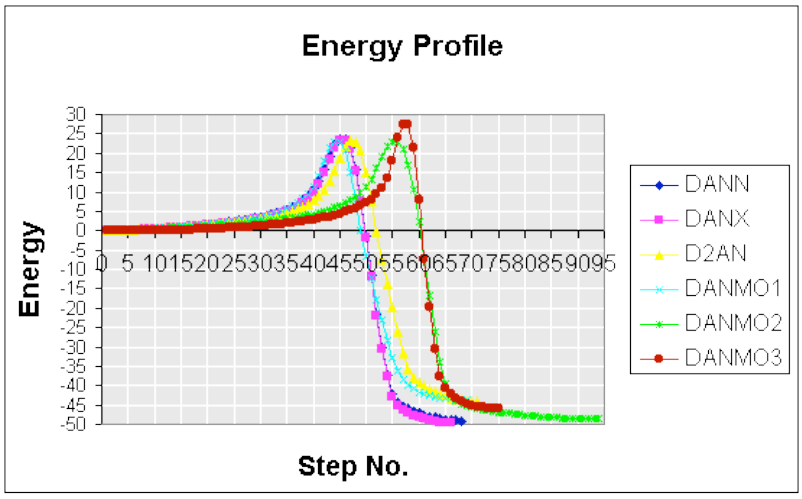
Chem 226/ Fall 2008 Dr. Rusay

Molecular Modeling: Diels Alder Reactions (I)

The energy profiles (reaction coordinate diagrams) below show the profiles of six reactions that involve 4 different dienes and 4 different dienophiles. The profiles have been normalized with the starting points set to zero. They approximate the relative vibrational energies of the reactions, but do not directly provide measureable energies of activation (E_a) or reaction free energies (ΔG_{rxn}). However, they allow a direct comparison between the reactions, which would not otherwise be possible. All of the reaction profiles are very similar yet subtly different.

The following molecular modeling computations were adapted from an undergraduate thesis: *A Computational Study of Molecular Vibrations and Reaction Pathways*, Barry McCarthy (1996) Brunel University, West London, U.K.

	Reactants	E_a (kJ)	ΔG_{rxn} (kJ)
DANN	(E)-1,3-pentadiene + acrylonitrile (1)	+23.5	-49
DANX	(E)-1,3-pentadiene + acrylonitrile (2)	+24.0	-49
D2AN	butadiene + trans-acrylodinitrile	+23	-43
DANMO1	butadiene + (Z)-2-methoxyacrylonitrile	+24	-44
DANMO2	1-methoxybutadiene + acrylonitrile	+22	-45
DANMO3	2-cyanobutadiene + ethene	+28	-46

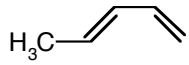
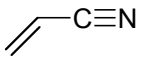
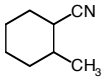


Refer to the on-line version for a better view of the Energy Profile diagram above.

1. Rank the reactions from fastest to slowest:

_____ >_____ > _____ > _____ > _____ > _____

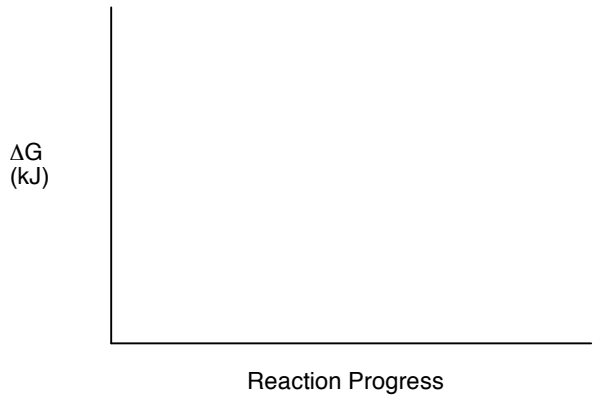
2. Complete the following table by providing structural drawings for the reactants and product in each respective reaction: (Stereochemistry is not necessary)

	Diene	Dieneophile	Major Product
DANN/DANX			
D2AN			
DANMO1			
DANMO2			
DANMO3			

Modeling data was generated using Spartan, a commercial computational progam that is similar to WebMO. The structures were computed and archived on the *Molecular Modeling Workbook* CD which is available 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. Click on each molecule and each transition state; then, in the menu click on Properties; read the energy value at the bottom of the screen. Complete the following table; use four decimal places for *au* values (1 *au* = 2625.5 kJ/mol). Answer the accompanying questions.

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]			

3. Assume that all of the reactions begin at the same relative energy state for the reactants and that $Ea = \Delta E_{(T.S.-Reactants)}$(kJ), which equals $\Delta G^{\ddagger}$. 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.

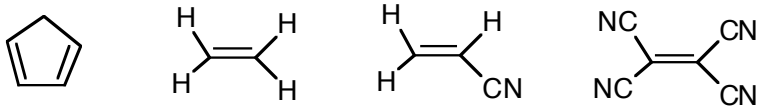
_____ < _____ < _____

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

4. Consider McCarthy's D2AN reaction. Where would it fit in the relative rates of reaction?
   Re-rank: A-B, A-C, A-D, and D2AN from slowest to fastest.

   _____ < _____ < _____ < _____

5. Observe the energy surfaces for the reactants from the CD. Red is more negative; blue more positive and green intermediate. Circle the atoms with the most intense blue and red regions and label them δ+ and δ- respectively in the following structures.



6. Consider D2AN; Draw its structure below and predict its energy surface by labeling its surface δ+ and δ- as above.

7. For the DANN and DANX reactions draw the respective transition states, DANN = endo, DANX = exo, show their stereochemistry.

   DANN: DANX:

Identify which transition state forms fastest. DANN or DANX (Circle one.)