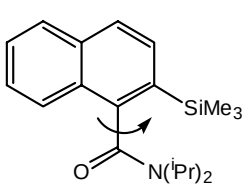
2ND YEAR ORGANIC PROBLEM CLASSES 2003/2004

Class 2. Dr Alan Spivey – Introduction to Stereoelectronics

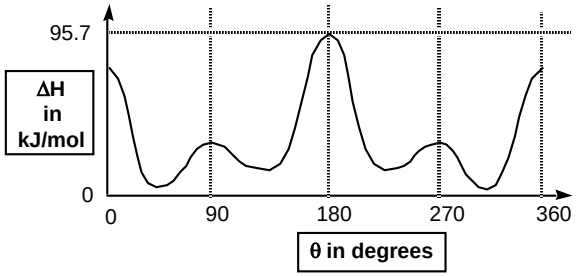
Class to be held at *3pm on Monday 17th November 2003* in normal tutors groups
Answers to be handed in to Dr Spivey's office – Room 834 (C1) *before 3 pm* on the day of the class. Late scripts will receive no credit.
Please write your own name AND YOUR TUTORS NAME on your script.

1. Answer **ALL** parts of this question.

(a) Compound **1** exhibits atropisomerism (i.e. hindered rotation) about the bond indicated and has an energy profile diagram as shown below. This diagram shows how the energy of this molecule varies as the indicated bond is rotated through 360° relative to the naphthalene ring at a temperature of 25°C. The dihedral angle (θ) = 0 for the situation where the naphthalene ring and amide function are co-planar as drawn.



(**1**)



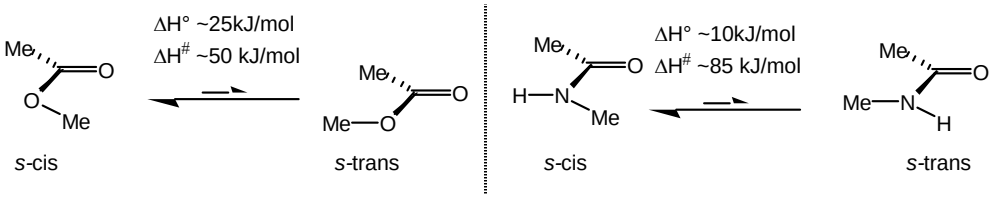
(i) What steric and stereoelectronic factors are responsible for the form of this energy profile diagram ? Account for the position of the *global* maxima and the *global* minima.

[4 marks]

(ii) What is the stereochemical relationship between the structures at θ = 90° and θ = 270° ?

[1 mark]

(b) Compare and contrast the thermochemical data given below for *s*-cis → *s*-trans isomerism in methyl acetate and methyl acetamide taking stereoelectronic, steric and dipole factors into account. As part of your answer draw annotated orbital diagrams of all four structures.



NB. $\Delta H^{\#}$ is the enthalpy of activation and ΔH° is the ground state enthalpy difference between the two conformers.

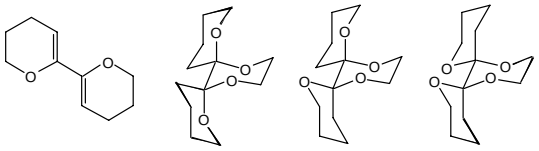
[15 marks]

PTO

(c) On heating bis-dihydropyran **1**, 1,2-ethanediol and a catalytic quantity of *para*-toluene sulfonic acid in toluene just one of the three possible diastereomeric products **2**, **3** and **4** is formed.

(i) Which is it ? [1 mark]

(ii) Why is the reaction so selective ? [4 marks]



1 **2** **3** **4**

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