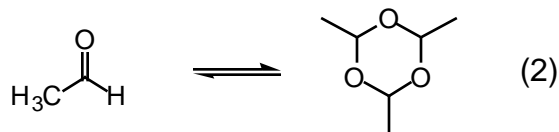
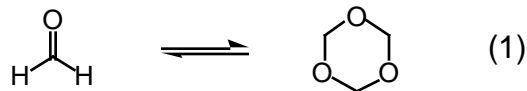


Answers to Problem Set 1: **NOTA BENE!!** I wrote this answer key before PC Model was upgraded from version 5.04 to version 7. There appear to have been some changes to the force field in the interim (NOT what one wants...), so certain numbers may be slightly different than what you obtained. Grading will take this into account.

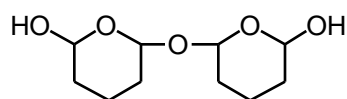
1. Consider the trioxane equilibria illustrated below (trioxane itself is a hypnotic agent used therapeutically). Use PC Model to compute the 298 K heats of formation of the monomers and the trioxanes in kJ mol^{-1} . Find the experimental gas-phase heats of formation (webbook.nist.gov might be a nice resource). How does PC Model do? Assuming the enthalpies are equivalent to free energies (they aren't, but let's make the assumption for the moment), what are the equilibrium constants for the two equilibria in the gas phase?



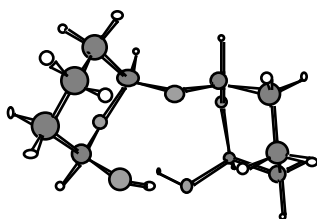
PCModel (the MMX force field) gives heats of formation for formaldehyde, acetaldehyde, trioxane, and 2,4,6-trimethyltrioxane of -120.0 , -169.3 , -486.2 , and $-647.3 \text{ kJ mol}^{-1}$, respectively. The experimental values on the NIST website are -115.9 , -170.7 , -465.8 , and $-636.2 \text{ kJ mol}^{-1}$, respectively. The average absolute error in the predicted values is thus 9.2 kJ mol^{-1} . This seems pretty good to me for a force field, and is only about thrice the experimental error in the measured values (not quoted) in some instances.

For these unimolecular processes, we have $K = \exp(-\Delta G / RT)$ where ΔG is the difference in free energies from left to right, R is the gas constant, and T is 298 K. Note that the problem set has implicit stoichiometry—the balanced equations have 3 monomers on the left going to 1 trimer on the right—so we need to multiply monomer heats of formation by 3. Plugging in numbers gives K values for reactions (1) and (2) of 8.0×10^{21} and 1.6×10^{24} , respectively, for MMX and 3.2×10^{20} and 3.5×10^{21} , respectively, for experiment. Obviously, these equilibria lie rather heavily to the right...

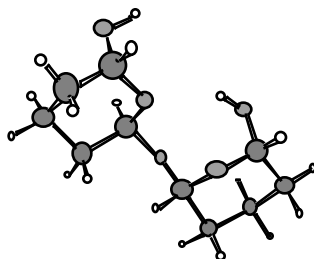
2. Shown below is a rather unusual sugar. Using PCModel, find the lowest energy stereoconformation for this molecule you can (i.e., you get to pick the stereochemistry of all stereogenic centers and the ring geometries, hydroxyl group rotations, etc.—I got down to $H_{f,298}^{\circ} = -247.5$ kcal mol⁻¹ without too much effort). Find two other stereoconformers as well. Using the term-by-term breakdown of the individual force field energies, explain in a chemical fashion the differences in energies for different conformers. To facilitate this analysis, it might be helpful to do some quick calculations on relevant monomers. Include with your answer printouts of the structures/energies for your conformers (note that a ball-and-stick structure is occasionally a bit easier to view than a wire structure for stereochemical purposes).



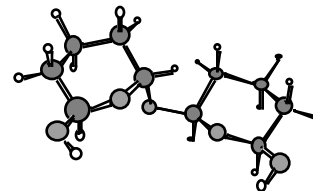
My three structures are show, with their heats of formation, below. The pictures are from Chem-3D, which I think renders better ball-and-stick images than PCModel (you can save from PCModel in Chem-3D format).

**A**

$$H_{f,298}^{\circ} = -249.1 \text{ kcal/mol}$$

**B**

$$H_{f,298}^{\circ} = -243.5 \text{ kcal/mol}$$

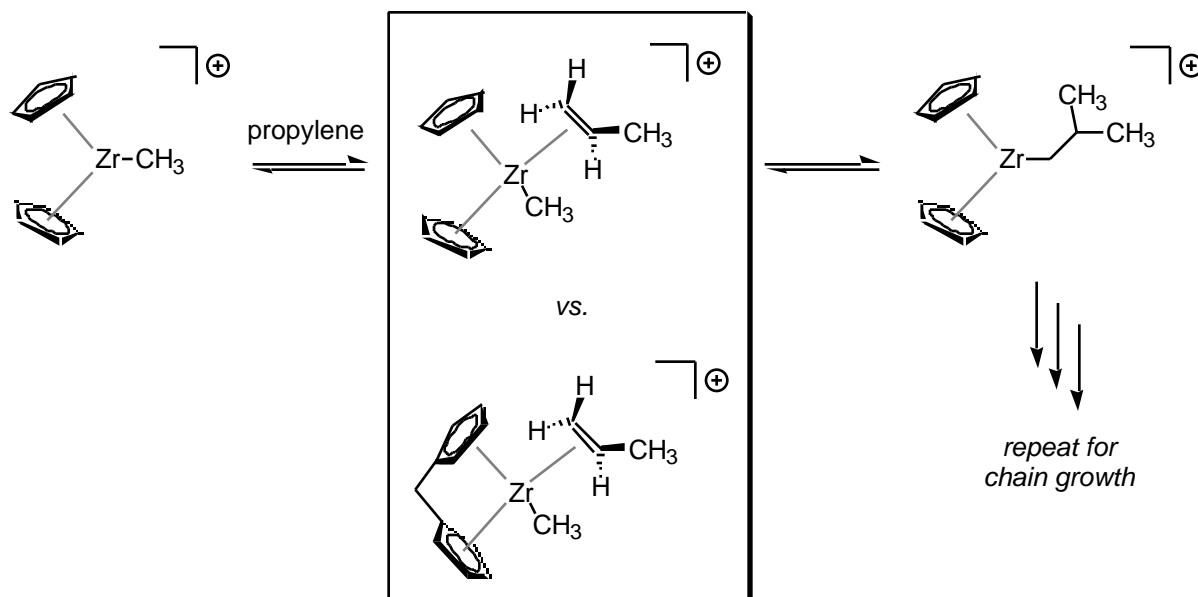
**C**

$$H_{f,298}^{\circ} = -238.7 \text{ kcal/mol}$$

The lowest energy is a bit lower than I got when I first wrote the problem set. In my 3 stereoconformers, the total stretching strain was effectively constant at 1.2 kcal/mol, the angle bending strain was about the same for **A** and **B**, but 1 kcal/mol smaller for **C**, which is consistent with all ring substituents but one being equatorial in **C**. Torsional strains were 11.6, 12.3, and 15.4 kcal/mol, respectively, for **A**, **B**, and **C**. Calculations on 2-hydroxytetrahydropyran show a difference of 1.2 kcal/mol between the axial and equatorial anomers (axial is lower) and that the difference is mostly in the torsional term (thus properly reflecting the anomeric effect). On going from **C** to **B**, three oxygen substituents go from equatorial to axial, so we might expect a drop of 3.6 kcal/mol. The

actual drop is 4.8. The remaining 1.2 kcal/mol can be ascribed to a favorable hydrogen bond from one hydroxyl group to the ring oxygen of the other ring (shows up in both *QQ* and *VDW* terms) which exceeds an unfavorable increase in angle bending strain for the more “compact” **B**. As for the additional 5.6 kcal/mol drop in energy on going from **B** to **A**, the illustrated arrangement of hydroxyl groups in **A** allows for another hydrogen bond in a “daisy chain” fashion (which is particularly favorable). Most of the difference is in *QQ* and *VDW*; there is also a small torsion energy difference favoring **A** (0.8 kcal/mol) but the overall structures are so different it is not obvious how to divide that amongst all the different bonds.

3. Zirconocenes are useful catalysts in the preparation of polypropylene. Shown on the next page is a structure for an intermediate thought to be important in the polymerization scheme. One of the interesting features about zirconocenes is that they can catalyze polypropylene production in a syndiotactic fashion, and it appears that one control element is the space available to incoming propylene based on the size and nature of the cyclopentadienyl (Cp) substituents. Some work has taken place with “bridged” Cp rings, which are designed to have different “bite angles”. Use PCModel to compute the structure of the indicated intermediate for simple Cp rings, and for the case where the two Cp rings are joined together by a methylene unit (CH₂). Report the following distances in each case (Å): Zr-CH₃, Zr-CH(CH₃), Zr-CH₂, and CH₃- - - CH(CH₃). Based on your results, how might you expect the reactivity of the two complexes to differ with respect to C-C bond formation? Justify your answer.



Technical notes: Metallocomplexes are slightly tricky in PCModel. The manual has a section on building ferrocene that you may find useful. Note that all Cp ring carbons should be defined as aromatic carbons (CA), the Zr-CH₃ bond is a “real” bond (just draw a connection) but all other Zr-C interactions must be set using the Mark (menu) Metal Coordination option, where the charge on Zr should be set to 1. As a check that you have not done something wrong, I note that optimized MMX energies in both cases should be around -115 kcal mol⁻¹.

Shown below are the two optimized structures from PCModel, with the relevant bond lengths indicated. Note that with the bridged Cps, the methyl and propylene ligands approach much closer to the Zr atom, as might be expected since simple inspection shows the bridging to pull the Cp rings towards one another compared to the unbridged case. The methyl/propylene separation is increased slightly.

In point of fact, it is impossible to determine how this change might affect the polymerization process. To understand the impact on kinetics, one would need to compute relevant transition states, which we can't do with a force field. To compute the effect on stereochemistry, we'd need much more data (and a different model system that would have stereochemical alternatives). Thus, any halfway reasonable speculation on your part will be treated respectfully in the grading process... If I were forced to speculate, I would say that the reduced encumbrance about the metal in the bridged zirconocene decreases the driving force for methyl migration, and reduces the reactivity of the intermediate (i.e., the polymerization slows down for the bridged case). Of course, this ignores possible electronic effects associated with the positions of the Cp rings, but it's a reasonable a proposal as any.

