Comparing the Stabilities of $[1_6]$- and $[1_4]$- Ketonands and Starands: An Ab Initio Study

Susan Lopez

Introduction:

Novel compounds closely related to crown ethers have been synthesized. Made from the oxidation of the benzylic methylenes of orthocyclophanes these compounds are deemed ketonands (cyclic polyketones) and starands (cyclic polyketals). Crown ethers having selective binding capabilities and molecular recognition properties, the authors are extremely interested in these new molecules. The internal 'cavities' of these being significantly different from the crown ethers might influence their host-guest behavior.

There is a synthetic preference for the formation of $[1_6]$starands over $[1_6]$ketonands, and for the formation of $[1_4]$ketonands over $[1_4]$starands. The authors hope to understand what factors are influencing the selective formation of one type over the other. To accomplish this ab initio calculations have been carried out to determine the lowest energy geometry and relative stability of each.

Computational Data:

Hartree-Fock (HF) calculations using a STO-3G basis set for the outer phenyl group and 3-21G basis set for the inner part (C=O of ketone in ketonand; COO of ketal in starand). Geometries were fully optimized for the $[1_6]$ketonand (S_6) and the $[1_6]$starand (D_{3d}). To ensure good reliability a larger basis set was used for representative models in which the phenyl rings were substituted by C=C bonds. The geometries of the models (as well as models for the $[1_4]$ketonand and $[1_4]$starand) were optimized at HF/3-21G. Moller-Plesset second-order perturbation (MP2) calculations at the optimized HF/6-31G* geometries were also done for the latter (MP2//HF/6-31G*).

Question Section:

(1.) Seeking Clarification (SCL)

There are three different basis sets used in this study, STO-3G, 3-21G and 6-31G*. Describe the differences in these basis sets, identifying what each component is in these notations. Are these basis sets appropriate for what molecules or parts of the molecules they are describing in paper? Why not do all of the calculations with the same basis set (i.e. explain the drawbacks in using each)?

(2.) Reasoning Using Quantitative Data (RQD)

Figure 1 (see below) shows a schematic that represents the relative energies of the $[1_6]$starand and $[1_6]$ketonand. What factors are responsible for these energy differences? Your answer should include a description of the different interactions involved and what specific factors such as geometry, etc. are influencing each of these.
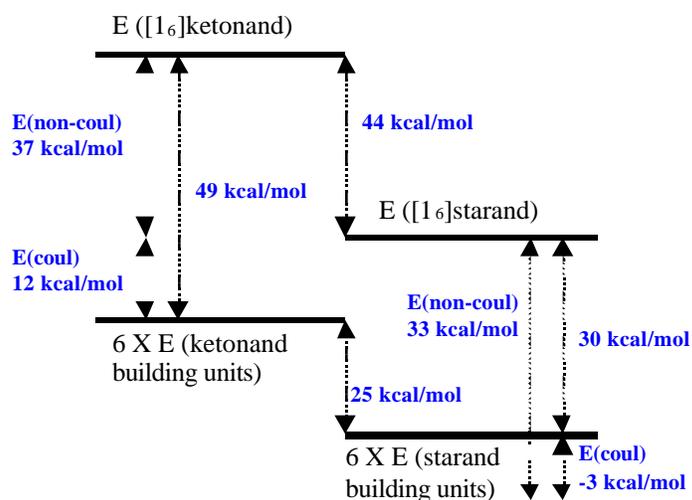

E ($[1_6]$ketonand)

E(non-coul)
37 kcal/mol

44 kcal/mol

49 kcal/mol

E ($[1_6]$starand)

E(coul)
12 kcal/mol

6 X E (ketonand building units)

E(non-coul)
33 kcal/mol

30 kcal/mol

25 kcal/mol

6 X E (starand building units)

E(coul)
-3 kcal/mol

(3.) Identification of components and Relationships (ICR)/ (RQD)

Construct an energy level diagram like that in Figure 1 for the $[1_4]$starand and $[1_4]$ketonand. All of the energy values you need are either specifically stated in the paper, or can be deduced from the information given. What similarities and/or differences are there between these two energy level diagrams? What is it about these molecules that yields this difference?

(4.) Flexibility and Adaptability of Scientific Reasoning (FAR)

Based on the information you have learned with regard to the stabilities of $[1_6]$- and $[1_4]$- starands and ketonands, what might you deduce for the hypothetical model compounds $[1_5]$- starand and ketonand? Which would you expect to be more stable? The $[1_8]$starand has been made, do you think that making the $[1_8]$ketonand is possible? Of course these answers require mostly speculation on your part since the molecules as of yet do not exist. Speculate on their relative stabilities by taking things like geometry, Coulombic repulsions and building-unit energies into consideration.

(5.) Identification of components and Relationships (ICR)

The $[1_6]$starand has a H^+ binding energy of -172kcal/mol. How does this affect its stability with respect to the ketonand? What is expected for the ketonand in the presence of H^+. Could this happen for the $[1_4]$ analogs? What about the $[1_8]$ analogs; the $[1_8]$starand has been synthesized as is stated in the paper, would it be possible to access the $[1_8]$ketonand by some means? Speculate in terms of energy and possible reaction pathways.