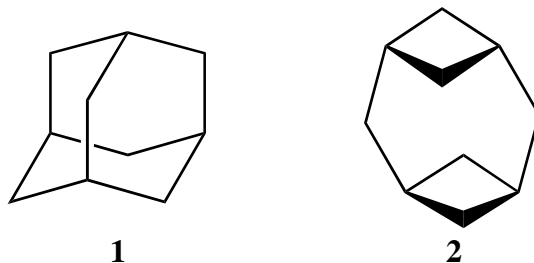


1. Below are two isomeric geometries that we previously examined in Problem Sets 1 and 2 as both $C_{10}H_{16}$ and $Si_{10}H_{16}$. It is time to (i) see how DFT does and (ii) discover whether the high-symmetry structures with which we have been working are really minima! To that end, we will first reoptimize all geometries at the TPSS/6-31G(d) level and then compute the vibrational frequencies. We will take advantage of the cubic scaling of local (i.e., non-hybrid) DFT by using an auxiliary density fitting basis set that will speed the calculation considerably. In order to do this, the correct specification of the theoretical level in Gaussian 03 is `tpsstpss/6-31g(d)/auto` (and, of course, you'll need to specify `opt` and `freq` to get the frequencies). Are all structures minima?



In addition, we should check the sensitivity to basis set by doing a single point calculation with a larger basis, in this case we will adjust the keywords to: `tpsstpss/6-311g(2df,p)/auto//tpsstpss/6-31g(d)/auto` `scf=tight` and guess the prior structure and wave function. Finally, we should check sensitivity to functional with this larger basis by performing a `mpw1pw91/6-311g(2df,p)//tpsstpss/6-31g(d)/auto` single point calculation (note that we can't use `auto` in this calculation because we have a hybrid functional).

Compare and contrast the DFT results for relative energies to prior results (found in the answer key to Problem Set 2). Comment as well on comparison of enthalpies and free energies from the TPSS/6-31G(d) level compared to simply electronic energies. If you had to make a best guess for the enthalpy differences, what would your guess be? What would your estimate of error in your guess be? How might you try to improve on your guess/error estimate with additional calculations? (You don't have to do them, just describe the plan.)

Using data courtesy of house elf, we have:

Level of Theory	$E(1)^a$	$E(2)^a$	$E(2) - E(1)$, kcal mol ⁻¹
<u>Carbon frame</u>			
AM1	-43.2	18.0	61.2
PM3	-34.6	6.3	40.9
HF/MIDI!	-385.688 27	-385.572 59	72.6
HF/6-31G(d)	-388.026 48	-387.928 14	61.7
MP2/6-311G(2df,p)// HF/6-31G(d)	-389.781 69	-389.680 53	63.5
TPSS/6-31G(d)/auto			
E	-390.802 62	-390.717 42	53.5
H_{298}	-390.552 15	-390.469 73	51.7
G_{298}	-390.858 60	-390.509 73	49.5
TPSS/6-131G(2df,p)/auto// TPSS/6-31G(d)/auto	-390.900 48	-390.815 03	53.6
$mPW1PW91/6-311G(2df,p)//$ TPSS/6-31G(d)/auto	-390.756 28	-390.663 06	58.5
<u>Silicon frame</u>			
AM1	70.4	91.2	20.8
PM3	6.7	16.8	10.1
HF/MIDI!	-2883.725 42	-2883.667 12	36.6
HF/6-31G(d)	-2898.529 99	-2898.480 58	31.0
MP2/6-311G(2df,p)// HF/6-31G(d)	-2899.944 92	-2899.894 31	31.8
TPSS/6-31G(d)/auto			
E	-9204.722 79	-2904.679 87	26.9
H_{298}	-2904.558 48	-2904.515 94	26.7
G_{298}	-2904.621 41	-2904.528 77	24.2
TPSS/6-311G(2df,p)/auto// TPSS/6-31G(d)/auto	-2904.974 66	-2940.931 68	27.0
$mPW1PW91/6-311G(2df,p)//$ TPSS/6-31G(d)/auto	-2904.846 14	-2904.799 50	29.3

^a Units are kcal mol⁻¹ for semiempirical levels of theory and E_h for ab initio and density functional levels of theory.

Some noteworthy observations:

- 1) Basis set effect is very small for TPSS energies, large vs. small. A good sign of convergence.
 - 2) Thermal contributions to free energy favor **2** over **1** by a rather large margin. Ordinarily, this might be unusual, but in this case **1** has very, very high symmetry, and that reduces its rotational entropy substantially. The cage is also very rigid, which reduces vibrational entropy. The effects are cumulative and amount to a full 4 kcal/mol in the case of carbon.
 - 3) The pure TPSS functional predicts **2** to be more stable relative to **1** than does the hybrid *mPW1PW91* functional, again by a substantial margin in the case of C, and a still noticeable margin in the case of Si. In general, hybrid functionals seem to give improved thermochemistries, and the closer agreement of the *mPW1PW91* results with the large-basis MP2 calculations suggests that this may be true in this case as well.
 - 4) My best estimate, with error bar, for the enthalpy difference between **1** and **2** would probably derive from taking an average of the MP2 and *mPW1PW91* results, correcting by the enthalpy vs. energy amount computed at the TPSS level, and taking the error to be one half the separation between the MP2 and *mPW1PW91* predictions times the square root of 2. For C, that is 59.3 ± 3.5 kcal/mol; for Si, 30.3 ± 1.8 kcal/mol.
 - 5) To do better, a composite level like MCG3, W2, BAC-MP4, etc. could be assayed.
2. Get a copy of Mochida, K.; Matsuhida, N.; Sato, R.; Nakadaira, Y. *Organometallics* **2006**, 25, 4231.
- a. Scheme 2 (page 4232) shows the reaction for the thermolysis of **1** to benzene and singlet dimethylgermylene, $\text{Ge}(\text{Me})_2$, and suggests a possible transition state (**3**). Determine whether **3** is really a transition state or whether it is a reactive intermediate (i.e., a high-energy minimum). A good first step might be first to optimize structures for **1**, benzene, and $\text{Ge}(\text{Me})_2$, and then use structural information from those structures to construct a guess geometry for **3** and see if it can be successfully minimized. Symmetry, possibly from employing a Z matrix, might prove useful in speeding up calculations. Ultimately use B3LYP/6-31G* for final calculations, but initial calculations at a lower level of theory could prove useful at your discretion. Is **3** a TS or minimum? If **3** is a minimum, find the transition state structure between **1** and **3**.

Structure **3** is actually a minimum, not a TS structure. A TS structure for the electrocyclic ring closure can be located.

- b. Using whatever transition state you find, compare your calculated ΔH^\ddagger to the experimental value given in the paper (assume the temperature difference between default 298 K in Gaussian and the experiment is negligible). Use ΔG^\ddagger to calculate the unimolecular rate constant, k , at 305.3 K. Include the equation that you used to get the rate constant. Do your errors seem reasonable given the method and basis set used?

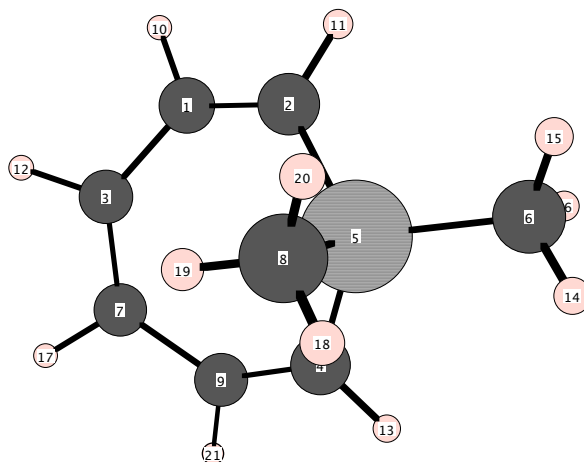
Structure	H, E_h	$H_{rel}, \text{kcal/mol}$
1	-2386.857 43	0.0
TS	-2386.817 39	25.1
3	-2386.834 46	14.4
Benzene and Ge(Me) ₂	-232.142 58 -2154.704 65	 6.4

The calculated ΔH^\ddagger of 25.1 kcal/mol may be compared to the experimental value of 20.5 kcal/mol. The difference of 4.6 kcal/mol is perhaps a reasonable error given the modest basis set that we used and that we are comparing gas-phase enthalpies to a reaction that takes place in solution. In the frequency outputs, we can also find free energy values. When the free energy of activation is used in the transition-state theory rate equation (Eq. 15.27 of the textbook) at 305.45 K, a rate constant of $1.77 \times 10^{-6} \text{ s}^{-1}$ is predicted. The experimental rate of $2.23 \times 10^{-4} \text{ s}^{-1}$ is two orders of magnitude larger, suggesting an error of about 3 kcal/mol in the free energy of activation (again, likely attributable to a small basis set and/or solvation effects).

- c. In the paper, it is mentioned that the progress of the reaction was followed via proton NMR, but the shifts that were observed are not described. Perform NMR calculations on all minima for this reaction (as single-point calculations on the geometries already optimized). Remember that NMR calculations require a much larger basis set in order to ensure accuracy. An appropriate basis set might be 6-311G(2df,p). A calculation of the TMS standard is also required, of course, in order to compute chemical shifts relative to the TMS protons (recall that a TMS example in glorious T_d symmetry is already helpfully available in your `templates` subdirectory). What shifts might an experimentalist use to evaluate if the reaction were to be proceeding? If **3** were to be present in sufficient concentration to observe its NMR spectrum, what peaks might one use to distinguish between **1** and **3**?

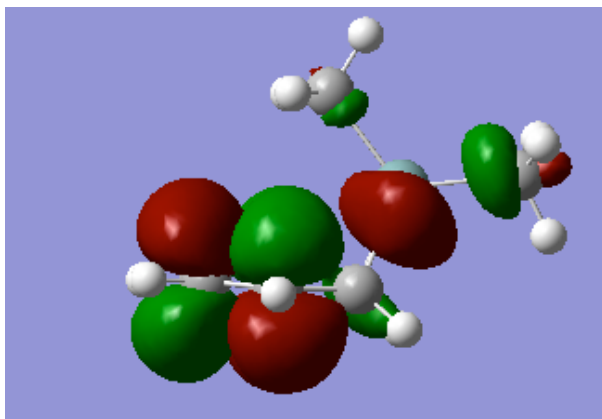
¹ H NMR			
Ring hydrogen	δ (ppm)		
	1	3	benzene
H11	6.00	2.06	7.68
H10	7.35	5.77	
H12	6.62	5.41	

In the conversion of **1** to benzene, one would see the three proton shifts from the ring of **1** merge slightly downfield into the one shift for benzene. If one was able to get a NMR spectrum of **3**, the easiest shift to identify it by would be of H11 which goes upfield by 4 ppm from complexes **1** to **3**.

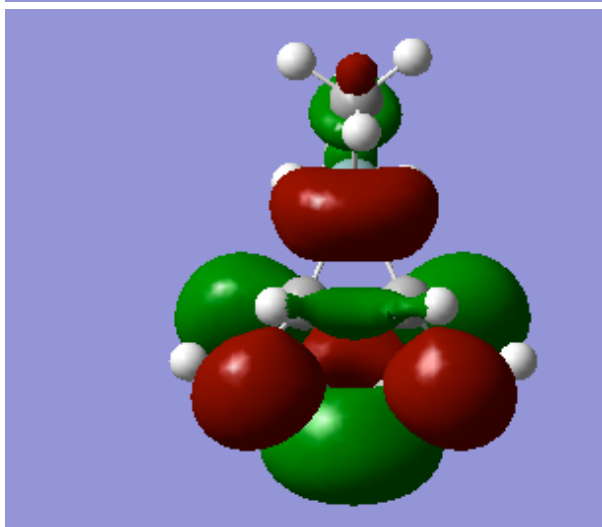


- d. Assume that **3** is a reactive intermediate that can be isolated. If **3** were to be reduced by one electron, would that tend to make easier formation of the reactant (**1**) or the products (benzene and Ge(Me)₂)? Explain your rationale based on inspection of a relevant molecular orbital of **3**; do not do expensive calculations on the radical anion.

Reduction adds an electron to the LUMO. So, by inspection of the LUMO, we should be able to make predictions. As noted in the orbitals below, the LUMO is predicted to be antibonding between the ring π system and the germylene lone pair, so that retrocyclization would be expected to occur with greater facility.



LUMO (side view)



LUMO (view from below)

3. Here continues a problem that will carry over to the final exam. We add to the data at:

pollux.chem.umn.edu/8021/C4H6S02/

Your present task is to update your structure on the potential energy surface (PES) with a calculation at the B3LYP/6-31G* level (since there is no double slash, this implies re-optimizing the geometry). The most efficient way to do this will be to read in the force constants and geometry from your RHF frequency calculation (i.e., `fopt=(readfc)` `geom=checkpoint`, `guess=read`) as keywords. Nota bene: if you were using `fopt=ts` you will need to continue to use `ts`, of course. Once you have a reoptimized structure, do a new frequency calculation at the B3LYP/6-31G* level and update your entry with the relevant thermochemical data requested by the DFT submission form.

Finally, compute the B3LYP/6-31G* aqueous solvation free energies for your DFT structures using the PCM model in Gaussian03 (as single-point calculations on the DFT optimized geometries). When the calculations complete, add the solvation free energies to the website data. Report only one position after the decimal place for the solvation free

energies in units of kcal/mol (the solvation free energy is the difference between what G03 reports as the “total free energy in solution: with all non electrostatic terms” and the electronic energy (*not* the free energy) of the optimized molecule in the gas phase).

Full credit for sensible data.