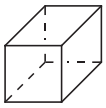
Chemistry 5021/8021 **Computational Chemistry** 3/4 Credits

Spring Semester 2003

ANSWER KEY

1. Cyclooctatetraene (COT) and cubane are two isomers of C_8H_8. To what point group does each molecule belong? What is the difference in their heats of formation predicted at the PM3 level (you do not need to impose symmetry in the PM3 calculations)? Is the sign of the difference (i.e., the prediction of which one is more stable) what you expected? Why or why not?

COT



cubane

COT belongs to the D_{2d} point group (like allene) while cubane belongs to the O_h point group. PM3 predicts COT to have a lower 298 K heat of formation than cubane by 47.1 kcal/mol. Given the enormous strain implicit in cubanes many fused 4-membered rings, it certainly seems reasonable that COT would be more stable, even though its "non-aromaticity" is evident in its non-planarity.

Now construct cartesian coordinate sets for the two molecules that *do* have the correct symmetry (hint: think about these molecules placed symmetrically around the origin in a 3-dimensional cartesian space. For every atom at a position (*x*,*y*,*z*), what other cartesian positions must be occupied by equivalent atoms?) You'll probably want to visualize your cartesians in Chem-3D to verify reasonable structures. Compute ΔE for COT and cubane at the HF/6-31G*, MP2/6-31G*//HF/6-31G*, and B3LYP/6-31G* levels. Comment on the values compared to one another and to PM3.

In the D_{2d} point group every point (a,b,c) must have corresponding points ($-a$,b,c), (a,$-b$,c), ($-a$,$-b$,c), (b,a,$-c$), ($-b$,a,$-c$), (b,$-a$,$-c$), and ($-b$,$-a$,$-c$), so once you pick one C and one H position, all the others can be generated by cut-and-paste in a word processor. In the O_h point group things are even easier as every point (a,b,c) generates all possible combinations of signs for the three coordinates (i.e., the same point is found in every cartesian octant).

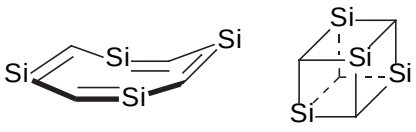
The energy differences predicted at the specified RHF, MP2, and B3LYP levels are 81.8, 68.7, and 58.3 kcal/mol, respectively. The last two

levels include electron correlation, where the first does not, and they agree slightly better with one another than either does with RHF, but not really by much. All levels give a larger difference than that predicted by PM3, although the B3LYP value is within about 11 kcal/mol of PM3. The broad range of predictions does not permit much confidence in any given value.

What is the experimental difference in the 298 K heats of formation for COT and cubane? How do the different levels of theory compare to experiment? Explain any particularly good or bad agreement. Although they are too expensive to have each student perform, the instructor has carried out G3 calculations on the two isomers, and you may find them in ~inst8021/PS2_data. How does the 298 K enthalpy difference at the G3 level compare to experiment? A possible criticism of our earlier analysis would be that we were using ΔE values from some levels of theory to compare to ΔH from experiment. Based on the data in the G3 output files, is this a significant criticism?

The experimental heats of formation for COT and cubane are 70.7 and 148.7 kcal/mol, respectively, for a difference of 78.0 kcal/mol. This value agrees rather poorly with any level of theory except RHF/6-31G*. Thus, there is some cancellation of errors associated with ignoring electron correlation and using a relatively modest basis set. The enthalpy difference predicted at the G3 level is 75.3, in reasonably good agreement with experiment (using much more complete levels of electronic structure theory and much larger basis sets makes a difference!) The G3 level predicts ΔH and ΔE to be very close to one another for these two molecules, so errors in the prior calculations are not associated with ignoring thermal contributions to enthalpy.

Now, consider the tetrasila analogs of COT and cubane below.



tetrasilaCOT tetrasilacubane

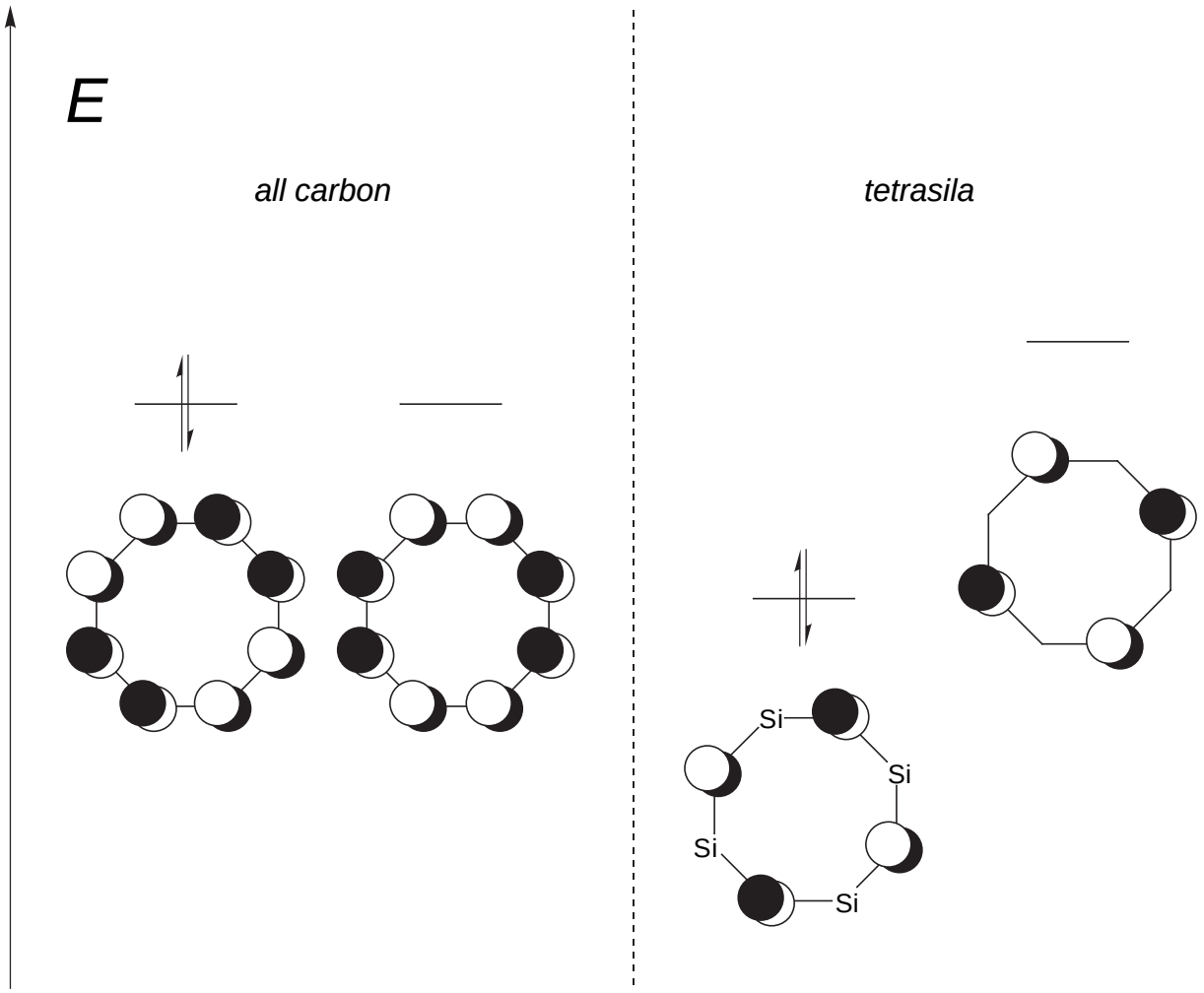
Repeat all of the calculations done above for these sila analogs (except that no G3 data need to be considered). Compare and contrast the two sets of systems: which features are similar and which are different? To what point groups do the optimized sila structures belong? Is there any disagreement on this point between different levels of theory? To better understand the structure of tetrasilaCOT, visualize its HOMO and LUMO. Explain

how these orbitals differ from the HOMO and LUMO of COT (you may visualize these too, or simply look in any standard textbook) and why this affects the geometry.

The PM3, RHF, MP2, and B3LYP levels all predict the *silacubane* to be more stable than the silaCOT by 95.9, 45.2, 57.8, and 62.5 kcal/mol, respectively. This reflects in part the strong preference of silicon to be sp^3 hybridized rather than sp^2. Longer C-Si bonds also reduce strain in cubane. Interestingly, although there is again substantial disagreement between different levels of theory, if we look at the *change* in relative stability on going from the all-carbon to the tetrasila system, it is predicted to be 143, 127, 127, and 121 kcal/mol at the same 4 levels of theory. Ignoring PM3, there is fairly good agreement, then, that the change is about 125 kcal/mol. We could then guess that the actual difference in heats of formation in the silasystem would be 125 kcal/mol different than experiment for the all carbon system, i.e., the cubane-like isomer will be more stable by 47 kcal/mol.

One reason to ignore PM3 is that it predicts a different geometry for tetrasilaCOT than the other levels. With PM3, it remains D_{2d}, but all other levels predict the ring to prefer to be planar with all equal bond lengths; this makes the molecular point group D_{4h} (the tetrasilacubane is T_d).

The ring prefers to be planar because the introduction of the silicon atoms lifts the frontier orbital degeneracy that causes all-carbon COT to be non-aromatic, and to distort to the tub-like geometry already noted above. As seen in the below diagram of the frontier orbitals, in the all-carbon case, when two electrons are singlet-coupled in a single orbital, that orbital causes true double bonds to form between p orbitals of like phase, and there is no balancing antibonding interaction because the other orbital is empty. This Jahn-Teller distortion further enhances bonding by bending common phases of pi clouds on opposite ring edges towards one another, creating the tub. But introduction of the Si atoms causes the frontier orbitals to be either entirely nonbonding on the carbon atoms or on the silicon atoms. The former is lower in energy because C is more electronegative than silicon. Bending of the ring is now disfavored because it raises the energy of lower ring pi orbitals.



2. In the attached communication from *Angewandte Chemie, International Edition in English*, Lambert et al. report the isolation and X-ray crystal structure of the pentamethylcyclopentadienyl (Cp*) cation. Note that Cp^{*+} is formally antiaromatic, so its been an attractive synthetic target for many years.

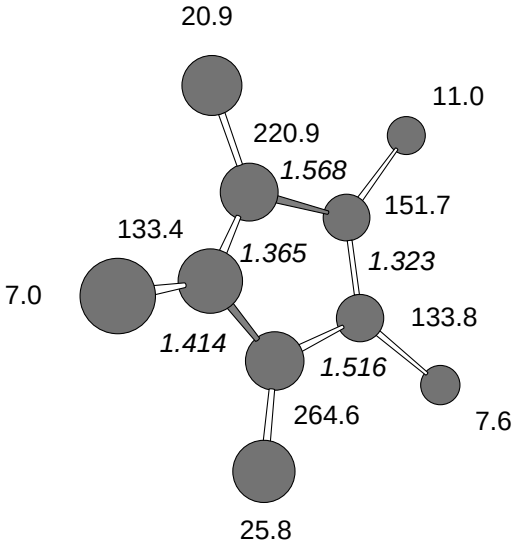
Lambert et al. report structural data and ^{13}C NMR data. Optimize the structure of the Cp* cation at the HF/6-31G* level (don't worry about trying to impose symmetry). How do your structural data compare to the reported data? Now compute the isotropic ^{13}C NMR chemical shifts for all carbons at the B3LYP/6-31G*//HF/6-31G* level (simply include the keyword `nmr` in a single-point calculation). Since NMR calculations provide *absolute* shieldings, you will also need to know the computed shieldings for tetramethylsilane (TMS, which is the standard for $\delta = 0$ on the ^{13}C chemical shift scale). I have done this calculation for you, and it may be found in the file ~inst8021/PS2_data/tmsnmr.out (note the lovely T_d symmetry!). A *de*shielding ^{13}C shift δ is then determined as shielding for

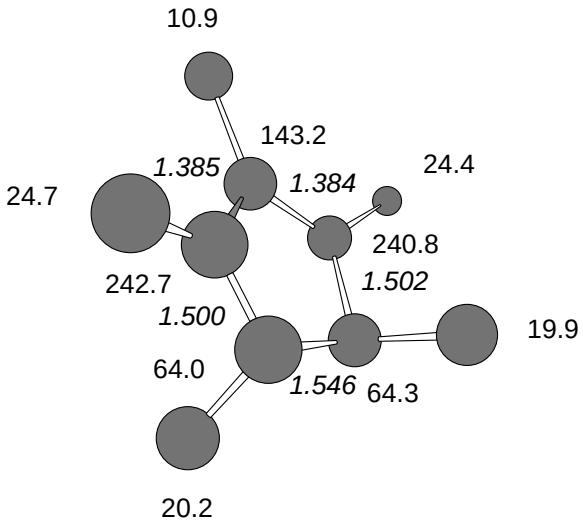
TMS minus shielding for carbon of interest. How do your data compare to those reported by Lambert et al.? (Use a picture to report your structural and NMR data).

Now consider the pentamethylcyclopent*en*yl cation (i.e., not *di*enyl, but just *mono*enyl; add the two H atoms trans to one another on adjacent carbon atoms). Compute structural and ^{13}C chemical shifts for this structure at the same levels of theory as already done for Cp^{*+}. How do your data compare to those reported by Lambert et al.?

Which of these two molecules do you think was actually made?

Bond lengths and 13C chemical shifts are noted in the below pictures (hydrogen atoms removed for clarity). Note that only in the mono-unsaturated ring does theory predict two methyl groups to be significantly out of the plane of the ring, as seen in the X-ray crystal structure. Agreement between theory and experiment is much better for the enyl system than for the dienyl system. To quantify this point, the RMS error in bond lengths for the most favorable overlap of the computed rings with the experimental one is 0.093 Å for the dienyl case and 0.022 Å for the monoenyl case. The RMS error in ring chemical shifts is 48 ppm for the dienyl case, and a mere 6.6 ppm for the monoenyl case.





So, what was really made? See Lambert and co-workers, *Angew. Chem., Int. Ed. Engl.* 114 (2002) 2275-2276 and 2278.

3. Here begins a problem that will carry over to the third problem set and ultimately the final exam. Take a look at

http://pollux.chem.umn.edu/8021/ProbSets-Exams/2003/C3H7NO/

Full credit for this problem simply involves submission of credible data.