

*This problem set will take longer than the last one in the sense that you may need to submit some jobs, leave, and check your results later. **Get started early.***

Some mechanical reminders: To run a G09 job, you must have the `gaussian` module loaded. After login, type `module list`—if you don't see `gaussian/g09.a02`, type `module load gaussian`, and then `module list` again, and now you should see it. Next, remember that your input files should be named, for example `myfile.com`. Issue the command `qg09 myfile.com` and the script will submit a 1 hour job to the devel queue (very responsive owing to one hour limit). For jobs that will take more than one hour (which should rarely be necessary) you can try `qg09 -q bladejr -t 5:00:00 myfile.com`, which will submit the job to the “normal” queue with a time limit of 5 hours (but you may have to wait for the job to start if the queue is already full). If you want to look at an output deck while a job is running, you can either `vi myfile.out` or `more myfile.out`. To examine the queue on the blade, the command is `qstat -a`; you may find that `qstat -a | egrep cm8021##` (where `cm8021##` is your userid (or the analogous `cm4021##`)) is also convenient. Links to `vi` commands and a unix primer are provided on the class webpage.

A nomenclature reminder: the notation $x/y//w/z$ means level of theory x using basis set y at a geometry optimized at level of theory w with basis set z . E.g., `MP4/6-311G(d,p)//MP2/6-31G(d)` means that the geometry was optimized at the `MP2/6-31G(d)` level but the energy (and/or other properties) are being calculated at the `MP4/6-311G(d,p)` level. The notation x/y in the absence of a trailing $//w/z$ implies optimization and energy evaluation were performed with the same level of theory.

Some quick notes/reminders with respect to *Gaussian 09*:

- 1) Various files have been provided in my directory `~cm8021pr/templates` — feel free to study them carefully to ensure that you have proper file formats, memory requests (`%mem=7gb`), parallel processor requests (`%nproc=4`), and checkpoint naming conventions (`%chk=myfile.chk`).
- 2) If you are entering geometric or basis set data in a G09 input deck (as opposed to reading it from the checkpoint file) you *must* end the input file with a blank line.
- 3) To find transition states *in the absence of a symmetry constraint*, use `fopt=(ts,calcfc)`. If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS

breaks the symmetry (in which case, use neither `ts` nor `calcfc` as keywords) or preserves it (in which case use both). If you are looking for a TS, you may often find it helpful to do `fopt=(ts,calcfc,noigentest)`. The other keywords besides `ts` request calculation of analytic force constants on the first step, and that the job not die if other than exactly one negative force constant is found at some step.

4) You can save a *lot* of time by using useful information from previous calculations stored in the checkpoint file. *Plan* your calculations to try to save time. You can also save a lot of time by using *symmetry* when appropriate. Consider this carefully for problem 2...

a) Keywords `guess=read` and `geom=checkpoint` get the wave function and the geometry, respectively, from the last completed calculation. So, if you have just done an optimization, and want to follow-up with a frequency calculation, for instance, you will certainly want to use these keywords. **Note: Frequencies *must* be calculated using the same level of theory with which the geometry was optimized to correspond to true IR frequencies!** (Note that if you know ahead of time you will want frequencies after a given optimization, you can simply include the `freq` keyword in the same job as `fopt`).

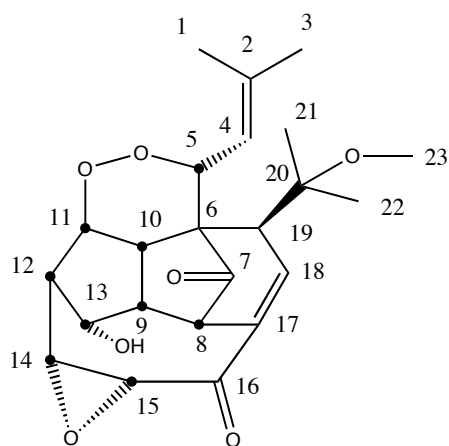
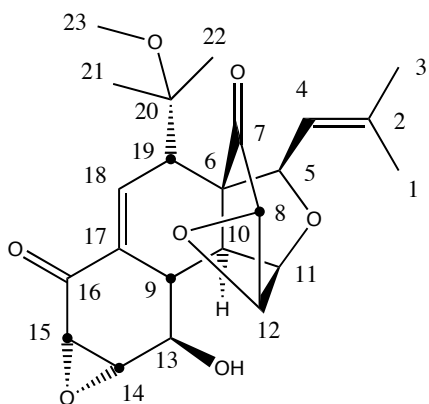
b) If you just optimized a geometry at one level of theory, and want to repeat that optimization at a different level, include `readfc` in the `fopt=()` keyword, e.g., `fopt=(ts,readfc)` for a second pass at a transition-state optimization. This causes the program to start with the force constants from the previous calculation, which is efficient. **It's usually a good idea to work your way up in a geometry optimization so you don't waste a lot of computer time because of a bad initial guess.**

***** THE PROBLEMS *****

1. We begin by following up on some work from the first class problem set. In particular, in `~cm8021pr/templates` I have placed PCModel text output files for the lowest energy structures of both **A** and **B** appearing in problem 3 of Problem set 1 (named `A_pcm.txt` and `B_pcm.txt`). For each of these structures (without reoptimization of the geometry), compute the ^{13}C NMR spectrum using the WC04 density functional together with the 6-31G(d) basis set (see Wiitala et al. *J. Chem. Theory Comput.* **2006**, 2, 1085 for details of the WC04 functional). You will find shieldings computed at this level of theory for tetramethylsilane (TMS) in `~cm8021pr/templates`, which you may want to use in order to compute the proper *deshielding* values δ for comparison to experiment. To assist in this comparison, report your deshieldings for the carbon atoms as numbered in the figure on the next page. (Those with good eyes will note that the stereochemistry at C-10 in **B** is different from that in Problem Set 1 – the structure here is

correct, and thus you should use *my* structures and not your own – this will have no effect on the grading of Problem Set 1.)

The experimental data are provided in the table below. They were originally assigned to structure **A** (see Schlegel et al. *J. Antibiot.* **2002**, 55, 814), but is structure **B** plausible? In addition to providing an answer to this question, together with justification for your response, outline what additional steps you could take to increase your confidence in making a final assignment.

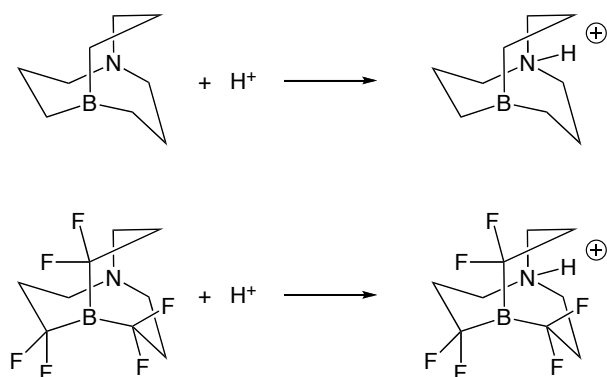
**A****B**

Experimental data

Carbon	δ , ppm
1	18.6
2	142.2
3	26.1
4	120.7
5	75.8
6	60.5
7	202.9
8	53.1
9	40.4
10	47.8
11	71.5
12	54.5
13	72.7
14	61.0
15	53.2
16	192.8
17	132.5
18	139.6
19	40.9
20	77.3
21	26.6
22	24.7
23	49.1

2. Consider the bicyclic borazane molecules on the next page, and in particular their basicities. Compute, at the levels indicated in the below tables, B–N bond lengths optimized at the indicated levels of theory (consider: are there possibilities for bond-stretch isomerism?) and proton affinities at the indicated levels of theory. In some detail, discuss your modeling strategy

and results, addressing in particular the chemistry, but also considering how the semiempirical models compare to the more complete levels of wave function theory. *Nota bene:* sensible attention to job ordering and symmetry will help you to stay within the development queue time limits as you work on this problem. Imagine that this problem was motivated by a question from an experimental colleague, namely, “How does the basicity of the borazane compare to that of the hexafluoroborazane?”



B–N Bond Lengths (Å) in Borazanes

	Bicyclo[3.3.3]borazane		Hexafluorobicyclo[3.3.3]borazane	
	Unprotonated	Protonated	Unprotonated	Protonated
AM1				
PM3				
PM6				
HF/3-21G				
HF/6-31G(d)				
MP2/6-31G(d)				

Computed Energies (E_h) of Borazanes

	Bicyclo[3.3.3]borazane		Hexafluorobicyclo[3.3.3]borazane	
	Unprotonated	Protonated	Unprotonated	Protonated
AM1				
PM3				
PM6				
HF/3-21G				
HF/6-31G(d)				
MP2/6-31G(d)//				
HF/6-31G(d)				
MP2/6-31G(d)				

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

pollux.chem.umn.edu/8021/PES/

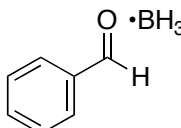
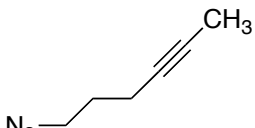
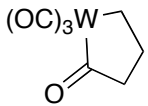
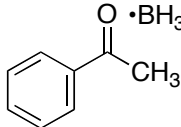
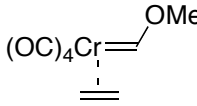
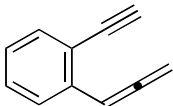
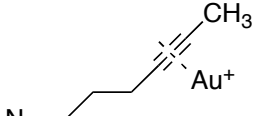
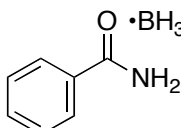
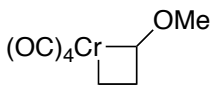
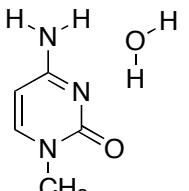
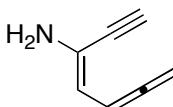
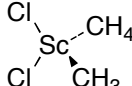
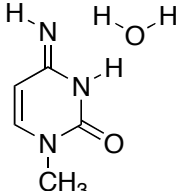
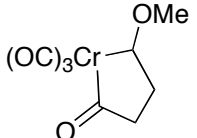
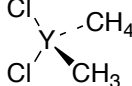
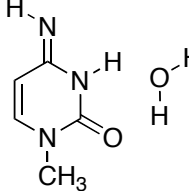
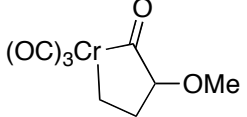
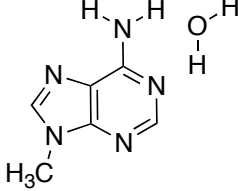
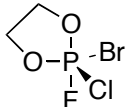
While there, select **View Surface**. You will see my contributions to detailing the energetics of select stationary points on various potential energy surfaces (click on either [93.html](#) or [94.html](#) to see them in 3D — you'll need a browser with Java capabilities — you'll also see text cartesian coordinates, which you can alternatively visualize by using the coordinates in a Gaussian 03 input file and using GaussView). My stationary points are for the van der Waals complex (minimum) of methane with methyllutetocene and the corresponding transition-state structure for C–H bond methathesis.

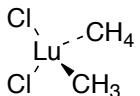
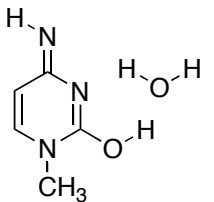
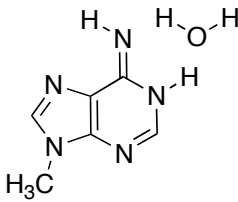
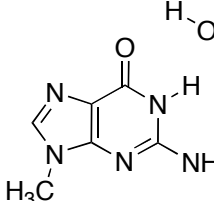
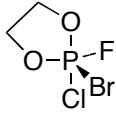
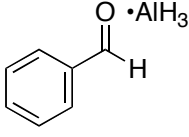

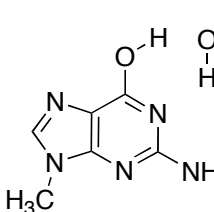
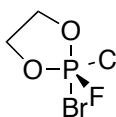
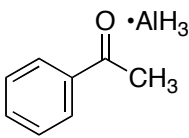
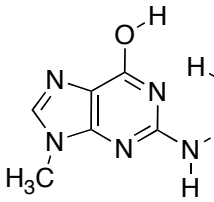
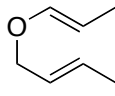
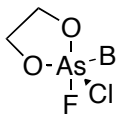
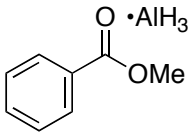
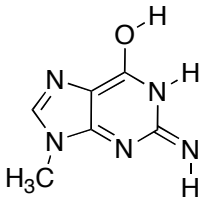
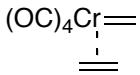
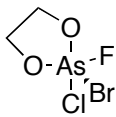
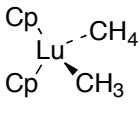

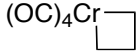
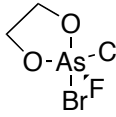
Your task is to find your own two stationary points—both a minimum and a transition-state structure—taken from the table starting on the next page. *You will receive by email the numbers of your two structures, which will be assigned randomly.* To complete each entry, you will need a frequency calculation at the HF level (and thus, of course, you will first have to have optimized the structure at this level of theory). When you have the data, click on **Submission Form** and paste in the number of imaginary frequencies (0 or 1), the HF energy, enthalpy, and free energy, and finally the optimized cartesian coordinates (you can cut and paste right from the output file *of the frequency calculation* following the instructions on the form). If you make any mistakes and fail to realize until after submission, contact me with the details and I will fix the website.

With respect to basis set, we will use the 6-31G(d) basis set for all atoms for which it is defined. If you have a molecule with an atom that is *not* defined in the 6-31G(d) basis (e.g., lutetium), then you should use the SDD basis set and associated pseudopotentials for those atoms, and 6-31G(d) for all the rest (see the *Gaussian 09* documentation for use of the **gen** basis set keyword). Note that you may find it more efficient to *start* looking for stationary points with a smaller basis set, and then finish with the larger one, but that is up to you.

Full credit for this problem simply consists of entering sensible data. In future exercises, we will make comparisons of different levels of theory and different congeners to learn more about the chemistry of the surfaces.

Class molecules:

- | | | | |
|--|--|---|--|
| <p>01 </p> | <p>26 Click [3+2] TS for 25</p> | <p>51 TS for carbonyl insertion of 50</p> | <p>76 Myers-Saito TS for 75</p> |
| <p>02 TS for addn of BH₃ to C=O of 1</p> | <p>27 </p> | <p>52 </p> | <p>77 Schmittel TS for 75</p> |
| <p>03 </p> | <p>28 Click [3+2] TS for 27</p> | <p>53 </p> | <p>78 </p> |
| <p>04 TS for addn of BH₃ to C=O of 3</p> | <p>29 </p> | <p>54 TS for [2+2] of 53</p> | <p>79 Myers-Saito TS for 78</p> |
| <p>05 </p> | <p>30 Click [3+2] TS for 29</p> | <p>55 </p> | <p>80 Schmittel TS for 78</p> |
| <p>06 TS for addn of BH₃ to C=O of 5</p> | <p>31 </p> | <p>56 TS for carbonyl insertion of 55 to 58</p> | <p>81 </p> |
| <p>07 </p> | <p>32 TS for tautomerization of 31–33</p> | <p>57 TS for carbonyl insertion of 55 to 59</p> | <p>82 Myers-Saito TS for 81</p> |
| <p>08 TS for symmetric CH bond metathesis in 7</p> | <p>33 </p> | <p>58 </p> | <p>83 Schmittel TS for 81</p> |
| <p>09 </p> | <p>34 </p> | <p>59 </p> | <p>84 </p> |
| <p>10 TS for symmetric CH bond metathesis in 9</p> | <p>35 TS for tautomerization of 34–36</p> | <p>60 </p> | <p>85 TS for tautomerization of 84–86</p> |

- | | | | |
|--|--|---|--|
| 11  | 36  | 61 pseudorotation
TS 60→62 | 86  |
| 12 TS for symmetric CH bond metathesis in 11 | 37  | 62  | 87  |
| 13  | 38 TS for tautomerization of 37-39 | 63 pseudorotation
TS 62→64 | 88 TS for addn of AlH3 to C=O of 87 |
| 14 [3,3] sigmatropic shift chair TS of 13 | 39  | 64  | 89  |
| 15 [3,3] sigmatropic shift boat TS of 13 | 40  | 65 pseudorotation
TS 64→60 | 90 TS for addn of AlH3 to C=O of 89 |
| 16  | 41 TS for tautomerization of 40-42 | 66  | 91  |
| 17 [3,3] sigmatropic shift chair TS of 16 | 42  | 67 pseudorotation
TS 66→68 | 92 TS for addn of AlH3 to C=O of 91 |
| 18 [3,3] sigmatropic shift boat TS of 16 | 43  | 68  | 93  |
| 19  | 44 TS for [2+2] of 43 | 69 pseudorotation
TS 68→70 | 94 TS for symmetric CH bond metathesis in 93 |
| 20 [3,3] sigmatropic shift chair TS of 19 | 45  | 70  | |
| 21 [3,3] sigmatropic shift boat TS of | 46 TS for carbonyl insertion of 45 | 71 pseudorotation
TS 70→66 | |

