This problem set will take longer than the last one in the sense that you will almost certainly 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` listed, 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 (usually 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 -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 standard 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 calhoun, 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, e.g., 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 `opt=(ts,calcfc)`. If you have a symmetry constraint, you need to decide whether the reaction coordinate for the TS structure *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 `opt=(ts,calcfc,noeigentest)`. The other keywords besides `ts` request calculation of analytic force constants on the first step (`calcfc`), and that the job not die if other than exactly one negative force constant is found at some step (`noeigentest`).

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. This will be especially true for Problem #3.

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 that you will want frequencies after a given optimization, you can simply include the `freq` keyword in the same job as `opt`).

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 `opt=()` keyword, e.g., `opt=(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.**

5) Serving GaussView across the local network can be slow owing to the massive amounts of graphics data being transferred. It will often be more convenient to transfer readable files to a local machine (e.g., a computer in Chemistry's Computer Lab) and run GaussView locally. In particular, output files (which are text) can be transferred easily. For inspection of molecular orbitals, it is convenient to transport a formatted checkpoint file. To generate such a file, the command is `formchk myfile.chk`, where `myfile.chk` is the name of the (binary) checkpoint file. A text formatted checkpoint file `myfile.fchk` will be created and can be moved in the same fashion as an output file. GaussView accepts .fchk as an option for file types to be opened.

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

1. In class, we went through Hückel theory as applied to the allyl cation in considerable detail (following the textbook). Consider if the central C–H fragment in the allyl cation were to be replaced by the isoelectronic N: (with an in-plane lone pair). The 2-azaallyl cation is easily generated by deprotonation of *N*-methylformaldimine. Now, here are a few experimental facts: (i) the ionization potential of the methyl radical is 9.8 eV, (ii) the ionization potential of the

amidogen radical is 10.8 eV, (iii) the rotational barrier of ethylene is 60 kcal/mol, (iv) the rotational barrier of formaldimine is 60 kcal/mol. Now, some questions: (i) what is the Hückel resonance energy for the 2-azaallyl cation? How do the 2-azaallyl system orbitals differ from the allyl system? Carry out AM1 calculations for the allyl and 2-azaallyl cations and visualize the orbitals; are they consistent with your predictions from Hückel theory? Compute the rotational barriers for a terminal methylene unit in allyl and 2-azaallyl; are they consistent with your predictions from Hückel theory?

2.   In Problem Set 1, we computed the internal hydrogen bond energies for the Kass polyol and its conjugate base alkoxide form. Based on the differential "internal" solvation energies, we estimated the energetic effect of hydrogen bonding on the acidity of the Kass polyol (just the parent compound—you need not do the various methylated species) compared to *t*-butanol. For your best extended and internally hydrogen bonded structures from PC Model, repeat these calculations at the AM1, PM3, PM6, HF/6-31G(d), HF/6-31+G(d), and MP2/6-31+G(2df,p)//HF/6-31+G(d) levels and report your results. Comment on variations between the models and any interesting price/performance issues. As we *are* now doing quantum calculations, how are the *absolute* deprotonation energies (which we couldn't really get from the force field)? For the HF/6-31G(d) level, compute frequencies and thermal contributions to free energy therefrom. By how much do these thermal contributions cause ΔG of internal hydrogen bonding to differ from ΔE? How do the IR spectra of the extended conformers differ, qualitatively, from those of the internally hydrogen-bonded conformers?

3.   Consider the bicyclic alazane molecules on the next page, and in particular their basicities. Compute, at the levels indicated in the below tables, Al–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 alazane compare to that of the hexafluoroalazane?"
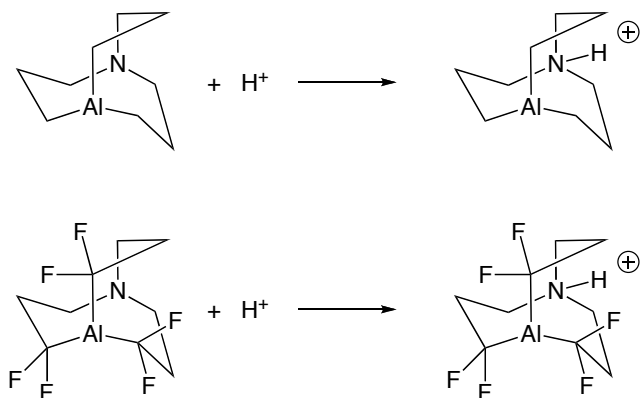
Al–N Bond Lengths (Å) in Alazanes

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

Computed Energies (E_h) of Alazanes

	Bicyclo[3.3.3]alazane		Hexafluorobicyclo[3.3.3]alazane	
	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)				

4.   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

`##.html` or `##.html`, where `##` refers to the list at the end of this problem set, to see them in 3D—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 a variety of minima and transition-state structures, and include more data than you will generate in *this* problem set, but you ultimately will create entries equivalent to my own.

Your task is to find two stationary points of *your* own—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; here, for example, is a correctly formatted copy ready to be pasted:
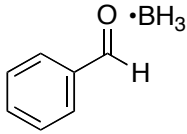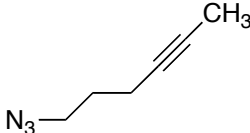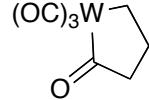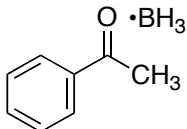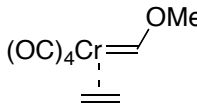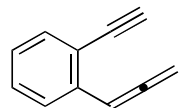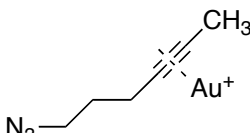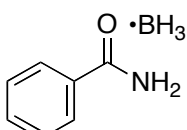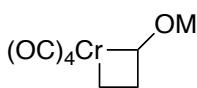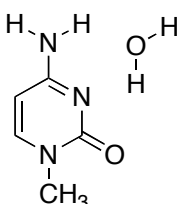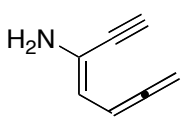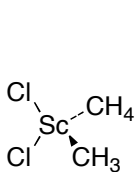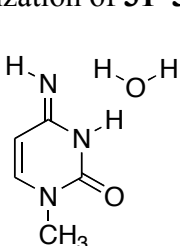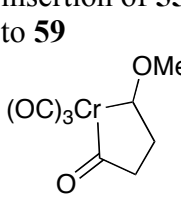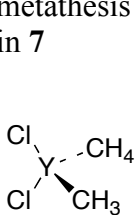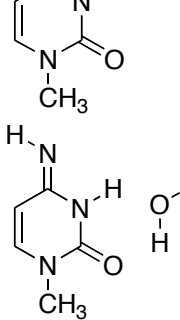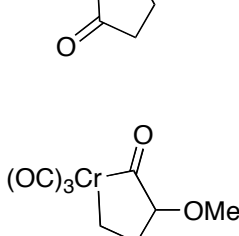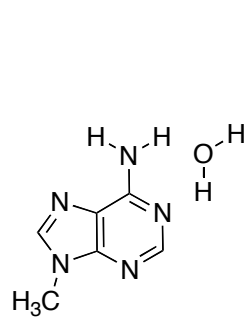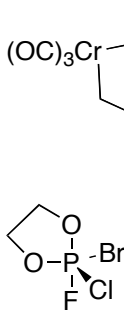
1	24	0	−0.064962	−0.034883	−0.096630
2	6	0	−1.141129	1.696746	−0.284156
3	6	0	−1.704425	−1.219553	−0.075460
4	6	0	−0.309697	−0.105930	−2.000636
5	6	0	2.247794	1.302449	0.456239
6	6	0	2.107300	1.423400	−0.863351
7	1	0	2.879366	0.545440	0.886439
8	1	0	1.845197	2.033939	1.133979
9	1	0	1.572343	2.243740	−1.303743
10	1	0	2.593114	0.756824	−1.548461
11	6	0	−0.078791	0.023111	2.023115
12	8	0	−0.120268	0.001756	3.135913
13	8	0	−2.637648	−1.824964	−0.203096
14	8	0	−1.744877	2.600319	−0.549794
15	6	0	1.211517	−1.645996	−0.290967
16	8	0	1.949469	−2.443506	−0.553117
17	1	0	−0.611209	−0.985150	−2.572495
18	1	0	−0.288539	0.728182	−2.704543
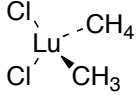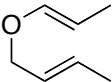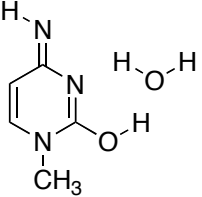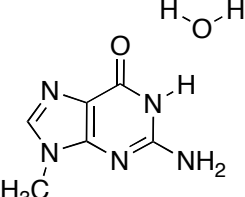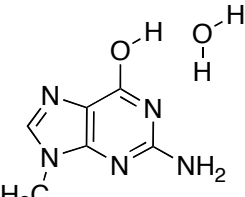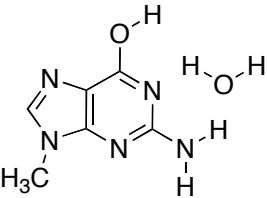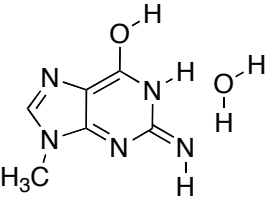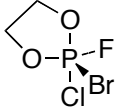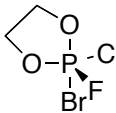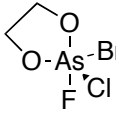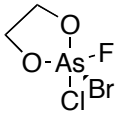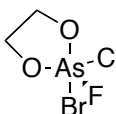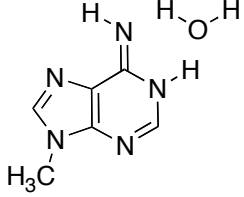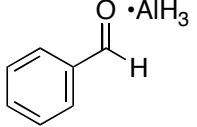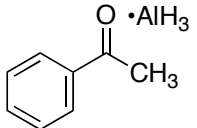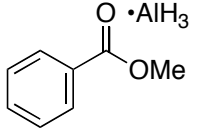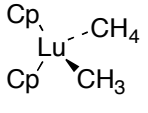
of course, you'll need to `vi` or `more` the output file (the *end* of the output file) to copy the optimized coordinates). If you make any mistakes and fail to realize until after submission, contact me with the details and I will fix the website.

With respect to basis set, we will use the 6-31G(d) basis set for all atoms for which it is defined (H–Kr). 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:

01	benzaldehyde O·BH₃ with H	**26**	Click [3+2] TS for **25**	**51**	TS for carbonyl insertion of **50**	**76**	Myers-Saito TS for **75**

01 O·BH₃

02 TS for addn of BH₃ to C=O of **1**

03 O·BH₃ CH₃

04 TS for addn of BH₃ to C=O of **3**

05 O·BH₃ NH₂

06 TS for addn of BH₃ to C=O of **5**

07 Cl Sc Cl CH₄ CH₃

08 TS for symmetric CH bond metathesis in **7**

09 Cl Y Cl CH₄ CH₃

10 TS for symmetric CH bond metathesis in **9**

26 Click [3+2] TS for **25**

27 CH₃, N₃

28 Click [3+2] TS for **27**

29 CH₃ Au⁺ N₃

30 Click [3+2] TS for **29**

31 H–N–H, O–H H, N, O, N, CH₃

32 TS for tautomerization of **31**–**33**

33 H–N, H–O–H, N–H, N, O, N, CH₃

34 H–N, N–H, O–H H, N, O, N, CH₃

35 TS for tautomerization of **34**–**36**

51 TS for carbonyl insertion of **50**

52 (OC)₃W, O

53 (OC)₄Cr=OMe

54 TS for [2+2] of **53**

55 (OC)₄Cr OMe

56 TS for carbonyl insertion of **55** to **58**

57 TS for carbonyl insertion of **55** to **59**

58 OMe (OC)₃Cr, O

59 O (OC)₃Cr, OMe

60 O–P–Br, O, F, Cl

76 Myers-Saito TS for **75**

77 Schmittel TS for **75**

78 (enediyne structure)

79 Myers-Saito TS for **78**

80 Schmittel TS for **78**

81 H₂N (enyne-allene)

82 Myers-Saito TS for **81**

83 Schmittel TS for **81**

84 H–N–H, O–H, N, N, N, N, H₃C, H

85 TS for tautomerization of **84**–**86**

11		**36**		**61**	pseudorotation TS **60→62**	**86**	
12	TS for symmetric CH bond metathesis in **11**	**37**		**62**		**87**	
13		**38**	TS for tautomer-ization 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 tautomer-ization 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**		

19

22	OMe structure	**47**	$(OC)_3Cr$ cyclopentanone structure	**72**	enyne-allene structure
23	[3,3] sigmatropic shift chair TS of **22**	**48**	$(OC)_4W{=}$	**73**	Myers-Saito TS for **72**
24	[3,3] sigmatropic shift boat TS of **22**	**49**	TS for [2+2] of **48**	**74**	Schmittel TS for **72**
25	N₃ pentynyl azide structure (H)	**50**	$(OC)_4W$	**75**	t-Bu enyne-allene structure