Problem 1 provides you with only very general instructions for certain tasks. You are not merely encouraged but expected *to ask for advice/help as you need it. Of course, first you should* think *about things, but after that, talk to me, Zahid, or a confident classmate.*

1.   Mixing $Ag(CN)_2$ and $Ni(CO)_4$ in chloroform under a CO atmosphere, you isolate a solid precipitate that microanalysis and mass spectroscopy indicate to be $NiC_4N_2O_2$. A ^{13}C NMR spectrum of the precipitate in chloroform with $Ni(CO)_4$ added as an internal standard shows a strong peak 6.6 ppm upfield from $Ni(CO)_4$ and a much smaller peak 8.4 ppm upfield from $Ni(CO)_4$. There is also a very strong peak 84 ppm upfield from $Ni(CO)_4$. An IR spectrum of the precipitate in a KBr pellet shows a strong absorption at 2154 cm^{-1} and very weak absorptions/shoulders at 2143, 2170, and 2188 cm^{-1}.

After three recrystallizations from diisopropyl ether, your solid is composed of beautifully twinned light orange crystals. NMR and IR spectra of the recrystallized solid show only the strong peaks noted above, and none of the weak ones.

An ultraviolet spectrum of the recrystallized solid in freon (who knew it would be soluble?) shows absorptions at 310 and 333 nm.

Here are the questions:

a. What is the structure of the molecules in the recrystallized solid? In a narrative fashion, describe in some detail how you came to your conclusion. Note that achieving 100% confidence can be very much more expensive than 99% confidence. It is perfectly OK to be satisfied with 99%.

b. To what electronic transitions do the two peaks in the UV spectrum correspond (show pictures of the orbitals)? Based on the nature of these transitions, how might you expect the geometries of the first and second excited states to differ from the ground state (don't do an excited-state geometry optimization, just infer from the orbitals).

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

pollux.chem.umn.edu/8021/C5H8N2/

Your present task is to update your structure on the potential energy surface (PES) with a calculation at the PBE1/6-31G* level (since there is no double slash, this implies re-optimizing the geometry; note that the G03 keyword for PBE1 is `pbe1pbe`). 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 PBE1/6-31G* level and update your entry with that data.

Finally, compute the PBE1/6-31G* aqueous solvation free energy for your DFT structure using the CPCM model in Gaussian03 (as a single-point calculation on the DFT optimized geometry). When the calculation completes, add the solvation free energy to the website data. Report only one position after the decimal place for the solvation free energy in units of kcal/mol (the solvation free energy is the difference between the total energy in solution and in the gas phase).