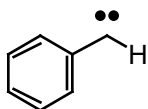
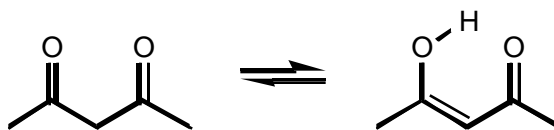


1. (G98) Optimize the geometries of singlet and triplet phenylcarbene at the HF/3-21G level (both states are planar, i.e., they have C_s symmetry)—note that HF will be interpreted as RHF for the singlet and UHF for the triplet, which is what you want for this problem. Which state is the ground state and what is the singlet-triplet (S-T) energy splitting? Compute the S-T splitting at the MP2/3-21G//HF/3-21G level. Now, compute the S-T splitting after optimizing the geometries at the BPW91/3-21G level. Experimentally, the triplet is the ground state by 2-6 kcal/mol (there is still a fair amount of uncertainty in the experimental value). What level of theory gives the best performance? What are the expectation values of S^2 for the determinantal wave functions formed from the UHF and UDFT orbitals?



phenylcarbene

2. (AMSOL) The tautomeric equilibrium between 2,4-pentanedione and its hydroxy-enol form is quite sensitive to solvation. Assuming internal hydrogen bonding for the enol, compute the 298 K equilibrium constant in the gas phase at the AM1 level (assume the heats of formation are free energies, or, more accurately, that the differences in the enthalpies and free energies are equal). Now, repeat your calculations optimizing the molecules in an aqueous medium represented by the SM5.4/AM1 solvation model. Express the difference in equilibrium constants as ΔG . Finally, repeat the calculations for cyclohexane as solvent. Experiment indicates the equilibrium constant to shift (relative to the gas phase) in favor of the enol form by 0.7 kcal/mol in cyclohexane, and in favor of the dione form by 2.4 kcal/mol in water. How does the solvation model do? Rationalize the observed effect. Visualize the geometries of the optimized diones in the gas phase, cyclohexane, and water. What is the dihedral angle between the two carbonyl bonds in each case? Explain any trend.



2,4-pentanedione

Note that the AMSOL calculations will require keywords associated with the solvation model. The correct sets of keywords are:

Gas: AM1

cHex: AM1 SM5.4A SOLVNT=GENORG

& IOFR=1.4266 ALPHA=0.00 BETA=0.00 GAMMA=35.5 DIELEC=2.02

(the ampersand at the start of the line above tells AMSOL the keywords are continuing on an additional line)

H₂O: AM1 SM5.4A SOLVNT=WATER

3. (G98) Here continues a problem that will carry over to the final exam. We add to the data at:

<http://pollux.chem.umn.edu/~kormos/8021/ProbSets-Exams/2000/C3H4N2O2/>

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 that data.

Finally, compute the aqueous solvation free energy for your DFT structure using the SM5.42R/B3LYP/MIDI! model in MN-GSM (MN-GSM is a solvation module for G98—MIDI! is a highly efficient basis set optimized for use in solvation calculations). A complete .dat file for accomplishing this can be gotten by issuing the command:

```
cp ~chem99/mysolv.dat .
```

Edit `mysolv.dat` to change the checkpoint file name to whatever your checkpoint file *is* named (and be sure you are in the same directory as your checkpoint file) and you should be able to submit the job immediately. When the calculation completes, add the solvation free energy to the website data.