**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?
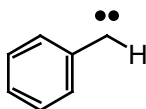

phenylcarbene

Level of Theory	Ground State	S-T splitting, kcal/mol	triplet $<S^2>$
HF	triplet	38.5	2.67
MP2	singlet	–1.8	2.67
BPW91	triplet	12.1	2.02

Notice that HF theory does a terrible job, partly because the basis set is small, but mostly because (i) the singlet has a small HOMO/LUMO separation, which HF is ill-designed to handle and (ii) the triplet has enormous spin contamination. MP2 is not necessarily in error by much, but this is pretty clearly pure luck. Perturbation theory works best for small perturbations, but here the change in S-T splitting is almost 40 kcal/mol! DFT overstabilizes the triplet a bit because of the very small basis set; if we had used a better basis set it would be quite accurate indeed.

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   G. 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
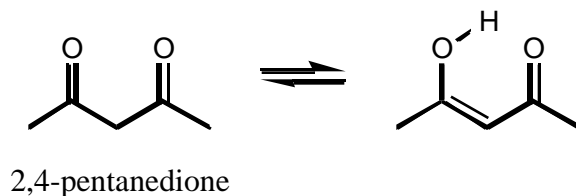
Medium	Equilibrium Constant	G° rel., kcal/mol	Dihedral angle, deg
Gas phase	0.310		137.4
Cyclohexane	0.188	0.3	125.5
Water	0.018	1.7	67.5

The solvation models do only fair jobs here. The trend is predicted to be in the wrong direction for cyclohexane, although the net error is only 1 kcal/mol. The correct direction is predicted for water, but the magnitude of the preference is underestimated by 0.7 kcal/mol. Note that as the dielectric constant of the solvent increases, the carbonyl dipoles in the dione come into closer alignment. Thus, in the gas phase they are pointed in roughly opposite directions (sterics prevents the otherwise ideal dihedral angle of 180 deg), in cyclohexane the angle is reduced by 12 degrees, and in water it reduces another 58 degrees! This is a good example of how solvation can move the location of a stationary point substantially, even for an uncharged solute. The trend overall is for more polar solvents to better stabilize the dione. This is rationalized by noting the greater polarity of two carbonyl groups compared to the internally hydrogen bonded enol (it is "self-solvated", if you like, and doesn't need much further help from a surrounding condensed phase).

3. (No analysis yet required)