Problem set 11: Chem 131b/231b

1. Formulate a pictorial representation for the intersystem crossing from a singlet n-\(\pi^*\) state to a triplet n-\(\pi^*\) state. Do the same for a singlet n-\(\pi^*\) to triplet \(\pi - \pi^*\) interconversion. In one case you will note that there is a change of spin as well as a movement of an electron from one orbital to another that is roughly oriented perpendicular to the first. The latter involves a change in orbital angular momentum while the former, a change in spin angular momentum. When they are coupled in this manner, that is when spin-orbit coupling occurs, intersystem crossing is facilitated. You will want to know that in answering this problem, you have formulated 'the gist of' El-Sayed's rule for intersystem crossing.

2. Here's an opportunity to use 'the conceptual results' of problem 1. Assume that the initial diyl (see below) exists as a singlet with the bisected geometry A. Examine the geometric changes that occur in progressing from A to the planar diyl (B), then to the 1,4-diyl formed from a 7-endo<trig cyclization (C). Do so, also, for its direct cyclization to the diyl, D. Now, think of what you learned in problem 1. In the blank spaces that have been provided, indicate whether the species, B-D, is likely to be a singlet or a triplet and provide (briefly) your reasoning. [JOC, 1994, 59 (8), 2270-2272]