Why does 5-methyl-2-pyrimidinone fluoresce? An ab initio study of the photophysics of a fluorescent DNA pyrimidine analog. KURT KISTLER, SPIRIDOULA MATSIKA, member — The photophysical properties of gas phase 5-methyl-2-pyrimidinone, a fluorescent DNA/RNA pyrimidine analog, have been calculated using multi-reference configuration-interaction with three levels of dynamical electron correlation included. The bright state at vertical excitation is \(S_2(\pi\pi^*)\) at 4.42 eV. An \(S_1-S_2\) seam originates close to vertical, and a gradient pathway from this seam leads to a global minimum on the \(S_1\) surface. A conical intersection between \(S_1\) and \(S_0\) (\(ci01\)) was found, but all levels of theory show that this conical intersection is significantly higher than the minimum, supporting fluorescence from \(S_1\). The details for this energetic inaccessibility, and the emission energy calculated (2.36 - 2.75 eV), depend on the level of theory used. Pathways along the \(S_1\) surface when no dynamical or intermediate dynamical correlation is included show a small barrier along with a second minimum in the \(S_1\) path from vertical to \(ci01\). When higher level of correlation is included (~130,000,000 configurations) the barrier vanishes, the secondary minimum becomes global, the energy of \(ci01\) increases, and the fluorescence energy becomes closer to experimental. Thus the importance of dynamical correlation when studying the photophysics of the DNA/RNA bases theoretically is underscored.