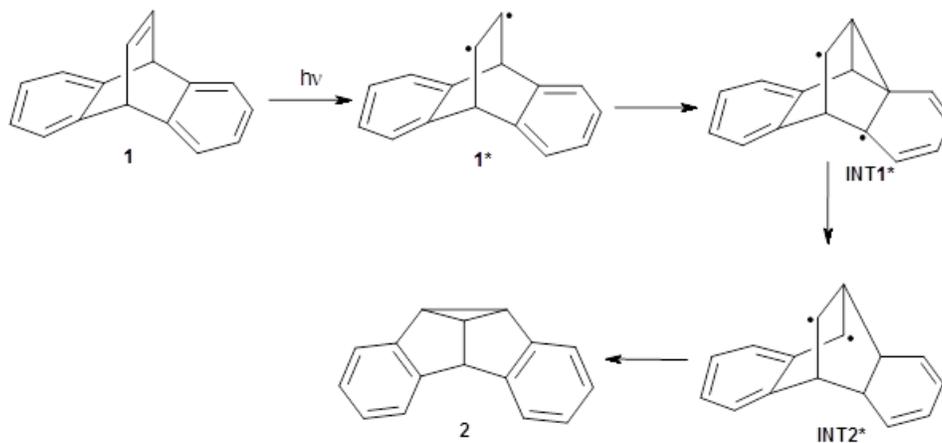
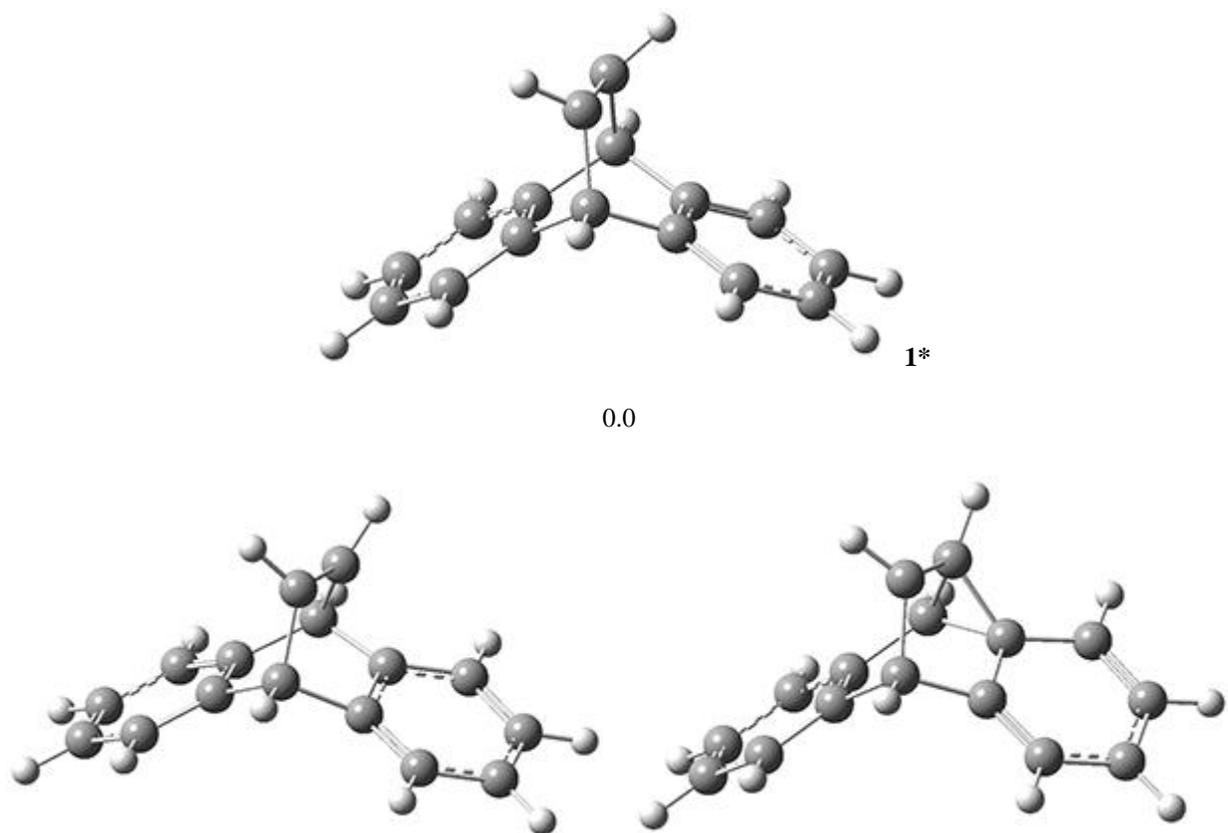


COMPETITION BETWEEN CONCERTED AND STEPWISE DYNAMICS IN THE TRIPLET DI- π - METHANE REARRANGEMENT

The di- π -methane photorearrangement has been known for many years, first studied by Zimmerman.^{1,2} The triplet photorearrangement gives an interesting rearranged product; and the mechanism of this photorearrangement of **1** into **2** has now been examined by the Houk group using computational techniques, including trajectory analysis. The proposed mechanism is that excitation to the triplet state **1*** is followed by rearrangement to the triplet intermediate **INT1*** which then rearranges to the triplet **INT2***. Intersystem crossing then leads to the singlet product **2**.



The PES for this rearrangement was explored³ at CASMP2(10,10)/6-31G(d)//CASSCF(10,10)/6-31G(d), with geometries and relative energies shown in Figure 1, as well as at (U)M06-2x/6-31G(d) and (U)B3LYP/6-31G(d); they all give qualitatively the same result. The first TS is the rate limiting step, and the second TS lies only 1-2 kcal mol⁻¹ above the intermediate **INT1**. So, the reaction appears to be two steps, but with such a low barrier for the second step, dynamic effects might be important as trajectories might cross **INT1*** and go over **TS2*** without residing in the intermediate well for any appreciable time – a seemingly one step reaction. Note than no TS for directly traversing from **1*** to **INT2*** was found.



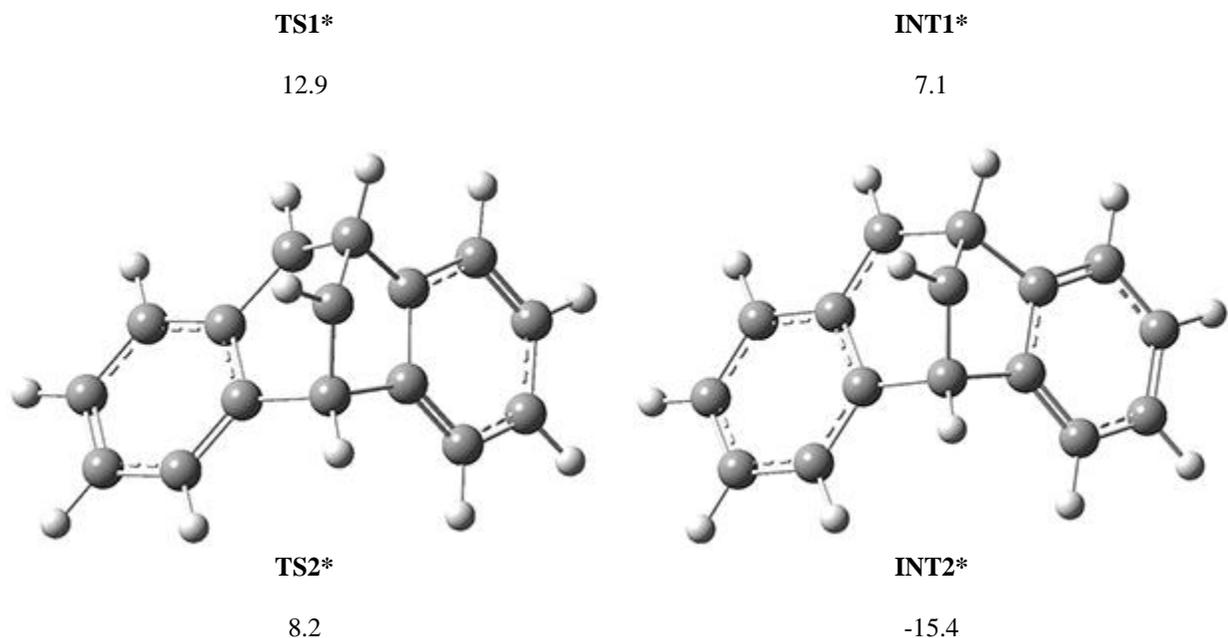


Figure 1. CASSCF(10,10)/6-31G(d) geometries and CASMP2 energies in kcal mol⁻¹.

Now in a follow-up study, Houk and co-workers⁴ performed trajectories analysis on the M06-2x/6-31G(d) PES. A total of 256 trajectories were initiated at **TS1*** and 241 ended at **INT2*** within 1500fs. Of these, 24 trajectories resided for less than 60fs within the region of **INT1**, a time less than a C-C vibration. Furthermore, the lifetime of **INT1** that is predicted by RRKM is much longer (about 500fs) than what is observed in the trajectories (about 200 fs). Thus, there is significant dynamic effects in this excited state rearrangement, though **INT1** is always sampled.

Source: <http://www.compchemhighlights.org/2014/10/competition-between-concerted-and.html>