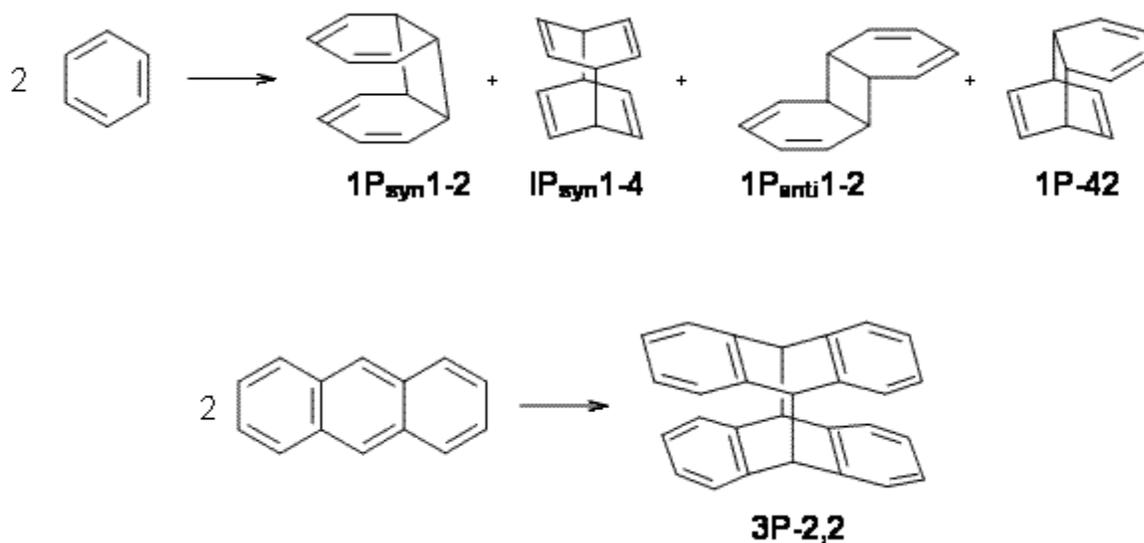
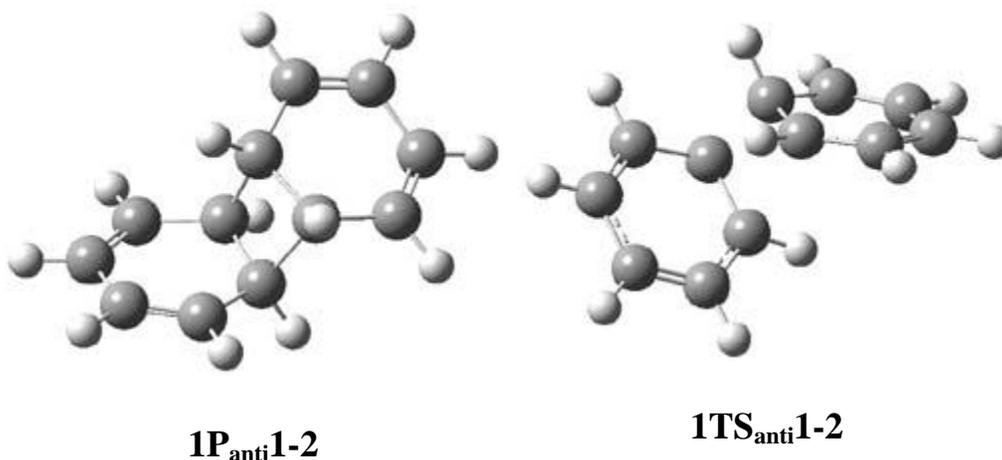


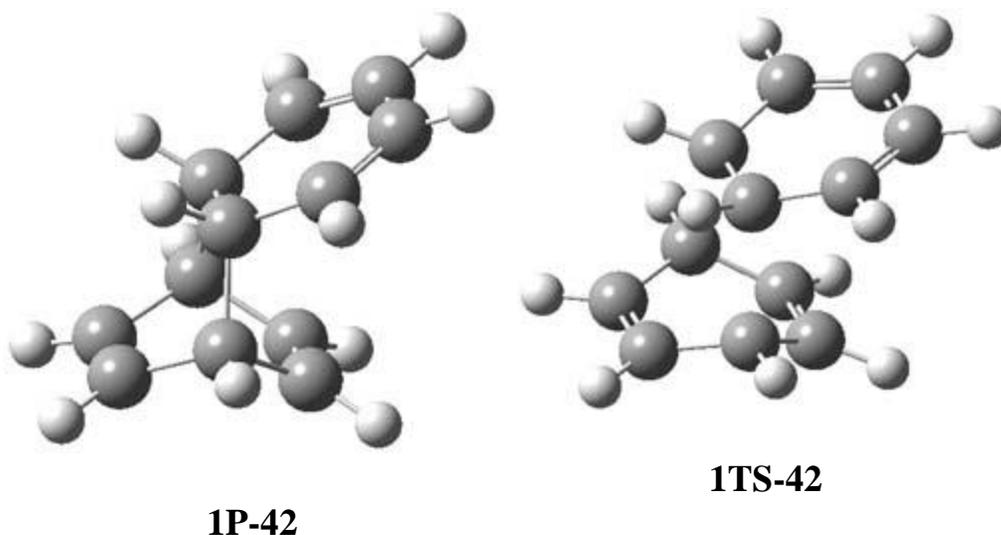
# ACENE DIMERIZATION

Bendikov and co-workers have examined the dimerization of linear acenes at M06-2x/6-31G(d).<sup>1</sup> They have looked at the formal forbidden [4+4] reaction that takes, for example, 2 molecules of benzene into three possible dimer products **1P<sub>anti</sub>1-2**, **1P<sub>syn</sub>1-2**, and **1P<sub>syn</sub>1-4**. The relative energies of these products increases in that order, and all three are much higher in energy than reactants; the lowest energy dimer is **1P<sub>anti</sub>1-2**, lying 47.4 kcal mol<sup>-1</sup> above two benzene molecules. Similarly, the dimerization of naphthalene is also endothermic, but the formation of the symmetric dimer of anthracene **3P-2,2'** is exothermic by 5.4 kcal mol<sup>-1</sup>. This gibes nicely with the best estimate of  $-9 \pm 3$  kcal mol<sup>-1</sup>.<sup>2</sup> Dimerization of the higher acenes are increasingly exothermic.



The transition state for the dimerization of benzene is concerted, though very asymmetric, as seen in Figure 1. Its energy is quite high ( $77.79 \text{ kcal mol}^{-1}$ ) and so this reaction can be completely discounted. The TS for the dimerization of naphthalene is also concerted and asymmetric, but the reaction pathway for the dimerization is stepwise, with a diradical intermediate. Furthermore, the highest barrier for this stepwise reaction is  $33.3 \text{ kcal mol}^{-1}$ . The activation energy of the back reaction (anthracene dimer to two anthracene molecules) was measured  $36.3 \text{ kcal mol}^{-1}$ ,<sup>3</sup> and the computed barrier of  $38.7 \text{ kcal mol}^{-1}$  is in nice agreement. The computed barriers for the dimerization of the higher acenes are predicted to be even lower than that of anthracene, consistent with the observation of dimers of these molecules.





**Figure 1.** M06-2x /6-31G(d) optimized structures.

I was curious that the authors did not consider the formally allowed [4+2] dimerization, leading for example to **1P-42**. So, I optimized this product and the concerted transition state leading to it. These are shown in Figure 1. The barrier through this transition state is still very large ( $54.1 \text{ kcal mol}^{-1}$ ) but it is  $23 \text{ kcal mol}^{-1}$  lower in energy than the barrier of the [4+4] reaction! The Product of the [4+2] is also lower in energy (by  $9 \text{ kcal mol}^{-1}$ ) than **1P<sub>anti</sub>1-2**. It seems to me that this type of dimerization is worth examining too – though I must say I have not as yet looked to see if anyone has explored this already.

Source: <http://comporgchem.com/blog/?p=1783>