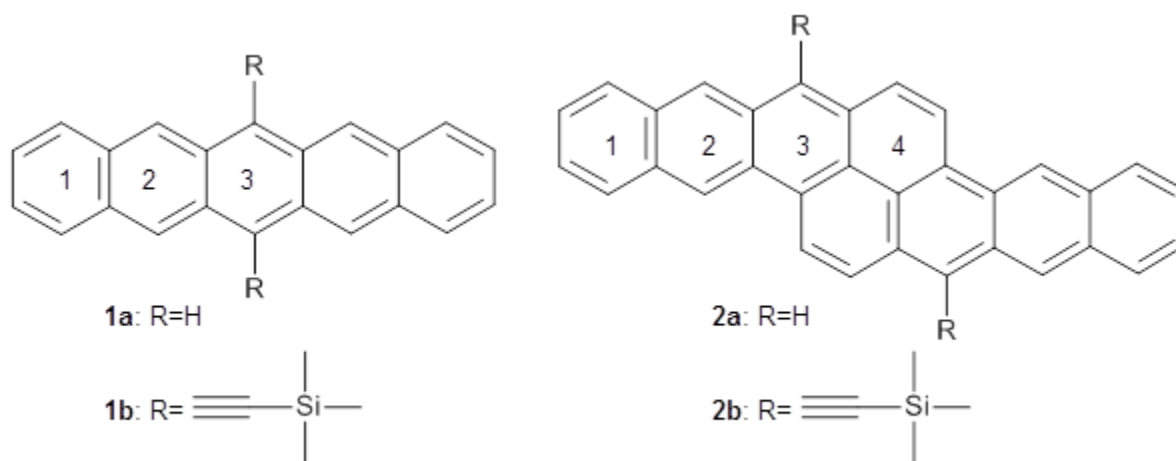


DIELS-ALDER REACTIONS OF FULLERENE

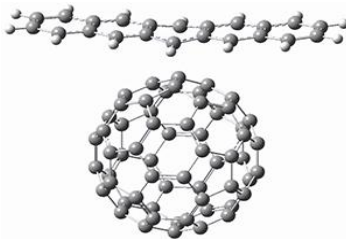
Diels-Alder reaction involving fullerenes have been known for some time. They occur across the [6,6] double bond of C_{60} , the one between two fused 6-member rings. Houk and Briseno report on the Diels-Alder reaction of C_{60} with pentacene **1** and bistetracene **2** and compare their computations with experiments.¹



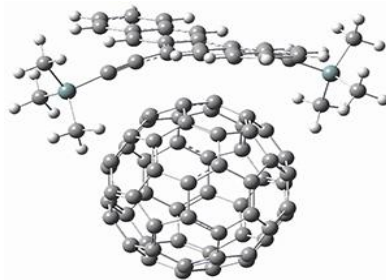
Pentacene and bistetracene ring numbering convention

Computations were performed for the reaction of **1** and **2** with C_{60} at M06-2x/6-31G(d)//M062x-3-21G*. The reaction can occur with the dienophile being either ring 1, 2, or 3 of pentacene and ring 1, 2, 3, or 4 of bistetracene. They located TSs and products for all of these possibilities. Select TSs and products are shown in Figure 1.

For the reaction of **1a**, the lowest energy TS is for the reaction at the central ring (ring 3), and the resulting product is the lowest energy product. The transition state (**PT_TS3**) is shown in Figure 1. This TS has the least distortion energy of the three possibilities, because reacting at this central ring destroys the least amount of aromaticity of pentacene. For the reaction of **1b**, the lowest barrier is again for reaction of ring 3 (through **TMSPT_TS3**). However, the product from the reaction with ring 2 (**TMSPT_P2**) is lower in free energy than **TMSPT_P3**, likely caused by steric interactions with the silyl substituents. This actually matches up with experiments which indicate that an analogue of **TMSPT_P2** is the kinetic product but **TMSPT_P3** is the thermodynamic product.



PT_TS3



TMSPT_TS3

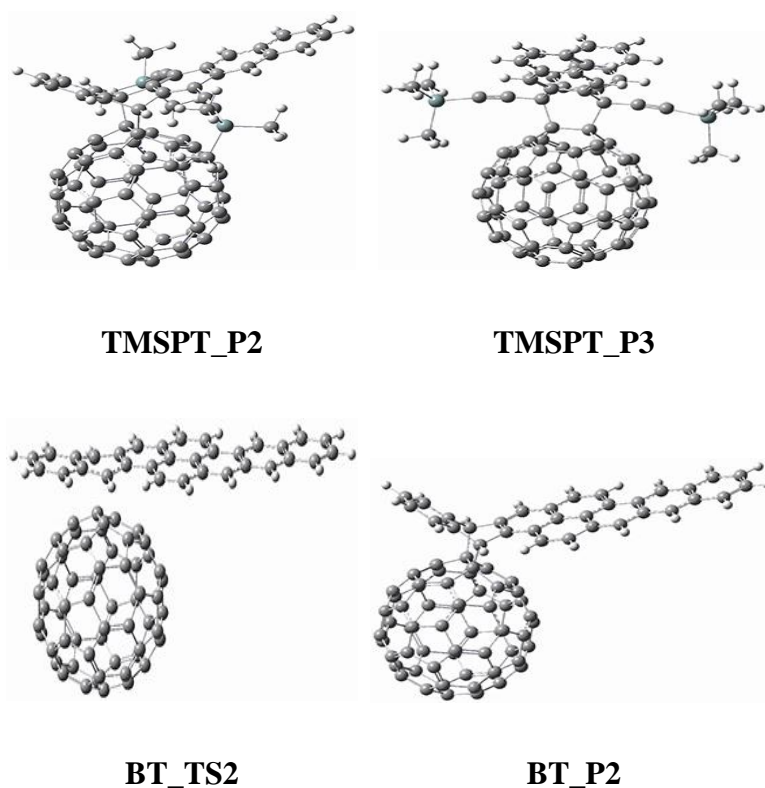


Figure 1. M06-2x/3-21G* optimized geometries.

(Once again a reminder that clicking on any of these structures will launch Jmol
and you'll be able to visualize and manipulate this structure in 3-D.)

The computations involving the Diels-Alder reaction of C_{60} with either **2a** or **2b** come to the same conclusion. In both cases, the lowest barrier is for the reaction at ring 2, and the product of the reaction at this same ring is the only one that is endoergonic. The geometries of **BT_TS2** and **BT_P2** are shown in Figure 1.

More importantly, the barrier for the Diels-Alder reaction involving **2a** and **2b** are at least 6 kcal mol⁻¹ higher than the barriers for the reaction of **1a** and **1b**, in complete agreement with experiments that show little reaction involving analogues of **2b** with C₆₀, while analogues of **1b** are reasonably rapid.

Source: <http://comporgchem.com/blog/?p=3226>