

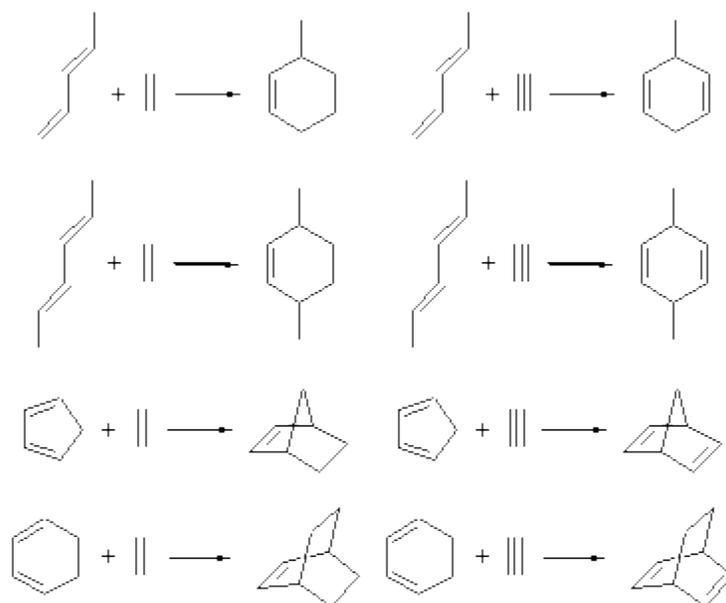
# ERRORS IN DFT: COMPUTATION OF THE DIELS-ALDER REACTION

Concern about the use of DFT for general use in organic chemistry remains high; see my previous posts (1, 2, 3). Houk has now examined the reaction enthalpies of ten simple Diels-Alder reactions using a variety of functionals in the search for the root cause of the problem(s).<sup>1</sup>

The ten reactions are listed in Scheme 1, and involve cyclic and acyclic dienes and either ethylene or acetylene as the dienophile. Table 1 lists the minimum and maximum deviation of the DFT enthalpies relative to the CBS-QB3 enthalpies (which are in excellent accord with experiment). Clearly, all of the DFT methods perform poorly, with significant errors in these simple reaction energies. The exception is the MO6-2X functional, whose errors are only slightly larger than that found with the SCS-MP2 method. Use of a larger basis set (6-311+G(2df,2p)) reduced errors only a small amount.

**Scheme 1**

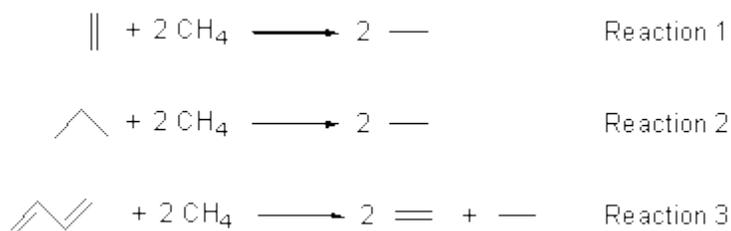




**Table 1.** Maximum, minimum and mean deviation of reaction enthalpies (kcal mol<sup>-1</sup>) for the reactions in Scheme 1 using the 6-31+G(d,p) basis set.<sup>1</sup>

<b>Method</b>	<b>Maximum Deviation</b>	<b>Minimum Deviation</b>	<b>Mean Deviation</b>
B3LYP	11.4	2.4	7.9
mPW1PW91	-8.7	-0.2	-3.6
MPWB1K	-9.8	-3.6	-6.2
M05-2X//B3LYP	-6.4	-1.6	-4.1
M06-2X//B3LYP	-4.4	-0.4	-2.5
SCS-MP2//B3LYP	-3.2	-0.5	-1.9

In order to discern where the problem originates, they next explore the changes that occur in the Diels-Alder reaction: two  $\pi$  bonds are transformed into one  $\sigma$  and one  $\pi$  bond and the conjugation of the diene is lost, leading to (proto)branching in the product. Reactions 1-3 are used to assess the energy consequence of converting a  $\pi$  bond into a  $\sigma$  bond, creating a protobranch, and the loss of conjugation, respectively.



The energies of these reactions were then evaluated with the various functionals. It is only with the conversion of the  $\pi$  bond into a  $\sigma$  bond that they find a significant discrepancy between the DFT estimates and the CBS-QB3 estimate. DFT methods overestimate the energy for the  $\pi \rightarrow \sigma$  exchange, by typically around  $5 \text{ kcal mol}^{-1}$ , but it can be much worse. Relying on cancellation of errors to save the day for DFT will not work when these types of bond changes are involved. Once again, the user of DFT is severely cautioned!

Source: <http://comporgchem.com/blog/?p=99>