Revisiting the Diels-Alder reaction: origin of selectivity and stability of *endo* adducts

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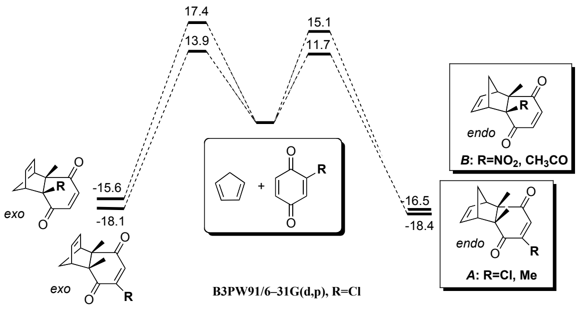
The Diels-Alder (DA) reaction is one of the most interesting and useful reactions found in organic chemistry. Despite the fact that it was discovered more than 80 years ago there is still no full understanding of the reaction mechanism. There are many suggestions, which attempt to explain *endo* selectivity in Diels-Alder reaction, but none of them are firmly established. As examples, arguments such as Secondary Orbital Interaction (SOI), difference in primary overlap, difference in volumes of activation, the polarity of the transition states and release of strain energy have been used.

The DA reaction between cyclopentadiene and *p*-benzoquinone was first described in 1906 and results in the *endo* adduct. In the case of substituted quinones, reaction with either substituted or unsubstituted double bond is possible. For example, 2-Methylquinone and 2-Chloroquinone [1] was reported to give the adduct that results from reaction with unsubstituted double bond (***A*** *a*dduct). 2-nitroquinone, 2-acetylquinone, 2-carbometoxyquinone react with cyclopentadiene by substituted double bond leading to the ***B*** adduct.



C–C bond in *exo* TS, Å		C–C bond in *endo* TS, Å	$\Delta E_{act(endo\text{-}exo)}$
2.153	PM3	2.152	0.29
2.123	AM1	2.115	0.99
2.227	HF/STO-3G	2.215	-2.05
2.261	B3PW91/6-31G*	2.243	-1.93
2.238	B3PW91/6-311+G(d,p)	2.218	-2.24
2.229	B3PW91/6-311+G(3df,2p)	2.209	-2.16
2.249	B3PW91/cc-pVDZ	2.233	-1.94
2.228	B3PW91/cc-pVTZ	2.208	-2.02
2.228	B3PW91/cc-pVQZ	2.207	-2.06
2.251	B3PW91/aug-cc-pVDZ	2.232	-2.19
2.272	MP2/6-31G*	2.262	-3.11
2.283	MP2/6-311+G(d,p)	2.272	-3.85
2.285	MP2/6-311+G(3df,2p)	2.275	-3.79

Our initial B3PW91/6–31G(d,p) calculations[1] suggest that the Diels-Alder reaction of 2-chloro-1,4-quinone with cyclopentadiene proceeds as an *inverse* Diels-Alder reaction. The formation of ***A***-type adduct is more favourable (both kinetically and thermodynamically) over the ***B***-type adduct. The lowest activation barrier is found to be 11.7 kcal/mol and corresponding transition state describes formation of the *endo*-***A***-type adduct.

Here we present results of our calculations (DFT, MP2, CASSCF) of DA reaction with 1,4-paraquinones with various substituents at 2 position. We note the absence of SOI and rather strong dependence of activation barriers and exothermicity of the reaction on basis set and level of theory.

[1] D.I. Sharapa, A.V. Gayday, A.G. Mitlenko, I.A. Levandovskiy, T.E. Shubina, *EJOC*, **2011**, ***ASAP***.