THEORETICAL STUDY OF DIELS-ALDER REACTION'S ASYNCHRONICITY WITH DFT AND TOPOLOGICAL DESCRIPTORS

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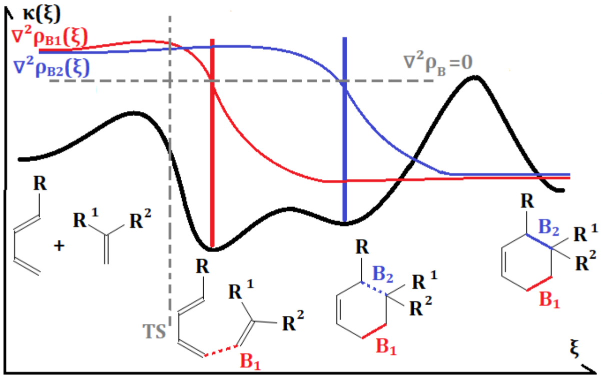
Other keywords : Diels-Alder, Asynchronicity

Abstract

Diels-Alder cycloaddition is one of the most powerful chemical reaction used by organic chemists. In most cases, it involves a concerted mechanism with two C-C bonds formed during the same elementary step. This explains the stereoselectivity observed. Nonetheless the concerted mechanism can be either synchronous with the two bonds forming exactly concomitantly or asynchronous with the two bonds created in two stages along the same elementary step. In extreme cases, a stepwise mechanism can be observed.



In this work we studied by DFT 16 Diels-Alder reactions covering a large range of degree of synchronicity using Gaussian09 (M06-2X/6-31G(d,p)). As expected, reaction profiles of the reaction force ($F(\xi)$) and more specifically of the reaction force constant$\kappa(\xi)$[1] highligthed these various degrees of synchronicity. More quantitatively, the width of the transition state region ($\Delta\xi$) revealed to be a good measure of the asynchronicity. We introduced a new index Θ from molecular orbital theory to predict the degree of synchronicity from the reactant's structures. Then we proposed a topological study based on QTAIM to analyze the bond's formations. We focused on the sign of $\nabla^2\rho$ at the bond critical point for each new bond[2].Interestingly, $\nabla^2\rho$ changes of sign coincide with kappa minima. It may help to analyze process composing a mechanism of concerted reactions.

References

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