Title: **Diels-Alder [4+2] cycloaddition: study of the butadiene - ethylene prototypical system.**

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The pericyclic reactions go through concerted transition states and can take place either thermally or photochemically. Cycloaddition reactions are pericyclic reactions where a n-π conjugated electron system reacts with a second m-π electron system generating a cyclic structure. The Diels-Alder [4+2] cycloaddition reaction is known as one of the most reliable six-membered cycle formation method in organic chemistry due to its good control over stereochemistry, which can be predicted with the Woodward-Hoffman rules. These rules establish that the reaction occurs following a process with orbital symmetry that determines the outcome stereochemistry of the reaction depending on the initiation.

Aiming at discriminating whether the progress of the thermal Diels-Alder [4+2] cycloaddition reaction between a diene and a dienophile is enhaced by either electron-donor or electron-withdrawing substituent groups on the dienophile, a computational study (DFT) has been done. In this study, 1,3-butadiene has been used as the diene and ethylene as the reference dienophile for a posterior comparison with the disubstituted ethylene of their respective potential energy surface. Firstly, it has to be fully characterized the minimum energy pathway for the simple reaction for future mechanistic and energy comparisons to two alternative reactions with the dienophile with amino groups as electron-donor substituent or nitrile groups as electron-withdrawing. Then, each reaction energy profile will be built and described in terms of which dienophile's stereoisomer favors kinetically and/or thermodynamically the reaction.

Keywords: Diels-Alder [4+2], Thermal cycloaddition, DFT, disubstituted dienophile, energy barrier, product stabilization, Woodward-Hoffman rules, energy balance.