"PUSH-PULL" π+/π- (PPππ) SYSTEMS: A NEW TYPE OF INTERACTION SYSTEM IN CATALYSIS

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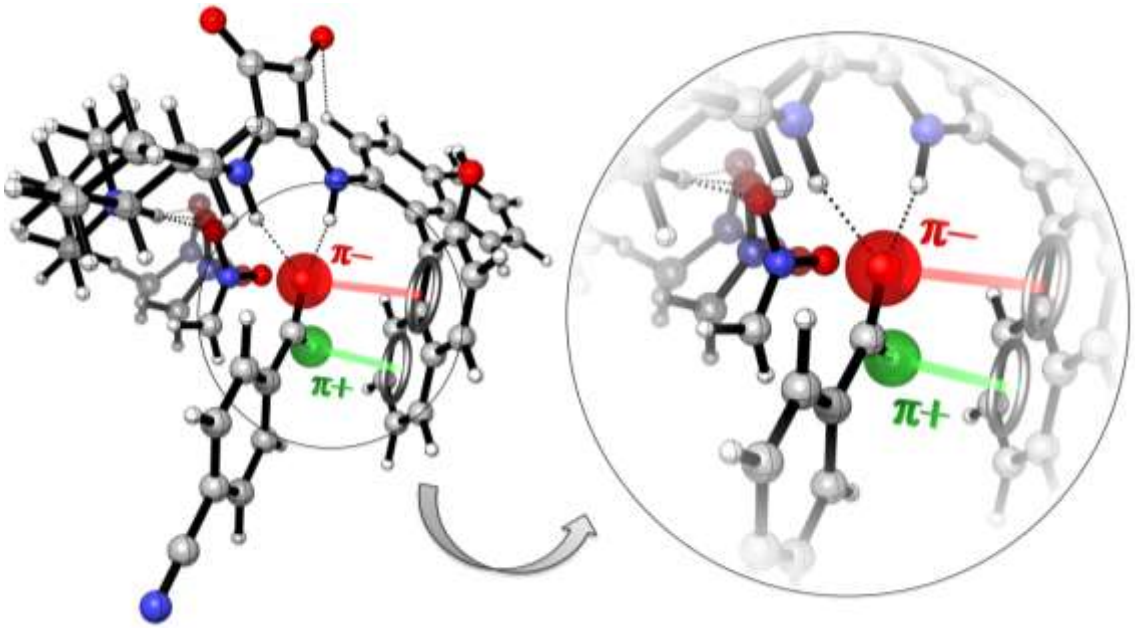
During this project, we studied computationally the mechanism of a Henry reaction catalyzed by a NOBIN-based squaramide. After a thorough comparison of the accuracy of different combinations of functionals and basis sets, we found that the ωB97X-D/6-311G(d) approach used with ultrafine grids and quasi-harmonic approximations showed the most precise results. This computational approach led to accurate calculated $\Delta\Delta G^{\ddagger}$ values with error margins lower than 1 kcal/mol in nine Henry reactions with different aldehydes [1].

Unexpectedly, during this computational study, two π-interactions were found that stood out over the rest of noncovalent interactions. These two π-interactions were created by one of the catalyst's naphthyl groups, a δ^+ atom (hydrogen atom) and a δ^- atom (oxygen atom), forming a PPππ system. The computational tests indicate that the energy of this system varies from 2.7 to 4.7 kcal/mol in the reaction steps studied (**Int1**, **TS1** and **Int2**), which is crucial for the differentiation in energy of **P1**, the most favorable pathway, over the rest of the pathways [2]. Additionally, diverse experiments were carried out in order to verify that π-interactions were formed during the reaction.

This squaramide-catalyzed Henry reaction represents the first example where a PPππ system has shown a concrete application in chemistry. Previously, only some of their characteristics such as their spectral properties had been studied but our study showed that this type of system has much unexplored potential for catalysis.



References

[1] J. V. Alegre-Requena, E. Marqués-López, R. P. Herrera, *Chemistry - A European Journal*, 2017, DOI: 10.1002/chem.201702841.

[2] J. V. Alegre-Requena, E. Marqués-López, R. P. Herrera, *ACS Catalysis*, 2017, 7, 6430.