On the importance of the novel RIRC technique to highlight the Hidden Intermediate of Reaction in the SNAr Reaction of piperidine on 2-bromo-3,5-dinitrothiophene

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Abstract

DFT/M062X/6-311+G(2d,2p) theoretical calculations have been applied to the reaction mechanism of the SNAr describing the action of the piperidine C5H10NH on the 2-bromo-3,5-dinitrothiophene. In a first predictive approach, the role of the ligand X in position 5 (X = NO2, CN and H) of the 2-bromo-3-nitrothiophene motif has been studied. Our results show that the dinitro compound represents the best element playing the role of electrophile. In a second part focused on this latter compound, we elucidate the aromatic substitution of bromide by piperidine mechanism. To do this, we first use the traditional tools such as the energy, force and internal coordinate profiles based on the intrinsic reaction coordinate. Then, we strengthen our study by tracing the atomic charge and Wiberg bond indice profiles. All the results demonstrate that we were in the presence of a concerted but asynchronous reaction. This excluded the zwitterion to act as a reaction intermediate. However, by using our new technique, called Reactive Internal Reaction Coordinate (RIRC), which gives access to the reaction path according to the selected active internal coordinates, we were able to locate without ambiguity a singular point associated with the Hidden Reaction Intermediate (HRI), compatible with the zwitterion structure. The latter compound corresponded to a long-lived transient species.

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