

Theoretical Study of the Mechanism of the Excited-state Double Proton Transfer in 7-azaindole Dimer

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Introduction

Proton transfer reactions play very important roles in physics, chemistry, and biology. Among them, excited-state double proton transfer (ESDPT) in 7-azaindole (7AI) dimer has been receiving particularly much attention, because this process has been taken as a model of the photo-induced mutation occurring in DNA base pairs. Thus this process has been intensively studied experimentally and theoretically for more than 40 years [1-3]. Through these studies, one major question has been put forward: Does the ESDPT follow a concerted mechanism or a stepwise mechanism? **Figure 1** shows schematic pictures of the mechanisms of the ESDPT in 7AI dimer from the normal dimer (ND) to the tautomer dimer (TD), derived from previous studies. In the concerted mechanism, two protons simultaneously transfer through a single transition state, without forming an intermediate for single-proton-transferred (SPT) component. In the stepwise mechanism, on the other hand, an intermediate is formed by the first SPT from ND, followed by the second SPT to TD. This intermediate can have either a zwitterionic character or a neutral character. The purpose of the present work is to clarify the mechanism of the ESDPT reaction in 7AI dimer more unambiguously by means of high-level quantum chemical calculations.

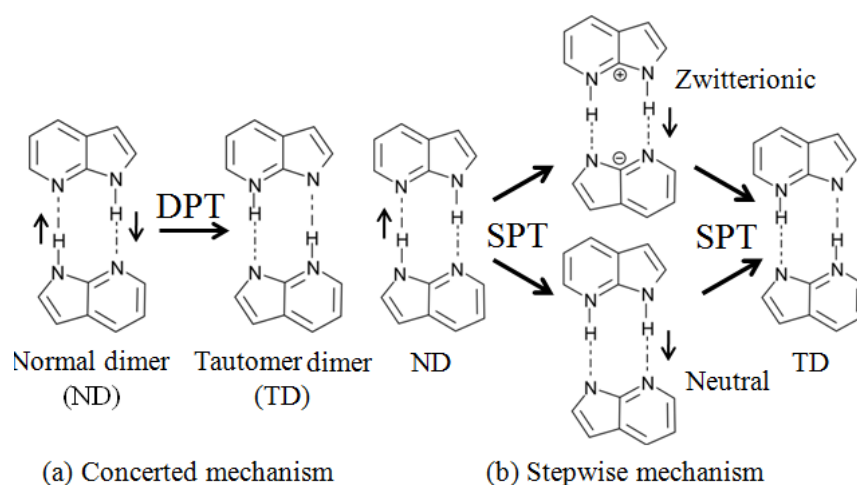


Figure 1. Concerted mechanism and step-wise mechanism of ESDPT in 7AI-dimer.

Computational Methods

The CASPT2 method and the long-range corrected TDDFT (LC-TDDFT) method are employed for geometry optimizations and energy calculations along the excited-state reaction paths. Potential-energy profiles are calculated for the ESDPT in the locally excited state as

well as in the charge transfer state in order to elucidate which mechanism in Fig. 1 is the most favorable.

Results and Discussion

Figure 2 shows the schematic pictures of the reaction paths of ESDPT in the 7-AI dimer. Three main reaction routes involving double proton transfer are located.

Route I: concerted mechanism: $\text{ND}_{\text{LE}} \rightarrow \text{TS}_{\text{LE}} \rightarrow \text{TD}_{\text{LE}}$.

Route II: stepwise mechanism via neutral intermediate: $\text{ND}_{\text{LE}} \rightarrow \text{IN}_{\text{CT}} \rightarrow \text{TS}_{\text{CT1}} \rightarrow \text{TD}_{\text{LE}}$.

Route III: stepwise mechanism via neutral intermediate: $\text{ND}_{\text{LE}} \rightarrow \text{IN}_{\text{CT}}' \rightarrow \text{TS}_{\text{CT2}} \rightarrow \text{TD}_{\text{LE}}$.

According to the energy profiles of the respective routes, it seems that the asynchronous concerted mechanism through **Route I** is definitely more likely to be followed than the stepwise mechanism with a neutral intermediate through **Route II** and **Route III** [4]. In the case of the gas phase, at least, one can say that the ESDPT in 7AI dimer proceeds with the concerted mechanism.

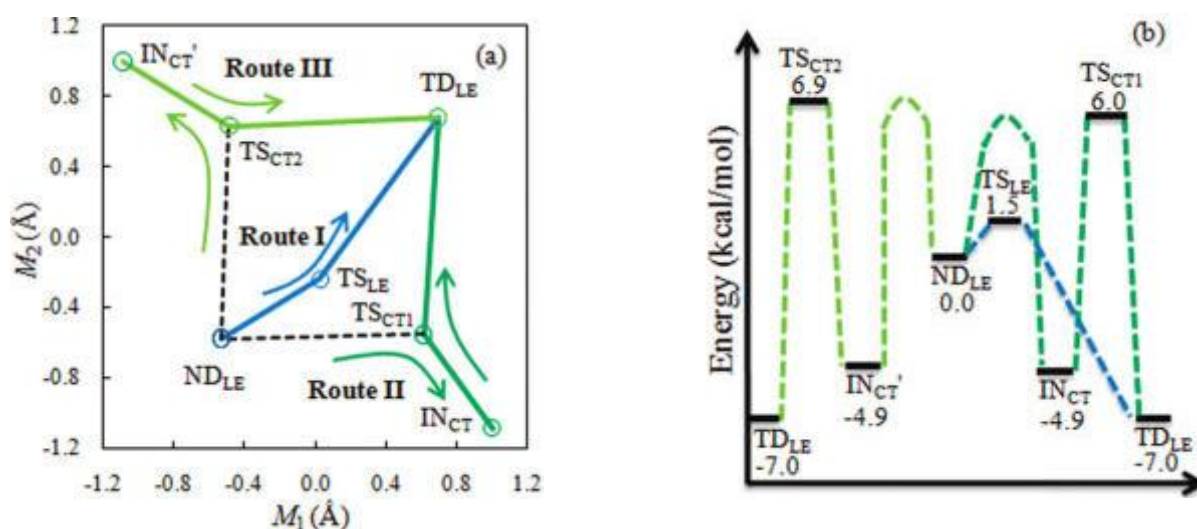


Figure 2. Schematic pictures of the reaction paths of ESDPT in the 7-AI dimer. (a) Reaction routes obtained by the LC-BLYP level optimization; and (b) energy diagram for reaction routes at the LC-BLYP level.

References

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