

## COMMUNICATION

# Straightforward Stepwise Excited State Dual Proton Transfer Mechanism for 9-10-HBQ System

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**Abstract:** A new molecule 9,10-dihydroxybenzo[h] quinoline (i.e. 9-10-HBQ) is focused in the present work about its excited state proton transfer (ESPT) mechanism. Though comparing potential energy barriers, it is found that the ultrafast ESPT process could occur in the  $S_1$  state without potential energy barrier along with hydrogen bond  $O_3-H_4\cdots N_5$  forming 9-10-HBQ-PT1 structure, subsequently, the second proton transfers via another intramolecular hydrogen bonded wire  $O_1-H_2\cdots N_3$  with a low potential energy barrier (about 7.69 kcal/mol) in the  $S_1$  state forming 9-10-HBQ-PT2 configuration. After completing excited state dynamical process, the  $S_1$ -state could turn back to  $S_0$  state with occurring reversed ground state proton transfer forming initial 9-10-HBQ structure.

**AMS subject classifications:** 65D18, 78M50, 74E40

**Keywords:** Proton transfer; frontier molecular orbital analysis; potential energy curves.

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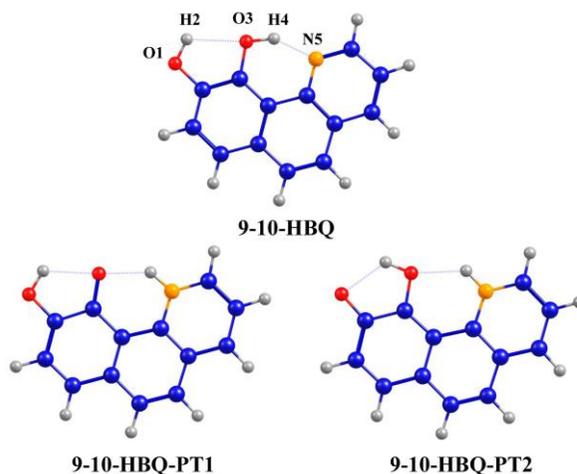
Due to its significance in nature, hydrogen bond has drawn great attention on the relevant topics [1-4]. Particularly, excited state hydrogen bond dynamics, elaborating properties involved in hydrogen bond in the excited state, plays important roles in many photophysical and photochemical processes, such as photo-induced electron transfer (PET), intra- or inter-molecular charge transfer (ICT), fluorescence resonance energy transfer (FRET), and so forth [5-8]. As one of the fast and quite complex reactions involved in hydrogen bond, the excited

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state intra- or inter- molecular proton transfer (ESIPT) is considered to be one of the most fundamental and important processes in chemistry, biology and materials [9-14]. Since half a century ago, the ESIPT process was firstly reported by Weller and co-workers in experiment with methylsalicylate [15], it has been a popular research [16-19]. The proton-transfer tautomerization form (normally named keto in the  $S_0$  state and keto\* in the  $S_1$  state) has charge redistribution characteristic, which are very fascinating towards the application of laser dyes, UV filters, fluorescence chemosensors, molecular switch, and so on [20-23]. Furthermore, some molecules are highly sensitive to the change in the microenvironments, based on which Sytnik *et al.* reported how the ESIPT chromophores can be used in the study of protein conformations and binding site polarity [24]. Indeed, a lot of spectroscopic techniques were applied to study the ESIPT process in recent years, however, only some indirect information about photochemical and photophysical properties could be provided through experimental investigations, and thus the explanation of ESIPT mechanism still have numerous challenges.

In effect, most of previous reports about ESIPT reactions are single-proton transfer, which occurs along with one intra- or inter- hydrogen bonded wire. Whereas only investigating about this kind of single-proton transfer process in the excited state is not enough, since more and more proton transfer processes in biological systems refer to multiple-proton transfer reactions [25]. Therefore, as a fundamental bridge, more and more inter- or intra- molecular systems containing double or multiple hydrogen bonds have been focused [26, 27]. Recently, as a kind of 10-hydroxybenzo[h]quinoline (10-HBQ) derivative, a



**Figure 1:** Views of optimized structures for 9-10-HBQ structures (9-10-HBQ-PT1: the single-proton transfer form; 9-10-HBQ-PT2: the double-proton transfer form) based on B3LYP/TZVP theoretical level. (Blue: C atom; Gray: H atom; Yellow: N atom; Red: O atom).