

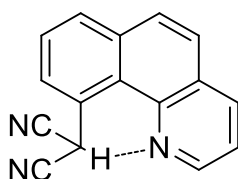
Acidic C-H bond as proton donor in excited-state intramolecular proton transfer (CHESIPT).

Numerous organic compounds possess both basic and acidic functional groups, whose properties may change (typically increase)ⁱ during the transition from ground state to the excited state. In the case where a simultaneous change of the proton donor and proton acceptor properties is significant enough, proton transfer process from acidic group to proton acceptor can occur. This process, known as an excited-state intramolecular proton transfer (ESIPT),^{ii,iii} continues to be the subject of intensive scientific research,^{iv,v,vi} even decades after the discovery of this phenomenon by Weller^{vii}. In the vast majority of described ESIPT-capable systems, phenolic –OH or acidic –NH serve as a proton donor group and heterocyclic nitrogen atom or carbonyl group as an acceptor of the proton.^{viii, ix, x}

The first example of “different” type of ESIPT (from phenolic -OH to a carbon atom) was discovered by Yates and co-workers^{xi} during the study photohydration reactions of o-hydroxystyrene. At the same time authors have shown that the reverse proton transfer (from C–H to phenolate oxygen) is highly unfavourable. Later Wan and co-workers^{xii} significantly expanded the range of compounds exhibiting this type of ESIPT showing the its possibility from phenol to a carbon atom that is part of an aromatic ring with high quantum efficiency.^{xiii, xiv}

Majority of ESIPT-capable systems can be classified as ‘flexible’ i.e. they can exist in several conformational states (part of which does not allow ESIPT).^{xv} The limited acidity of C-H bonds prompted us to focus on ‘rigid’ (inflexible) systems maintaining one conformational state. Since the classical and the most explored example of such molecules is 10-hydroxybenzo[*h*]quinolone,^{xvi, xvii, xviii, xix}

Herein we report the first attempt to create a model constituting the first example of fundamentally new type of ESIPT – transferring of the proton in excited state from acidic C-H to heterocyclic nitrogen atom based on benzo[*h*]quinolone core.



ⁱ Ireland, J. F.; Wyatt, P. A. H. *Adv. Phys. Org. Chem.* 1976, 12,131–221.

ⁱⁱ Demchenko, A. P.; Tang, K.-C.; Chou, P.-T. *Chem. Soc. Rev.* 2013, 42, 1379-1408.

ⁱⁱⁱ Zhao, J.; Ji, S.; Chen, Y.; Guo, H.; Yang, P. *Phys. Chem. Chem. Phys.*, **2012**, **14**, 8803-8817.

^{iv} Hsieh, C.-C.; Chou, P.-T.; Shih, C.-W.; Chuang, W.-T.; Chung, M.-W.; Lee, J.; Joo, T. *J. Am. Chem. Soc.*, **2011**, **133**, 2932–2943.

^v Mutai, T.; Sawatani, H.; Shida, T.; Shono, H.; Araki, K. *J. Org. Chem.*, **2013**, **78**, 2482–2489.

^{vi} Chou, P.; McMorro, D.; Aartsma, T. J.; Kasha, M. *J. Phys. Chem.* **1984**, **88**, 4596-4599.

^{vii} Weller, K. *Naturwissenschaften* **1955**, **42**, 175.

^{viii} McMorro, D.; Kasha, M. *J. Phys. Chem.* **1984**, **88**, 2235-2243.

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- ^{ix} Ciuciu, A. I.; Flamigni, L.; Skonieczny, K.; Gryko, D. T., *Phys. Chem. Chem. Phys.*, **2013**, *15*, 16907-16916.
- ^x Henary, M. M.; Wu, Y.; Cody, J.; Sumalekshmy, S.; Li, J.; Mandal, S.; J. Fahrni, C. J. *J. Org. Chem.*, **2007**, *72*, 4784–4797.
- ^{xi} M. Isaks, K. Yates and P. Kalanderopoulos, *J. Am. Chem. Soc.*, 1984, **106**, 2728;
- ^{xii} Matthew Lukeman and Peter Wan *J. Am. Chem. Soc.*, **2002**, *124*, 9458
- ^{xiii} Mitchel Flegel, Matthew Lukeman, Lawrence Huck, and Peter Wan *J. Am. Chem. Soc.*, **2004**, *126*, 7890
- ^{xiv} Nikola Basaric and Peter Wan *J. Org. Chem.* **2006**, *71*, 2677
- ^{xv} Mutai, T.; Sawatani, H.; Shida, T.; Shono, H.; Araki, K. *J. Org. Chem.*, **2013**, *78*, 2482–2489.
- ^{xvi} Martinez, M. L.; Cooper, W. C.; Chou, P.-T. *Chem. Phys. Lett.* **1992**, *193*, 151-154.
- ^{xvii} Chou, P.-T.; Chen, Y.-C.; Yu, W.-S.; Chou, Y.-H.; Wei, C.-Y.; Cheng, Y.-M. *J. Phys. Chem. A* **2001**, *105*, 1731-1740.
- ^{xviii} Chen, K-Y; Hsieh, C-C; Cheng, Y-M; Lai, C-H; Chou, P.-T. *Chem. Commun.* **2006**, 4395-4397.
- ^{xix} Piechowska, J.; Gryko, D. T. *J. Org. Chem.* **2011**, *76*, 10220-10228.