

Structural and Electronic Properties of 1- and 2-Naphthylamines in Aqueous Solutions

Manuel Martinović^a, Josip Draženović,^b Nikola Basarić^b and Nađa Došlić^a

mmartin@irb.hr

^a*Department of Physical Chemistry, Ruđer Bošković Institute, HR-10000 Zagreb, Croatia*

^b*Department of Organic Chemistry and Biochemistry, Ruđer Bošković Institute, HR-10000 Zagreb, Croatia*

Previous studies of *ortho*-, *meta*-, and *para*-aminobiphenyl [1] isomers have demonstrated distinct photochemical pathways involving proton transfer or water-assisted proton transfer from the NH₂ group to an aromatic ring carbon atom. While all isomers undergo water-assisted excited-state proton transfer (ESPT), the *meta*- isomer uniquely exhibits an additional photoredox pathway mediated by proton-coupled electron transfer (PCET), leading to water splitting. Motivated by the relevance of photocatalytic water activation, we investigate analogous processes in simpler organic chromophores.

Here, we examine 1- and 2-naphthylamine using a combined computational and experimental approach, focusing on isomer- and conformer-dependent photochemistry, including microsolvated water clusters. Our results reveal distinct excited-state deactivation pathways for the two isomers. In aqueous environments, 1-naphthylamine undergoes both water-assisted ESPT and a PCET-mediated photoredox process, whereas 2-naphthylamine exhibits exclusively ESPT reactivity. These differences are attributed to the intrinsic electronic characteristics of the La and Lb excited states in the two isomers. More broadly, our findings raise the question of whether such divergent photochemical behavior can be rationalized in terms of excited-state antiaromaticity relief.

Acknowledgement. This research has been supported by the Croatian Science Foundation grants (HRZZ-IP-2019-04-8008, HRZZ-IP-2022-10-4658, and HRZZ-IP-2024-05-8565) and the ADRIS foundation.

References:

[1] J. Draženović, C. J. Laconsay, N. Došlić, J. I. Wu, N. Basarić, *Chem.Sci.* **15** (2024) 5225–5237.