Proton Transfer in Aminonaphthols

Laura Cotter, 2018

Proton transfer (PT) is a fundamental process in both chemistry and biology, with examples such as tautomerization and the Electron Transport Chain[1]. Since many biological examples of PT are highly complex, we aim to develop a simple model that captures the effects of structure and the surrounding environment on PT. Since PT equilibrates very quickly, this makes it difficult to study. Photoacids, a class of molecules that become more acidic under excitation with light, enable us to overcome this difficulty by allowing control over when the PT event occurs.

The Takematsu Lab uses aminonaphthols, a particular set of photoacids, to study PT. These molecules have both a basic amine group and an acidic alcohol group, similar functional groups to those of amino acids. Aminonaphthols have three possible protonation states in the ground state, a cation, neutral, and anion, and a fourth zwitterion state that is only accessible under excitation. By varying the substitution of these two groups around the naphthalene framework, we can characterize the structure-reactivity relationship. Additionally, aminonaphthols are small molecules, allowing us the ability to perform theoretical calculations. Initial studies have used water as the solvent in order to mimic a biological system.

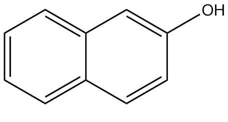

Figure 1. 2-Naphthol

This summer, I began by characterizing 2-naphthol (Figure 1), as it is well studied in literature[2] and as a way to isolate the effect of the alcohol group. Through absorption spectroscopy, I was able to calculate a ground state pK_a of 9.5, consistent with the literature value of 9.47[3]. Using steady-state emission spectroscopy and applying the Förster Cycle, I obtained an estimated pK_a^* of 2.93. Time resolved emission measurements using Time-Correlated Single Photon Counting (TCSPC) allowed the calculation of rate constants and the kinetic calculation of a pK_a^* of 2.78, which is again consistent with the literature value of 2.8[4].

Once I developed an understanding of 2-Naphthol and established a protocol, I used many of the same procedures to begin characterizing aminonaphthols, starting with 8-amino-2-naphthol (8N2OH) and 7-amino-2-naphthol (7N2OH, Figure 2). For 8N2OH, I found ground state pK_a values of 4.3 ± 0.2 for the amine and 9.5 ± 0.1 for the alcohol and for 7N2OH, I calculated ground state pK_a values of 4.4 ± 0.2 for the amine and 9.6 ± 0.1 for the alcohol. In the ground state, it appears that the addition and substitution of the amine does not affect PT.

In the excited state, there is a difference in the emission spectra between 8N2OH and 7N2OH. There was difficulty in assigning the emission spectra of 7N2OH with the corresponding protonation state, particularly with the zwitterion and neutral species. Ideally, 7-methoxy-2-naphthylamine (7N2OMe) would be used as a comparison molecule, since it has the same chemical structure as 7N2OH, with the exception that the alcohol functional group is now methylated and cannot undergo PT. The methylated version should behave very similarly to 7N2OH, but since it can only form the cation and neutral species, 7N2OMe should allow us to identify the emission peaks of 7N2OH.

Since 7N2OMe is not commercially available, I am in the process of optimizing a synthesis using microwave irradiation on the Bucherer reaction[5]. I plan to continue optimization in the fall, as well as characterizing excited state PT in 7N2OH. In the future, I also hope to perform computational calculations and characterize PT in 3-amino-2-naphthol.

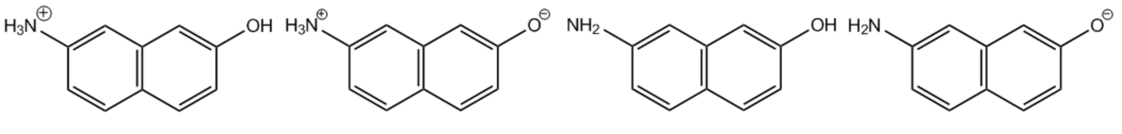

Figure 2. The four protonation states of 7N2OH (left to right): cation, zwitterion, neutral and anion.

Faculty Mentor: Kana Takematsu
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References
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