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Takematsu Lab, Summer 2022:
Exploring Schiff Base Chemistry as a Synthesis Platform for Photoacid Candidates

Photoacids are compounds that undergo excited state proton transfer (ESPT) and become more acidic upon absorbing light.[1] Photoacids are used to spatially and temporally control the pH of biological and chemical processes, such as acid-initiated protein folding and acid-catalyzed polymerization.[2] In order to control finely-tuned processes, the photoacids themselves must be designed carefully. The Takematsu lab is interested in how the structure of a photoacid can affect its ESPT mechanism and kinetics.[3]

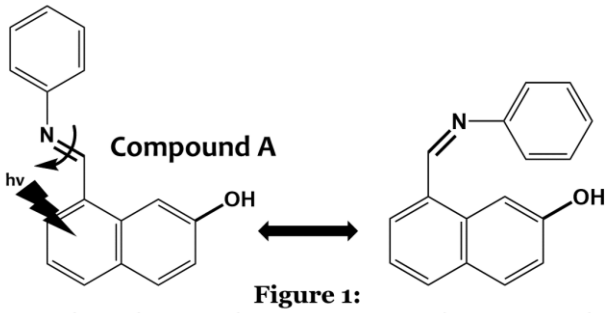

Figure 1:
Compound A undergoing photoisomerization. This new excited-state pathway may impact the ESPT of Schiff base photoacid candidates.

This summer, I explored Schiff base chemistry as a synthesis platform for potential photoacid candidates, specifically 8-phenylimino-2-naphthol (compound A) [Figure 1] and its control, 1-naphthalaniline (compound B) [Figure 2]. Schiff bases are characterized by their imine, or carbon-nitrogen double bond. These photoacid candidates introduce a new photoinduced pathway: photoisomerization in the form of a rotation about its double bond [Figure 1]. [4] Introducing a new excited state pathway may impact the ESPT mechanism.

I developed a synthesis protocol for control compound B using Schiff base chemistry [Figure 2]. Compound B was synthesized as a photoisomerization control as it has no potential ESPT pathway. Schiff base synthesis is highly customizable. By reacting specific amines and aldehydes, various target compounds can be synthesized with a simple reflux procedure.[4] Following synthesis, I used Nuclear Magnetic Resonance Spectroscopy (NMR) to confirm compound B was synthesized successfully [Figure 3]. I also began investigating compound B using absorption and steady-state emission spectroscopy in various solvents, including acetonitrile, methanol, and water. I established a strong foundation to begin my honors project in the upcoming fall 2022 semester. I will employ the skills I developed this summer to synthesize compound A and investigate its excited-state pathways.

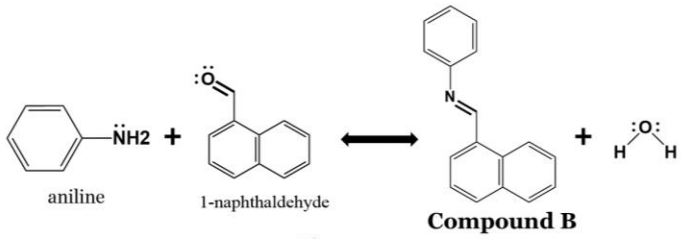

Figure 2:
Schiff-base synthesis of the control compound B, using aniline as the amine and 1-naphthaldehyde as the aldehyde. Equimolar amounts of reactants in methanol, catalyzed by a few drops of acetic acid, were refluxed to produce the Schiff base product B.

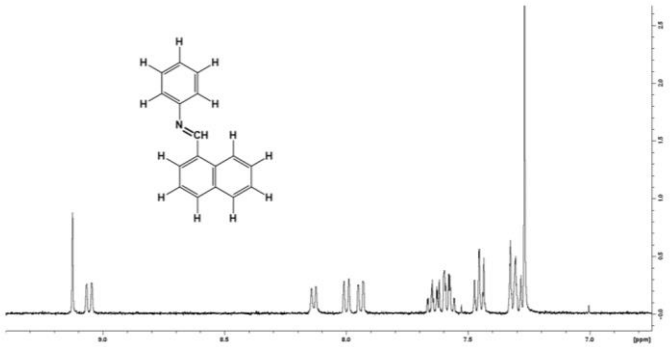

Figure 3:
1H NMR spectra of control compound B in $CDCl_3$ synthesized using Schiff base chemistry.

Citations: **(1)** Agmon, Noam. J PhyChem A 2005 109, no. 1: 13–35. **(2)** Sambath, Karthik, et al. Org Let 2020 22 3, 1208-1212 **(3)** Nix, Oliver. Bowdoin College. **(4)** G.Y. Nagesh. J of Molec Struc, 2015, Volume 1085.