

Investigating the Photoacidity of 8-benzylideneamino-2-naphthol

Oliver Nix, Class of 2022

Acids are an essential part of many chemical and biological processes, either catalyzing reactions, directly reacting with species, or simply changing the pH of a system. The strength of an acid is characterized by its pK_a , which indicates the extent to which the acid dissociates into H^+ and its conjugate base. Photoacids are a group of molecules which become more acidic when excited by a light source, or their excited state pK_a^* is much lower than their ground state pK_a . Photoacids are useful experimental tools, as they provide temporal and spatial control over local pH and as such can be used to control a variety of processes. Additionally, photoacids can be used to explore concepts such as proton transfer and excited state acidity.

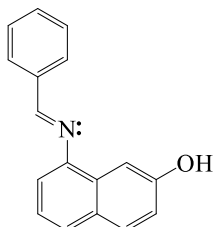


Figure 1:
8-benzylideneamino-2-naphthol

2-naphthol, a known photoacid, has a pK_a of 9.52 and a pK_a^* of 2.8, and has spectral properties well suited for photochemical studies, such as high emissivity and distinct spectral features between its acid and conjugate base forms. Additionally, 2-naphthol can undergo aromatic substitutions, allowing for a host of functional groups to bond to and influence the photoacidity of 2-naphthol. 8-benzylideneamino-2-naphthol (8BN2OH, Fig 1) is especially interesting as its benzylidene functional group is a combination of an imine and an aromatic ring and as such can be both isomerized and fully conjugated with 2-naphthol. The goal of this project was to characterize the ground and excited state chemistry of 8BN2OH through a combination of absorption and emission spectroscopy and to elucidate the effect of the benzylidene functional group on the photoacidity of 2-naphthol.

Samples were prepared in quartz cuvettes using 40 μ M solutions of 8BN2OH in water, methanol and acetonitrile. To test the stability of 8BN2OH in the ground state, UV-Visible absorption spectra were taken with the Agilent 8453 UV-Visible Spectrophotometer. To understand the excited state pathways of 8BN2OH, steady-state fluorescence spectra were obtained with the Hitachi F-2500 Fluorescence Spectrophotometer, and time-resolved fluorescence spectra were obtained with Horiba DeltaFlex Fluorescence Spectrophotometer. Programs were written in Matlab for data analysis.

In neutral pH water, 8BN2OH is not stable, and readily decomposes into 8-amino-2-naphthol and benzaldehyde. However, 8BN2OH is stable in both acetonitrile and methanol, and have identical absorption spectra across the two solvents (Fig 2). When concentrated triflic acid is added, 8BN2OH decomposes in acetonitrile and methanol. The decomposition is proposed to be at the imine, as imines are susceptible to acid and water catalyzed decomposition.

Time-resolved fluorescence measurements were obtained of 8BN2OH in dry acetonitrile. While all absorption spectra indicated a single species in the ground state, the fluorescence decay of 8BN2OH was fit to a multiexponential function, suggesting the existence of multiple reaction pathways in the excited state. 8BN2OH may be able to act as a photoacid in acetonitrile upon excitation, but more control experiments are needed. In the fall, I plan to investigate these pathways using chemical controls and computational calculations.

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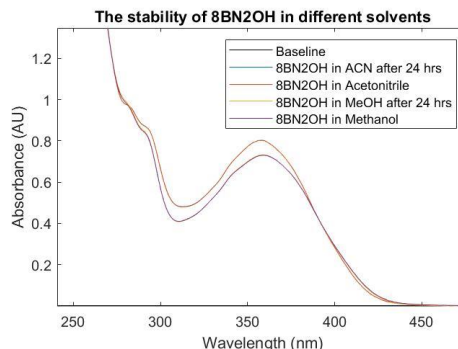


Figure 2: The stability of 8BN2OH samples in different solvents over time.