

Bifunctional Heteroaromatic Compounds as Irreversible Photooxidants

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Background and Objective: Nitrogen substituted aromatic heterocycles contain a fragmentable nitrogen-oxygen bond with a bond energy of $\sim 301 \pm 16$ kJ/mol. The first excited singlet state of these cationic molecules is dissociative, the N-O bond cleaves homolytically to yield a heteroaromatic radical cation and an oxygen centered radical. These highly reactive, transient species can irreversibly oxidize DNA and thus are useful tool in modern spectroscopy.

Methods: The interaction of the nitrogen onium salts with DNA is examined in binding and cleaving studies. Emission and absorption as well as CD spectroscopy are used to evaluate ground state association and solvent interaction.

Results: The addition of a DNA-binding moiety (naphthalimide) is essential for efficiency of the nitrogen onium salts. Addition of a positive charge increases ground-state association with DNA dramatically, as expected. Absorption and emission is strongly dependent on the hydrogen-bond ability of the solvent. The quantum yield of radical cation formation is 0.6. Energy wasting steps are geminate pair recombination to several positions of the aromatic heterocycle.

Discussion and Conclusions: The bifunctional salts can serve as irreversible photooxidants. The energy wasting geminate pair recombination must be avoided by using different heterocycles. This would also switch the excitation wavelength of naphthalimide and onium salts.

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