Photoreduction of oxoisoaporphines by amines: Laser flash and steady-state photolysis, pulse radiolysis, and TD-DFT studies

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Photoreduction of oxoisoaporphine (OIA) (l-aza-benzo-[de]anthracen-7-one) and its 5-methoxy (5-MeOOIA) derivative by selected amines (two non-a-hydrogen-donating amines (l,4-diaza[2.2.2]-bicyclooctane (DABCO) and 2,2,6,6-tetramethylpiperidine (TMP)) and three a-hydrogen-donating amines (triethylamine (TEA), diethylmethylamine (DEMA), and dimethylethylamine (DMEA))) has been studied in deaerated neat acetonitrile solutions using laser flash and steady-state photolysis. The triplet excited states of OIA and 5-MeOOIA are characterized by intense absorption maxima located at ?max = 450 nm and lifetimes of 34.7 ± 0.5 and 44.6 ± 0.4 ?s, respectively. In the presence of tertiary amines, both triplets are quenched with a rate constant that varies from the near diffusion limit (>10 9 M-1 s-1) to a rather low value (?10 7 M-1 s-1) and shows the expected dependence on the reduction potential for one-electron-transfer reactions. The transient absorption spectra observed after quenching of the resp