

Time Resolved UV-vis and IR Spectroscopic Studies on A Singlet 1,2-Diazacyclopentane-3,5-diyl Diradical: Notable Nitrogen-Atom Effects on the Reactivity of the Singlet Diradical

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Bond cleavage and bond formation processes play a central role in chemistry. Localized singlet diradicals are key intermediates in the homolytic reactions. Last decade, the relatively long-lived singlet carbon-carbon diradicals S-C-DR (up to $\sim 5 \mu\text{s}$ at 293 K, $\lambda_{\text{max}} \sim 570\text{-}600 \text{ nm}$) were discovered by this laboratory by introducing the dialkoxy groups at C(2) position and the aryl groups at C(3) position in the cyclopentane-1,3-diyl skeleton, *Chem. Rev.* **2013**, *113* (9), 7011-7088. Our computational calculations revealed that the σ -bonded compound was calculated to be stable than the open-shell species by ca. 63 kJ mol^{-1} . More recently, a notable nitrogen atom effect was found by this laboratory to increase significantly

the lifetime of a singlet 1,3-diyl **S-DR2a** ($\sim 10 \text{ ms}$ at 293K in toluene; $\lambda_{\text{max}} \sim 670 \text{ nm}$), *ACIE*, **2006**, *45*, 7828-7831. The major product isolated in $\sim 70\%$ after the denitrogenation was surprisingly not the ring-closed compound **N-CP** but the oxygen-migrated compound **MG**. In this study, the time-resolved absorption and infrared spectroscopic analyses at nanosecond time scale was performed in the photochemical denitrogenation of **AZ2** in detail, which revealed that **N-CP** was actually formed as a transient species that was equilibrated with the singlet diradical **S-DR2**.

