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

Shouhei Yoshidomi,^a Megumi Mishima,^a <u>Manabu Abe</u>,^a* Yoshihisa Fujiwara,^b Shin Seyama,^c and Taka-aki Ishibashi^c*

^aDepartment of Chemistry, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan

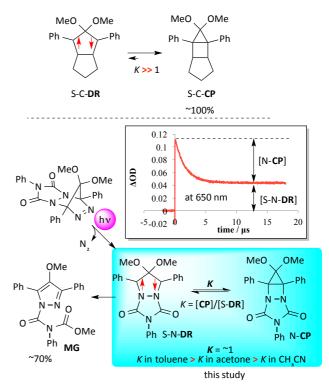
^bDepartment of Mathematical and Life Sciences, Graduate School of Science, Hiroshima University, 1-3-1 Kagamiyama, Higashi-Hiroshima, Hiroshima 739-8526, Japan

^cDepartment of Chemistry, Graduate School of Pure and Applied Sciences, University of Tsukuba,

1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan

(mabe@hiroshima-u.ac.jp)

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 ~5 μ s at 293 K, λ_{max} ~570-600 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** (~10 ms at 293K in toluene; $\lambda_{max} \sim 670$ nm), *ACIE*, **2006**, *45*, 7828-7831. The major product isolated in ~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**.