

学位論文要旨

Reactivity of Singlet Diradicaloids Embedded in Macrocyclic Skeleton and Non-Aufbau Electronic Configuration of Triplet Diradicals

(マクロ環状骨格を有する一重項ジラジカルの反応性及び三重項ジラジカルの非
Aufbau 電子構造)

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Chapter 1. General Introduction

Localized diradicals having two unpaired electrons are well-known chemical species in the denitrogenation of azoalkanes or bond homolysis reactions. Diradicals have two spin states, a singlet and a triplet. Due to the ferromagnetically coupled of two electrons, triplet diradicals show great potential for application to molecular magnetic materials. On the other hand, singlet diradicals are key intermediates in the bond homolysis processes, thus, elucidating their chemistry will provide a deeper understanding of the fundamental processes of bond-formation and bond-breaking processes. Recently, the non-linear optical properties and singlet-fission phenomenon were found in open-shell singlet species. So, singlet diradicals have attracted attentions not only in fundamental chemical research but also in the field of materials science.

Chapter 2. Reactivity of Singlet Diradicaloid Embedded in Macrocyclic Skeleton

Singlet cyclopentane-1,3-diyl diradicaloids with bonding orbital in the highest occupied molecular orbital (HOMO) are promising candidates for carbon-carbon π -single bonding species. Such species possess extremely small HOMO-LUMO gap, which show unique chemical properties such as high redox activity and non-linear optical property. Generally, the localized singlet diradicaloids having π -single bonding character are highly reactive species to give the corresponding σ -bonding compounds. The short-lived character hampers experimental investigations of their nature. In the past two decades, continuous efforts were devoted to stabilizing such highly reactive species. By introducing phenyl rings to the radical carbon atoms, singlet diradicaloids could be thermodynamically stabilized by electron delocalization. On the other hand, the kinetic stabilization of singlet diradicaloids has been achieved by introducing bulky groups to destabilize the transition states and products of intramolecular radical-radical coupling reaction.

In this chapter, we implemented the approach of “stretch effect” for cyclopentane-1,3-diyl diradicaloids to access kinetically stabilized singlet diradicaloids. The stretch effect induced by macrocyclic skeleton can suppress the bond-formation process by pulling the two radical carbons into the opposite direction against the bond-formation. Thus, the transition states **TS** and σ -bonded products **CP** are supposed to be destabilized, and singlet diradicaloid **S-DR**

could be kinetically stabilized. To this end, a macrocyclic structure was designed to generate the long-lived singlet diradicaloid, enabling the experimental investigation on the singlet diradicaloid with π -single bonding character.

Quantum chemical computations were conducted for molecular design of long-lived singlet diradicaloid with “stretch effect”. The kinetically stabilized diradicaloid **S-DR2** was generated by the photochemical denitrogenation of azoalkane **AZ2** to exhibit a small carbon–carbon coupling reaction rate of $6.4 \times 10^3 \text{ s}^{-1}$ (155.9 μs), approximately 1000 times slower than that of the parent system without the macrocycle **S-DR1** ($5 \times 10^6 \text{ s}^{-1}$, 209 ns) at 293 K in benzene. In addition, a significant dynamic solvent effect was observed in the intramolecular radical–radical coupling reactions. The lifetime of singlet diradicaloid **S-DR2** showed a longest lifetime up to 400.2 μs in viscous glycerin triacetate ($\eta = 23.00 \text{ cP}$) at 293 K. Furthermore, the σ -bonded product **CP2** was highly destabilized by the stretch effect, it decomposed immediately after exposing to air atmosphere, although the σ -bonded product with no-macrocyclic structure **CP1** was stable under air. The theoretical and experimental studies demonstrate that the stretch effect and solvent viscosity play important roles in retarding the σ -bond formation process, thus enabling a thorough examination of the nature of the singlet diradical and paving the way toward a deeper understanding of reactive intermediates.

Chapter 3. SOMO–HOMO Conversion in Triplet Cyclopentane-1,3-diyl Diradicals

According to the Aufbau principle, singly occupied molecular orbitals (SOMOs) are energetically higher lying than the highest doubly occupied molecular orbital (HOMO) in the electronically ground state of radicals. However, in the last decade, SOMO–HOMO energy converted species have been reported in a limited group of radicals, such as distonic anion radicals and nitroxides. This unusual electronic configuration plays an important role in switch bond dissociation energy, generation of high-spin species in the low oxidation state, and light emission in the near-infrared region.

In chapter 2, we discussed about the singlet cyclopentane-1,3-diyl diradicaloids, the HOMO and SOMOs of these diradicaloids are at separated position, thus, it is possible to generate SOMO–HOMO-converted diradicals by increasing HOMO energy and/or decreasing SOMO/SOMO–1 energies. In this study, SOMO–HOMO conversion was found in triplet 2,2-difluorocyclopentane-1,3-diyl diradical **DR3F** by theoretical computations, which contains the anthracyl unit at the remote position. The SOMO–HOMO conversion vanished in dihydro-substituted or naphthyl-substituted triplet diradicals, indicating that the high HOMO energy in the anthracyl moiety and the low-lying SOMO–1 due to the fluoro-substituent effect are the keys to the SOMO–HOMO conversion phenomenon. Furthermore, the cation radical generated through the one-electron oxidation of neutral diradical was optimized to a SOMO–HOMO-converted monoradical, and the dication **DR3F**²⁺ was a diradical with triplet ground state. This computational study provides an approach for molecular design of SOMO–HOMO-converted species.