



In recent years, low-valent chemical species such as radicals and carbenes, which have been recognized as short-lived intermediates, have been isolated by appropriate molecular design, and their chemical properties have been investigated in detail experimentally. In particular, the discovery of isolable carbenes, which are now widely used as indispensable ligands in coordination chemistry and synthetic organic chemistry, has enabled the development of novel highly active catalysts.



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Manabu Abe was born in Osaka, Japan. He received his Ph.D. from the Kyoto Institute of Technology with Professor Akira Oku, in 1995. In 1995, he became a faculty staff at Osaka University (Prof. Masatomo Nojima's group). From 1999 to 1998, he was an Alexander-von-Humboldt fellow with Professor Dr. Waldemar Adam at the Universität Würzburg. He was also a visiting researcher at the LMU München (Professor Dr. Herbert Mayr) in 2007. He moved to Hiroshima and became a full-time professor of Organic Chemistry at the Department of Chemistry, Hiroshima University in 2007. His research focuses on reactive intermediates chemistry, especially on diradicals.



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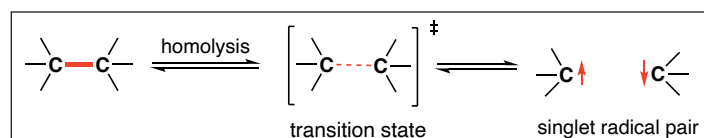


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IN OUR RESEARCH, we have focused on the singlet state of radical pairs that are always involved in the homolysis of bonds but are difficult to observe directly because of their extremely short lifetimes (Scheme 1); moreover, we have been working to elucidate their chemical properties and develop their functions by increasing their lifetimes. In this article, we first review the chemistry of localized singlet 1,3-diradicals intervening in the bond homolysis process of carbon-carbon bonds. Further, we discuss our recent findings on (1) controlling the ground state spin multiplicity (singlet versus triplet); (2) a novel bonding mode (C- π -C); (3) effects of substituents, macrocycles, and solvent viscosity; (4) the nitrogen-atom effect; and (5) the third intermediate in the bond homolysis process.



Scheme 1 Bond homolysis.

New Insights into Bond Homolysis Process and Discovery of Novel Bonding System (C- π -C) by Generating Long-lived Singlet Diradicals

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Chemistry of Localized Singlet Diradicals (singlet radical pair)

It has recently been discovered that in some cases, three energy minima may be observed in the bond homolysis process; nevertheless, it is generally believed that there are two energy minima in this process. For example, homolytic cleavage of the carbon-carbon σ -bond of the ethane molecule ($\text{CH}_3\text{-CH}_3$) generates a singlet radical pair of two methyl radicals ($\cdot\text{CH}_3$) (Scheme 1) whose energy difference is approximately equal to the bond dissociation energy of the σ bond, approximately 85 kcal mol^{-1} . If we can directly observe the thermal equilibrium process between these two states, we can examine the solvent and substituent effects on the equilibrium process and clarify the details of the bond homolysis process experimentally. However, since the activation energy of the σ -bond formation reaction between methyl radicals is almost zero, it is extremely difficult to directly observe the singlet radical pair in a simple manner. To achieve the direct observation of singlet radical pairs based on kinetic stabilization, the authors focused on singlet diradicals in a cyclic framework (Scheme 2).

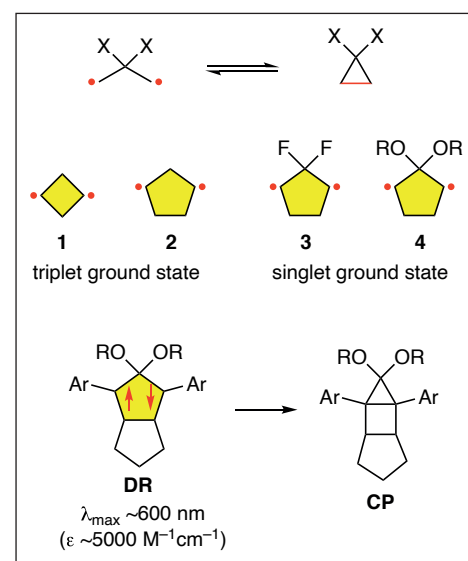
Prior to the study on singlet diradicals by the present authors, Kistiakowsky¹, Hoffmann^{2,3}, Closs^{4,5}, Schaefer⁶, Berson⁶, Adam⁷, Dougherty^{8,9}, and Borden¹⁰ reported on the reactivity and ground state of 1,3-diradicals in the 1930s, 1960s, 1970s, 1980s, and 1990s, respectively. The role of 1,3-diradicals in the

thermal isomerization of cyclopropane to propene was first proposed by Kistiakowsky et al. (Scheme 2), and theoretical and experimental studies were performed by Hoffmann and Berson et al. The triplet ground states of cyclobutane-1,3-diyl-diradical **1** and cyclopentane-1,3-diyl-diradical **2** were discovered by Closs, Adam, and Dougherty, and the ground state of 2,2-difluoro-1,3-diradical **3** was found to be singlet by Borden et al. To study the reactivity of singlet 1,3-diradicals experimentally and to clarify the bonding homolysis process, the present authors deemed it essential to extend the lifetime of the singlet diradicals by stabilizing them kinetically. In the latter half of the 1990s, we began to study 1,3-diradicals **4** with oxygen functional groups at the 2-position, keeping in mind that the molecular design of long-lived singlet diradicals requires (1) a singlet ground state and (2) the easy synthesis of a variety of derivatives. As a result, we succeeded in generating localized singlet diradicals **DR** that can be easily observed by time-resolved spectroscopy owing to their strong absorption peak around 600 nm in the visible region, which quantitatively gives the σ -bonded product **CP**.¹¹⁻¹³

Ground state spin multiplicity of 1,3-diradicals

Closs et al. found that when the substituents at the C2 position of 1,3-diradicals are hydrogen atoms ($\text{X} = \text{H}$), the most stable spin

multiplicity of the diradical is a triplet (Table 1).^{4,5} This is because the energy difference between the two orbitals ψ_{S} and ψ_{A} , which the two electrons of the 1,3-diradical occupy, becomes small due to the orbital interaction between ψ_{S} and the pseudo- π orbital σ_{CH} at the second position.³ The triplet state becomes energetically stable when one electron occupies $\psi_{\text{S,H}}$ and $\psi_{\text{A,H}}$ each according to Hund's rule (Figure 1). In other words, by increasing the energy



Scheme 2 Localized 1,3-diyl diradicals in cyclic structures.

levels of the two orbitals occupied by two electrons, diradicals can be created with a singlet ground state. Indeed, Borden et al. found that diradical **3** with an electron-withdrawing fluorine atom at the C2 position (X = F, singlet-triplet energy difference $\Delta E_{ST} = -9.7$ kcal mol⁻¹)¹⁴ is a singlet-state molecule.

We focused on the oxygen functional group, for which an increased number of derivatives are possible, and examined the most stable spin multiplicity of 4 (Table 1). As a result, we found that 4a (X = OH) with an oxygen functional group is indeed a singlet ground-state molecule that is a candidate for the experimental verification of the π -single bond (vide infra). Interestingly, **5** (X = SiH₃) with an electron-donating substituent, SiH₃, was also found to have a singlet ground state.¹⁵

These substituent effects can be explained by the pseudo- π orbital interaction at the C2-position of the 1,3-diradical and the spiro-conjugation effect (Figure 2). In the case of the oxygen functional group, the interaction between ψ_S and the pseudo- π orbital σ_{CO}^* at the C2 position stabilizes the ψ_S orbital (Figure 2a, left), resulting in a singlet ground state with π -single bonding wherein two electrons selectively occupy the $\psi_{S,OR}$ orbital. In the case of 4a with X = OH, a CASSCF(2,2) calculation shows that the two electrons are accommodated

in the $\psi_{S,OR}$ orbital with 81% probability, and the bond order between C1 and C3 is 0.62. The electronic absorption spectrum was predicted by TD-DFT calculations, and 4a was found to be a species exhibiting strong absorption at 420 nm (oscillator intensity (*f*) = 0.32); furthermore, the absorption at 420 nm was found to be due to the $\pi \rightarrow \pi^*$ transition of the π single bond.¹⁶ In addition to the pseudo π interaction, spiroconjugation plays a role in increasing the energy gap between $\psi_{S,OR}$ and $\psi_{A,OR}^*$, thereby increasing it to the energy spacing ΔE_{ST} of 4b (Table 1, Figure 2a).

In the case of **5** with the introduction of electron-donating silicon functional groups, the singlet was estimated to be the most stable spin multiplicity (Table 1), and CASSCF calculations revealed that an electron configuration in which the electrons occupied the antibonding orbital (π^*) $\psi_{A,Si}$ with 71% probability was favorable (Figure 2b). This substituent effect was attributed to the strong interaction of the electron-donating σ_{CSi} with the ψ_S orbital, resulting in $\psi_{A,Si}$ as the HOMO and $\psi_{S,Si}$ as the LUMO. This indicates that the singlet state of **5** exists without π -single bonding in the frontier orbitals, in contrast to the case of **4a,b**, where π -single bonding is introduced by the electron-withdrawing substituents.

Novel π -Single Bond (C- π -C)¹⁷⁻¹⁹

The present author's research group has been promoting research with the aim of not only understanding the process of bond homolysis, but also developing new chemistry based on the unexpected discoveries made in such research. In this regard, an unexpected finding in our research was that the localized singlet diradical exhibited strong absorption in the visible region (around 600 nm in the case of diradical **6**), whereas the corresponding triplet diradical **7** showed absorption in the ultraviolet region (around 350 nm). (Figure 3). To investigate the origin of the remarkable spin multiplicity effect on the absorption wavelength of the diradical species, we computed the orbitals corresponding to the electronic transitions using quantum chemical calculations (Figure 3).

The absorption in the visible region around 600 nm is computed to be mainly due to the electronic transition from the π -bonding orbital (π) to the antibonding orbital (π^*) between C1 and C3 based on a high-level ab initio method (CAS(2,2)+DDCI3) (Figure 3). Thus, the singlet diradical **6** entails π -bonding between C1 and C3, although an open-shell singlet structure exists. In other words, the localized singlet 1,3-diradical with an electron-withdrawing substituent at the C2-position has a novel bonding system with a π -single bond (C- π -C) between C1 and C3. This new group of compounds has a planar four-coordinated carbon atom, which is different from the generally known molecular structure. Very recently, a new bonding system has been reported for heterocyclic systems.²⁰⁻²⁸ In addition, despite a small π -electron system, they exhibit strong absorption in the visible region and are expected to provide new photoantenna sites that absorb abundant solar energy. Furthermore, as recently proposed by Nakano and co-workers,²⁹ the open-shell π -bond is expected to have a high two-photon absorption capacity because of the third-order nonlinear effect; once π -single bond (C- π -C) compounds are isolated, they may function as next-generation optical materials.

Kinetic Stabilization of π -Single-Bonded Compounds based on Substituents and Solvent Viscosity

The singlet diradical **6** is stable for at least a day in the low-temperature matrix state (77 K) but has a lifetime of approximately 200 ns at room temperature.¹³ Therefore, it is difficult to handle the chemical species at room temperature. To extend the lifetimes of π -single-bonded compounds, we investigated the substituent effects of the alkoxy and aryl groups, which can be relatively easily modified (Figure 4).

Although diradical **8**, which has a planar cyclic acetal skeleton at the C2 position,

	X,X	E_{ST}^* in kcal mol ⁻¹	ground state
2	H,H	+0.9	triplet
3	F,F	-9.7	singlet
4a	OH,OH	-6.7	singlet
4b		-12.2	singlet
5	SiH ₃ ,SiH ₃	-5.2	singlet

* $\Delta E_{ST} = E_S - E_T$. E_S : singlet energy; E_T : triplet energy

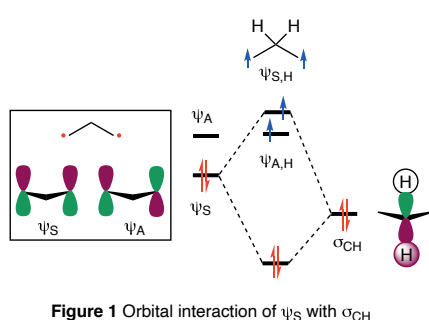


Figure 1 Orbital interaction of ψ_S with σ_{CH}

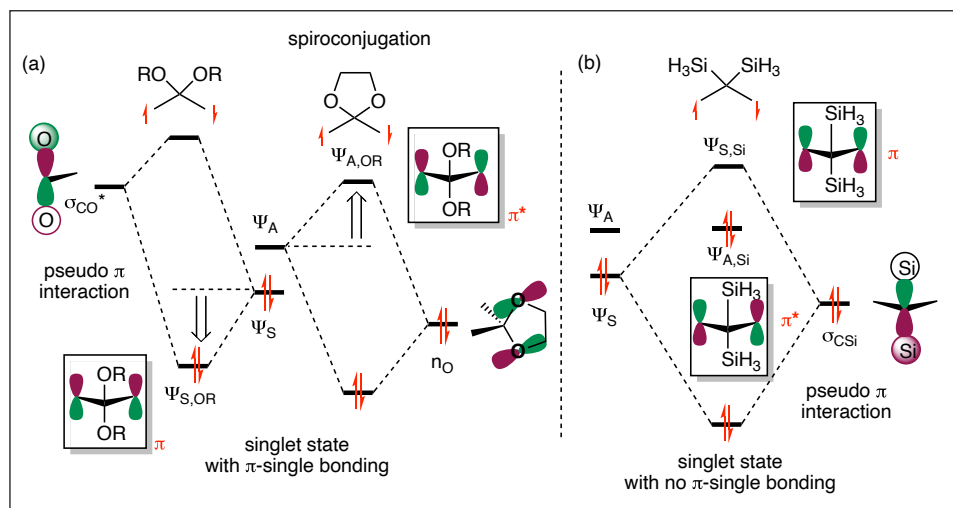


Figure 2. (a) alkoxy group effect and (b) silyl group effect on the singlet ground state of 1,3-diradicals

has a large singlet–triplet energy gap and absorbs light at around 500 nm, its lifetime is two orders of magnitude shorter than that of **6**, which is approximately 2 ns. This indicates that the steric hindrance between the acetal skeleton and the phenyl group at the C2-position raises the energy barrier for the transformation from the π -bond to the more stable σ -bond. In the case of **9** with OC_3H_7 , the lifetime was one order of magnitude longer than that of **6**. When the aryl group was also modified with substituents that increased the steric hindrance, relatively long-lived singlet diradicaloids **10** and **11** with lifetimes of 5 and 24 μs , respectively, were obtained. Thus, the introduction of a bulky aryl group and an alkoxy group enables the elongation of the lifetime of the π -single-bonded species. Recently, the present author's group observed a notable effect of viscosity on the lifetime of the singlet diradicaloid **11**, which increased to 2 s in 2,4-dicyclohexyl-2-methyl pentane (DCMP, $\eta = 38.7$) at 4000 atm and 293 K.³⁰ This phenomenon is understood as the dynamic solvent effect. That is, for reactions that require a large reaction space, the logarithm of the reaction rate is proportional to the logarithm of the reciprocal of the viscosity.³¹ The bond formation process of **11** should involve the movement of bulky aryl groups having a large space. This implies that the reaction requires sufficient reaction space. In fact, when the viscosity of the solvent was increased at atmospheric pressure, the lifetime of **11**, which is the inverse of the reaction rate, became longer (Figure 5a). Under high pressure conditions with viscous solvents, which are known to increase in viscosity with increasing pressure, the logarithm of the lifetime of **11** was proportional to the induced pressure (Figure 5b).

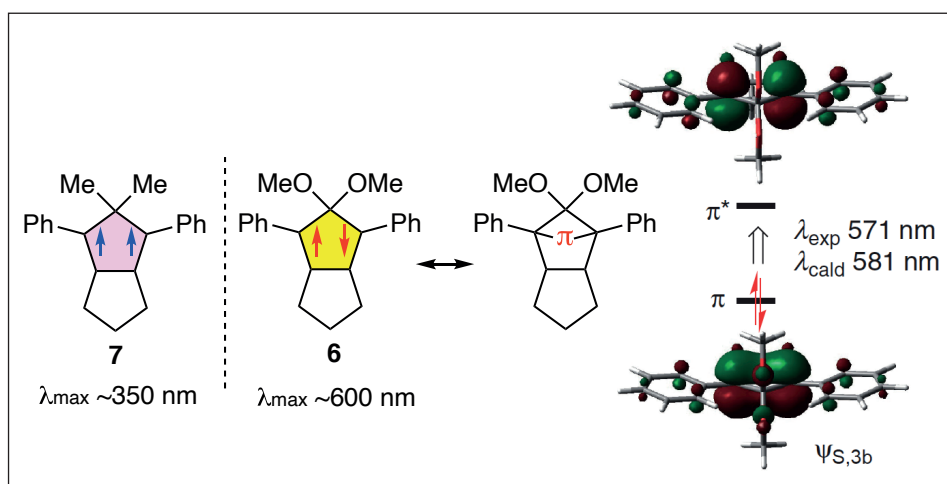


Figure 3. Electronic absorption characteristic in the singlet and triplet diradicals.

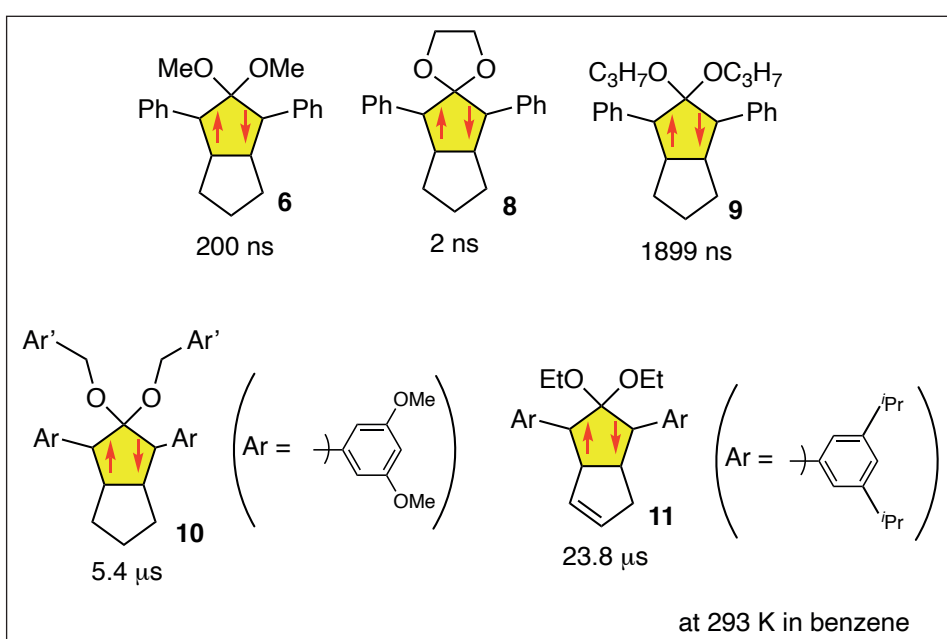


Figure 4. Substituent effect on the lifetime of singlet diradicaloids with π -single bond

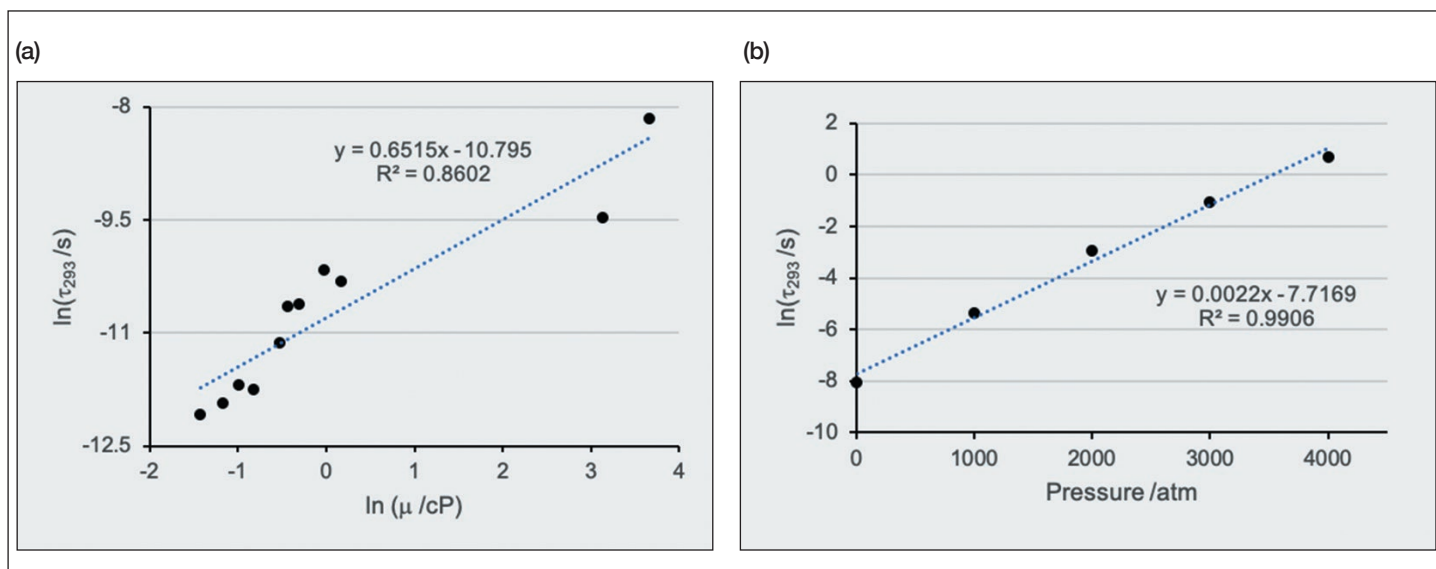


Figure 5. (a) The solvent dependency of the lifetime of **11** at 293 K and atmospheric pressure. (b) The pressure dependency of the lifetime of **11** at 293 K in DCMP.

Kinetic Stabilization of π -Single Bonded Chemical Species Using Macrocylic Stretching Effect³²

We further aimed to determine whether the longevity of π -single-bonded chemical species can be achieved by kinetic stabilization through a novel molecular design. In this context, inspired by recent synthetic studies on cyclic paraphenylene,^{33–36} we designed a molecule with a diradical skeleton in the macrocyclic ring (Scheme 3)³⁷. Specifically, the diradical skeleton has a planar structure and a larger macrocyclic ring than the corresponding ring-closing structure; therefore, we expected it to be less molecularly distorted and thus more kinetically stabilized in the reaction yielding the ring-closed product. The distorted macrocyclic skeleton was expected to have a stretching effect, pulling the C1–C3 bonds of the ring closure outward. As a model molecule, we designed a ring skeleton at the meta-position of the phenyl group in the radical moiety to minimize thermodynamic stabilization. Further, the macrocyclic effect

on the kinetic stabilization of diradical **12** was investigated using quantum chemical calculations.

In the case of **12a** (R = H), which has a biphenyl group as a substituent, the ring-closed compound **13a** was found to be more stable than **12a** by 9.6 kcal mol⁻¹. In the case of **13b**, in which a benzene ring was introduced between the biphenyl groups, the energy difference was slightly smaller, estimated to be 7.0 kcal mol⁻¹. When a naphthyl group with a more planar π -system was introduced, the energy difference between the diradical structure **12c** and the ring-closed structure **13c** was found to be much smaller, 1.0 kcal mol⁻¹, indicating that the kinetic stabilization of the diradical **12c** was expected. The stretching effect of the ring-closing structure was suggested by the fact that the C1–C3 bond distance of **13c** was calculated to be 162 pm, which was longer than that of **13a** (158 pm). Furthermore, the transition state energy of the ring-closing reaction was estimated to be 5.8 kcal mol⁻¹ for the transformation from **12a** to

13a, but it was 9.2 kcal mol⁻¹ for the cyclization from **12c** to **13c**. It is clear that the introduction of the macrocyclic ring kinetically stabilized the diradical.

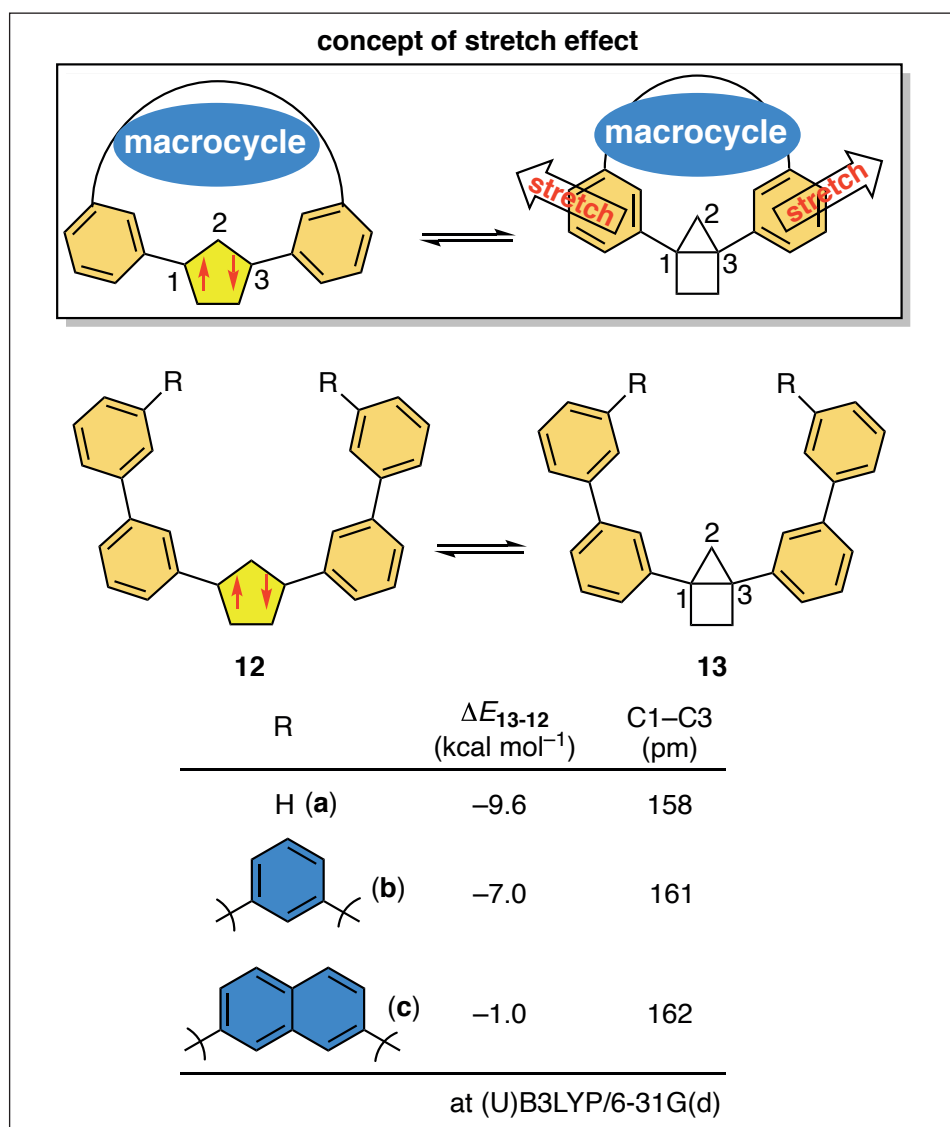
Recently, we succeeded in synthesizing azo compounds **14a**³⁷ and **14b**,³⁸ which can experimentally verify the macrocyclic effect on the kinetic stabilization of diradicals, and examined its reaction behavior (Scheme 4). When we attempted to generate diradicals **15** from **14** by the laser-flash-photolysis (LFP) method, we observed an absorption maximum around 600 nm, which is characteristic of singlet diradical species. Further, transient species with an absorption maximum around 600 nm, characteristic of singlet diradical species, were successfully observed (Figure 6). The lifetimes of the transient species **15a** and **15b** were determined to be 14.0 and 156 μ s at 293 K, respectively, which are two-three orders of magnitude longer than that of **6**. The transient species near 600 nm was identified as the singlet diradical **15**; this is because the photodenitration of **14** produced a quantitative ring-closed product **16** and the signal near 600 nm was not quenched by molecular oxygen.

The macrocyclic stretching effect could not be directly estimated from the reaction energy because the thermal equilibrium process between **15** and its ring-closed form **15b** could not be observed, as in the case of diradical **28** (Figure 9). A close examination of the reactivity of ring-closed compound **15b** showed that its chemical reactivity was strongly influenced by the stretching effect of the macrocyclic ring. Thus, **15b** was stable under degassed conditions but gradually transformed into oxidation products **18–20** under an oxygen atmosphere. Under the same conditions, **21** was stable, suggesting that the high reactivity of **15b** was due to the macrocyclic effect.

The dynamic solvent effect (viscosity effect) has also been confirmed for the case of macrocyclic singlet diradicaloid **16**. Diradicaloid **16** lasts up to 400 μ s in the high-viscosity solvent triacetin (GTA, $\pi^* = 0.63$ kcal mol⁻¹, $\eta = 23.0$ cP), which is 2.5 times longer than in benzene ($\pi^* = 0.55$ kcal mol⁻¹, $\eta = 0.65$ cP) at 293 K. On the other hand, in low-viscosity acetone ($\pi^* = 0.62$ kcal mol⁻¹, $\eta = 0.32$ cP), whose polarity is very close to that of GTA, the lifetime **16** was as short as 27.9 μ s. This indicates that the viscosity of the solvent plays an important role in determining the lifetime of the singlet diradical. During the ring closure reaction, the movement of the macrocyclic skeleton is inhibited in the viscous solvent, resulting in a longer lifetime of the singlet diradicaloid **16**.

Nitrogen Atom Effect on the Reactivity of Singlet Diradicals

As typified by N-heterocyclic carbenes (NHCs), the reaction behavior of carbenes is known to change dramatically with the



Scheme 3 Concept of “stretch effect” for the kinetic stabilization of singlet diradical.

adjacent nitrogen functional groups.^{40–44} Considering this, we investigated the effect of nitrogen atoms on the reactivity of localized 1,3-diradicals (Figure 7).^{45,46} As mentioned above, diradical **2** is a triplet ground-state molecule, but the ground state of **22** changes to a singlet when nitrogen atoms are introduced in the five-membered ring, as in carbene. However, the ground state of carbene is a closed-shell singlet, while the ground state of **22** ($\Delta E_{ST} = E_S - E_T = -2.7 \text{ kcal mol}^{-1}$ in C_2) is an open-shell singlet. Diradicals **23** and **24**, with highly electronegative F or OH groups introduced on the carbon sandwiched between the radical moieties of **22**, show larger singlet–triplet energy differences, $\Delta E_{ST} = -19.7$ and $-14.9 \text{ kcal mol}^{-1}$ in C_2 , respectively; moreover, an increase in these energy differences suggests that the singlet becomes more stable upon introducing the electron-withdrawing groups.

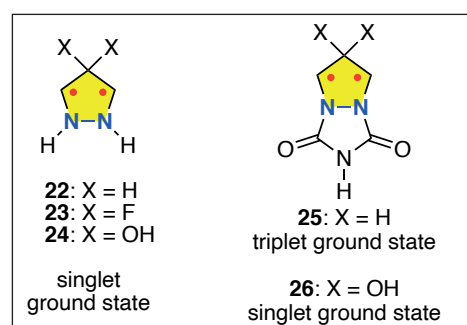


Figure 7. Nitrogen-atom effect on the ground state spin-multiplicity.

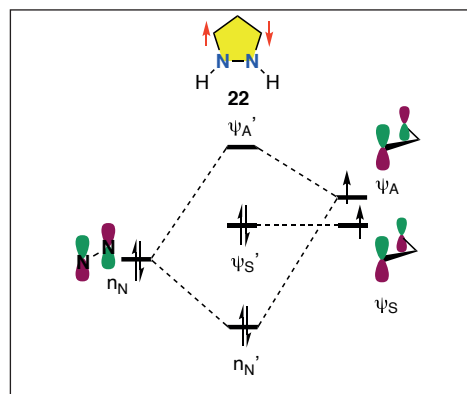


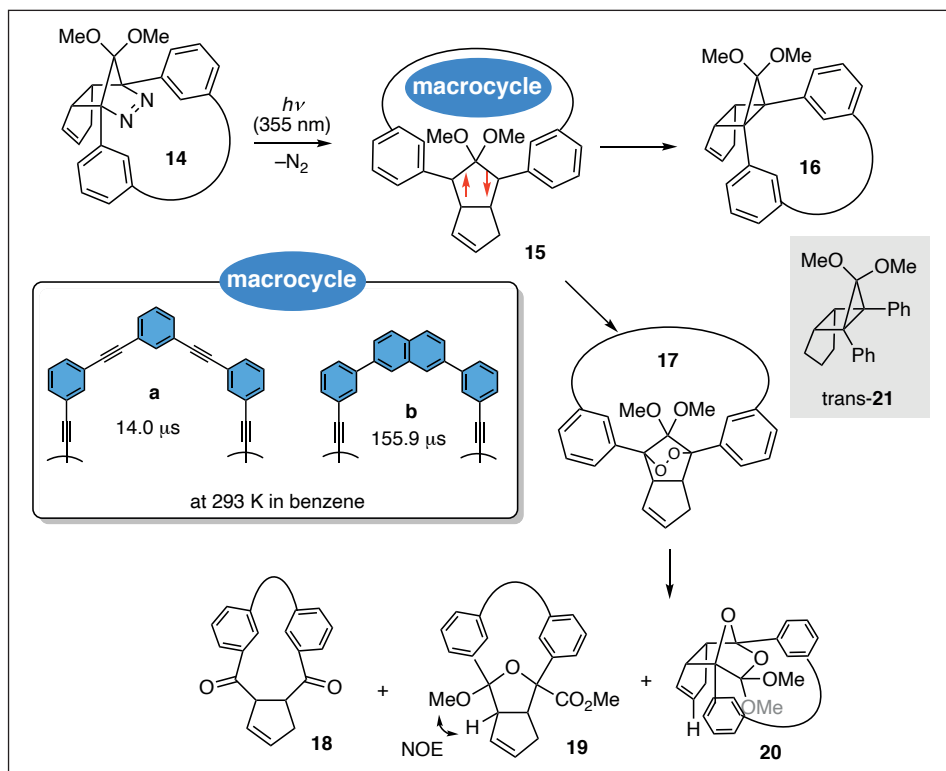
Figure 8. Nitrogen-atom effect on the singlet ground state

The nitrogen-atom effect can be understood by the fact that the interaction between the orbitals n_N and ψ_A increases the energy difference of ψ_S and ψ'_A occupied by the two radical electrons, as shown in Figure 8. This is supported by the shorter nitrogen–nitrogen bond distance of diradical **22** (1.355 Å) than that of pyrazolidine (1.521 Å). The orbital interaction shown in Figure 8 is also proved by the fact that the triplet becomes the ground state for diradical **25**, in which the electron-withdrawing group is introduced on the nitrogen atom. Interestingly, diradical **26**, in which the electron-withdrawing substituent is introduced at the C2 position of the 1,3-diradical, changes to

the singlet-ground-state diradical. Surprisingly, the 1,3-diradical with an electron-withdrawing substituent at the C2-position was found to be more energetically stable than the corresponding closed-ring form.

To experimentally investigate the effect of nitrogen on the reactivity of 1,3-diradicals, we attempted to synthesize azo compounds **27** that can clean the diradical (Scheme 5). The cycloaddition of pyrazole with PTAD afforded azo compound **27** in a quantitative yield, and the denitrogenation of **27** led to the generation of derivative **28** of diradical **26**.

The reaction dynamics of diradical **28** were investigated by the laser flash photolysis (LFP) of **27** (Figure 9). As a result, we observed a chemical species exhibiting a strong absorption peak near 650 nm in the visible region, which is characteristic of singlet diradical species (Figure 9a). Interestingly, the species with absorption around 650 nm entailed two decay processes: a fast decay process (microseconds) and a slow decay process (milliseconds), as shown in Figure 9b. The species was determined to be the singlet diradical **28** because it was not quenched by molecular oxygen and



Scheme 4. Generation of **15** with a macrocyclic structure.

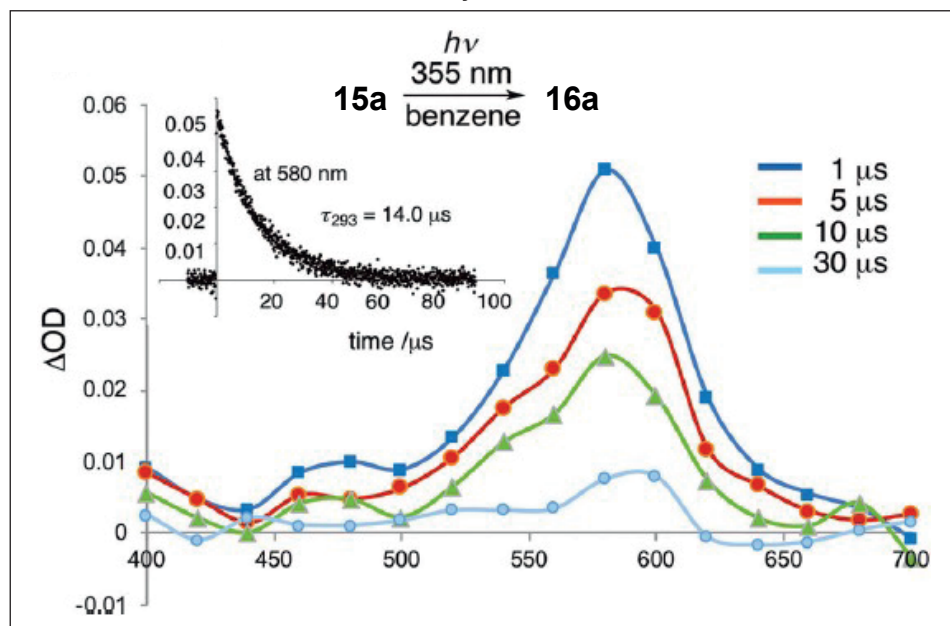


Figure 6. LFP study on **15a** at 293 K in benzene.

was electron spin resonance (EPR)-silent, which is consistent with the prediction of quantum chemical calculations that **28** exhibits strong absorption at around 700 nm.

Product analysis of the photo-denitrogenation reaction of **27** showed that the cyclized product **29** of **28** was not isolated, but the product **30** obtained by methoxy group rearrangement was identified as the main product. This experimental result is consistent with the fact that cyclized compound **29** is more energetically unstable than **28**, as mentioned above. From the results of this product analysis and quantum chemical calculations, the reaction behavior of **28** observed by the LFP method can be understood by the reaction mechanism shown in Scheme 5. Diradical **28** generated by the LFP method from **27** first reaches thermal equilibrium with the ring-closing compound **29** within a lifetime of approximately microseconds, and then gives the rearrangement product **30** in a reaction lasting for approximately milliseconds (Scheme 5). Therefore, nanosecond time-resolved infrared absorption (IR) spectra were measured to confirm the formation of ring-closing compound **29** in the reaction system. The fast decay process of **28** was experimentally identified as a radical recombination process to yield compound **29**,

and the activation parameters ΔH^\ddagger and ΔS^\ddagger of the ring-closing reaction were found to be 37.6 kJ mol⁻¹ and -2.6 J K⁻¹ mol⁻¹ in toluene and 36.4 kJ mol⁻¹ and -4.6 J K⁻¹ mol⁻¹ in acetonitrile, respectively. These results are in good agreement with the activation energy of 42.4 kJ mol⁻¹ obtained by quantum chemical calculations. The thermal equilibrium process ($K = k_{29}/k_{28}$) between the singlet diradical and σ -bonded product was experimentally observed for the first time in this study. Although the solvent effect on the equilibrium constant K was small, it was found to be smaller for the polar solvent acetonitrile (ACN) than for the nonpolar solvent toluene (TOL); $K_{\text{TOL}} = 1.54$, $K_{\text{ACN}} = 0.72$, and the zwitterionic nature of the singlet diradical was experimentally clarified (Scheme 5). Because the contribution of the zwitterionic structure of the singlet diradical was further enhanced by the nitrogen atom adjacent to the radical site, the energy difference between the singlet diradical and its ring-closed form became small, and the bonding homolysis process could be directly observed.

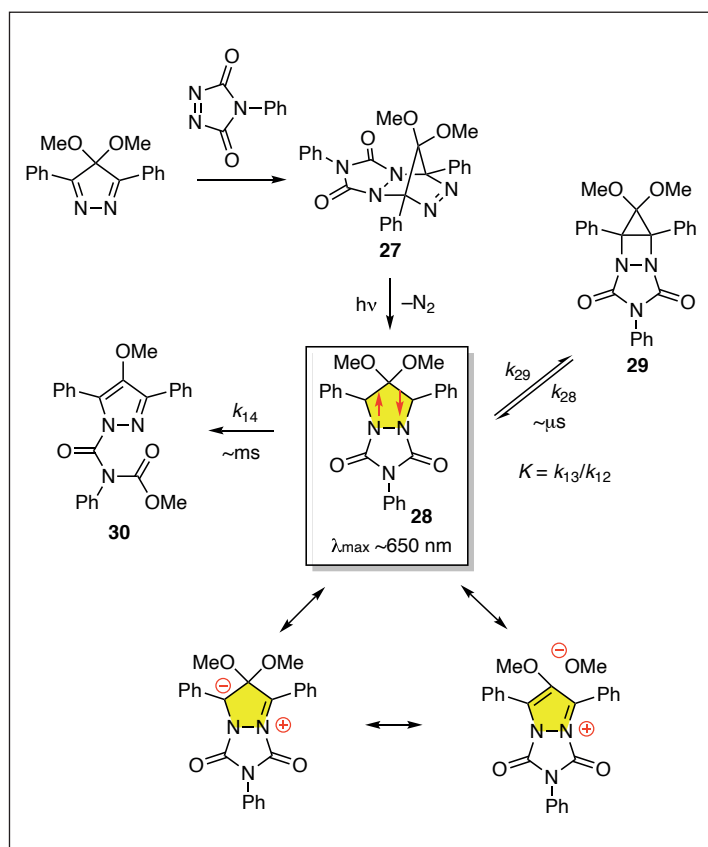
Third Energy Minimum of the Bond Homolysis Process⁴⁷

In general, there are two energy minima in the bond homolysis process: the singlet radical pair

and the sigma-bonded compound. Herein, we describe the recent discovery of a third energy-minimum structure in the bond homolysis process, a puckered-type intermediate **33**. The discovery of this intermediate allows us to understand the spin-multiplicity effect on the stereoselectivity of the ring-closing product **32** produced in the denitrogenation of azo compound **31** and the emission observed from **32** at unusually long wavelengths (Scheme 6).

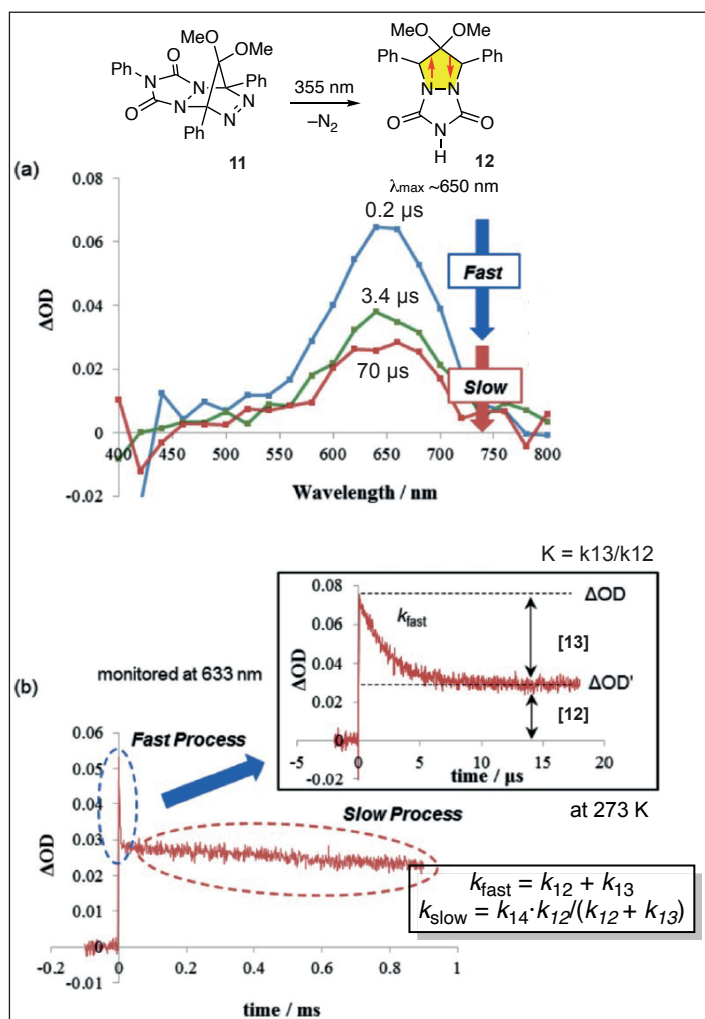
As shown in Scheme 6, when the photo-denitrogenation of **31** was performed by the direct electronic excitation of the azo functional group (-N=N-), trans-**32**, which retains the stereochemistry of **32**, is preferentially obtained (trans/cis-**28** = 85/15), whereas the denitrogenation of the excited triplet of the azo moiety using a triplet sensitizer such as benzophenone yielded cis-**32** exclusively. To investigate the effect of spin multiplicity on the stereoselectivity of this radical coupling reaction, the reaction behavior of the previously known planar singlet diradical **6** was first investigated by quantum chemical calculations using the broken symmetry method (BS-DFT) (Figure 10).

As a result, even though trans-**32** is more stable thermodynamically than cis-**32**, the transition state cis-**TS** giving cis-**32** is approximately 20 kJ mol⁻¹ more stable than the



Scheme 5 (above). Generation of singlet diradical **28** and its reactivity.

Figure 9.(right) (a) LFP study on **28** at 293 K in toluene; (b) Time profile of 633 nm species after LFP of **27**.



transition state **trans-TS** giving **trans-32**, indicating that **cis-32** is kinetically favored. These calculations indicate that **cis-32** was formed exclusively in the triplet-sensitized denitrogenation of **31** because of the intersystem crossing (ISC) of the planar triplet diradical **36** to the more stable **6**, which selectively leads to **cis-32**. Experimentally, the activation energy barrier of the radical coupling reaction in **6** was found to be 41.4 kJ mol⁻¹, which is similar to the activation energy barrier for the transformation from **6** to **cis-32** determined by quantum chemical calculations. When we started the IRC calculation from **trans-TS**, it was suggested that there is a third intermediate **33** between **trans-32** and **trans-TS**, which had not been observed in the bonding homolysis process. Quantum chemical calculations (BS-UB3LYP/6-31G(d)) showed that the energy of **33** was approximately 36.8 kJ mol⁻¹ higher than that of **6**. It was also found that there was almost no energy barrier to **trans-32**, and **trans-32** was quickly obtained when **33** was generated (Figure 10). In other words, in the direct excitation of **31**, **34** generated in the stepwise denitration process preferentially gives **trans-32** via the puckered-type intermediate **33** (Scheme 7). By contrast, in the triplet sensitization reaction, **cis-32** is exclusively generated from the triplet intermediate **36**, which has a long lifetime and can change its conformation to the most stable planar diradical **36**. After intersystem crossing to **6**, **cis-32** was selectively formed in the ring-closing reaction.

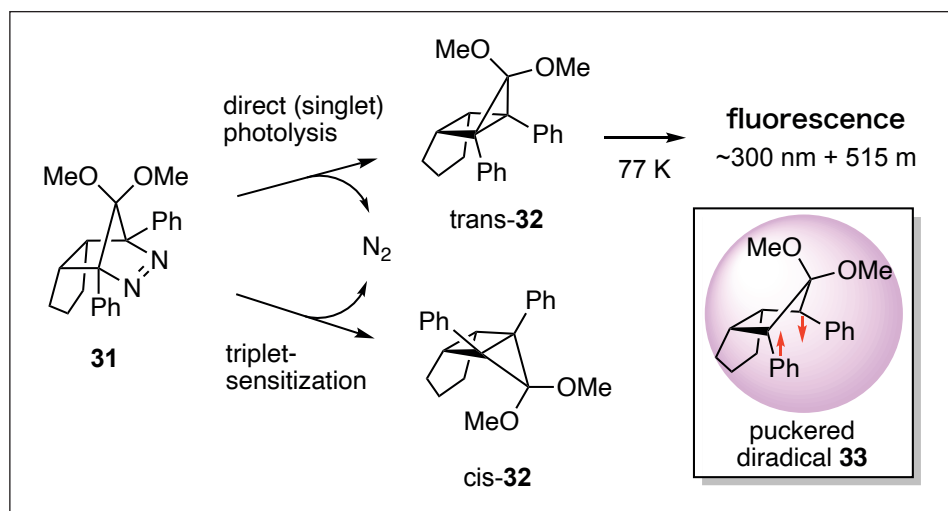
As shown in scheme 7, the mystery of the remarkable spin multiplicity effect on stereoselectivity observed in the photo-denitration reaction of **31** seems to be solved by assuming the intervention of a previously unobserved puckered-type singlet diradical. However, there is no direct experimental evidence for the existence of such a diradical, and the analogy is based on DFT calculations, which are inherently unable to treat open-shell singlet diradicals with theoretical precision. The present author aimed to experimentally capture the third structure **33** intervening in the bond homolysis process. Therefore, we attempted to stabilize the puckered structure by introducing a bulky substituent, as is usual, and directly observed the derivative of **33** ($\lambda_{\text{calcd}} = 480 \text{ nm}$), which is expected to appear at wavelengths shorter than those of **6** ($\lambda_{\text{calcd}} = 580 \text{ nm}$) in our calculations (Figure 11).

Azo compound **35** was synthesized by introducing $-\text{OCH}_2\text{Ph}$ as a bulky substituent in the alkoxy moiety and a meta-dimethoxyphenyl group ($-\text{C}_6\text{H}_3(\text{OMe})_2$) as an aryl group. The photodenitrogenation reaction was conducted in a low-temperature organic glass matrix using 2-methyltetrahydrofuran (MTHF, melting point 137 K). At 110–120 K, where a soft matrix was obtained, a strong absorption around 580 nm corresponding to a planar singlet diradical was observed and attributed

to **37**. At temperatures below 98 K, where the matrix is hard, no absorption near 580 nm was observed, and a chemical species with electronic absorption near a shorter wavelength of 450 nm was observed instead of **37**. Because of the good agreement with the calculated absorption wavelength of **36** and the silence in the electron paramagnetic resonance (EPR) spectrum, the absorption near 450 nm was assigned to the third minimum-energy structure, a puckered-type singlet diradical **36**.

Anomalous long wavelength emission from **trans-32**

The puckered-type diradical **33** is the third minimal-energy structure found in the ground-state bond homolysis process and is an important intermediate that controls the stereoselectivity of radical coupling reactions. To determine whether the puckered-type structure exists in the bond dissociation process in an electronically excited state, we measured the emission spectrum of **trans-32** (Figure 12).⁴⁷



Scheme 6. Puckered diradical **33** as a new intermediate of bond homolysis.

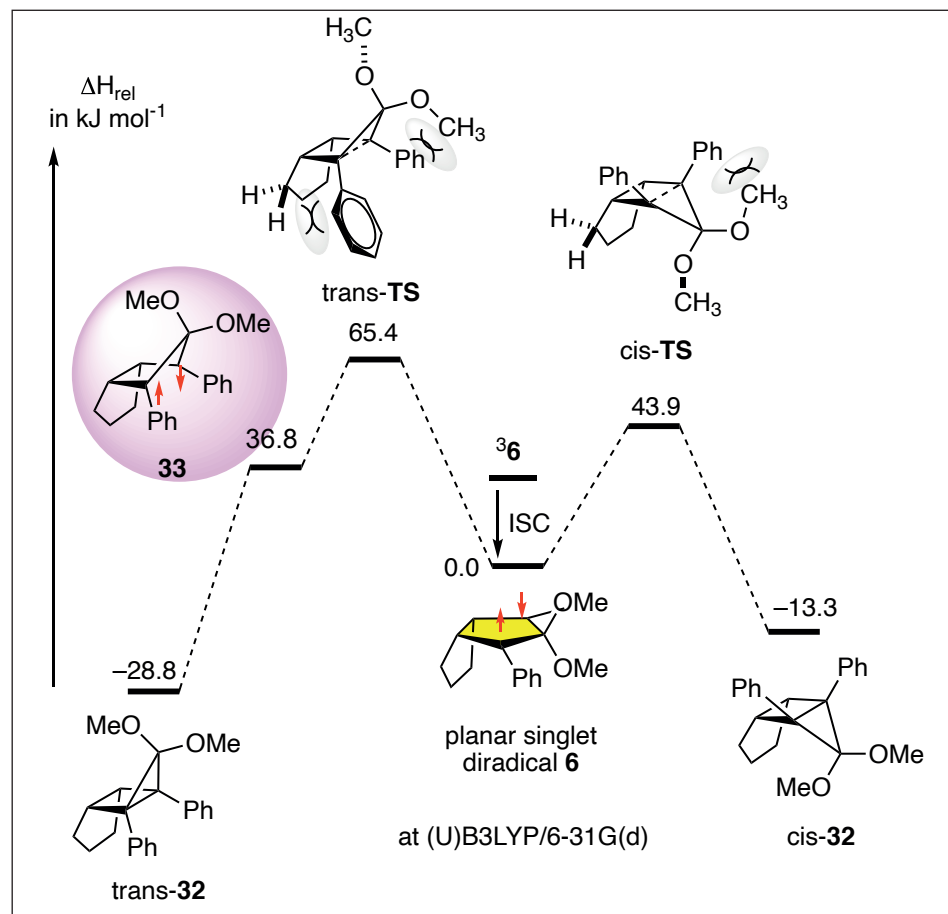
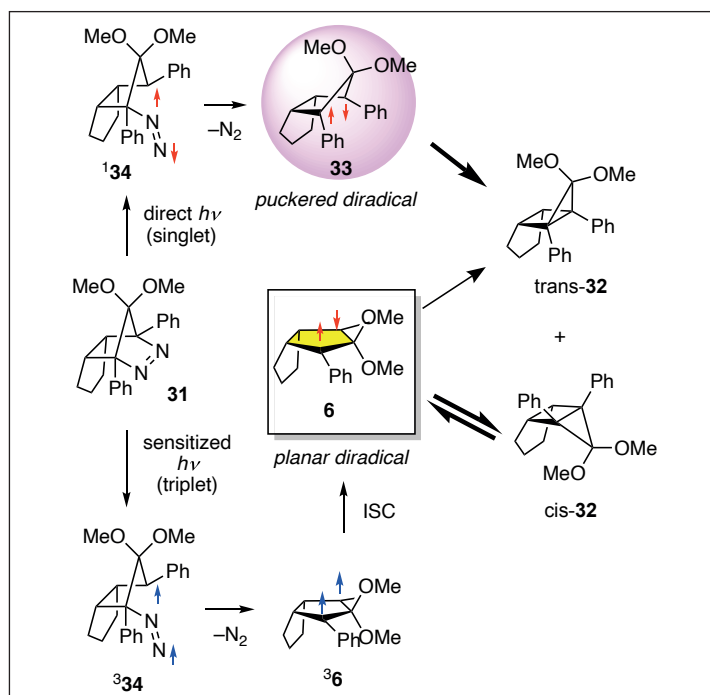


Figure 10 Computational study on reactivity of planar singlet diradical **6**.

The fluorescence spectrum (250 nm excitation) of a solution of trans-**32** (1.5×10^{-5} M) in 3-methylpentane (3-MP) was measured at liquid nitrogen temperature (77 K). Interestingly, fluorescence corresponding to a phenyl-group-derived vibrational structure was observed around 280–360 nm (lifetime 8.7 ns, Figure 12a) and broad fluorescence with no vibrational structure was noticed at 460–660 nm (lifetime 7.9 ns, Figure 12b). The excitation spectra of these two types of emission (Figures 12a and 12b) were consistent with the absorption

spectrum of trans-**32**. These observations indicate that not only the fluorescence at shorter wavelengths but also the fluorescence with emission maxima around 515 nm originates from the electronically excited state of trans-**32**. Considering the results of quantum chemical calculations shown below, we conclude that the long-wavelength emission originates from the electronically excited state **33*** of the Packard-type diradical, which is generated from the electronically excited state of trans-**32** via an adiabatic σ -bond cleavage process.

Similar long-wavelength fluorescence was not observed for trans-**38**, an analog of **32**; only fluorescence from the phenyl group (260–355 nm, 9.2 ns) was observed. The substituent effect on the emission spectra observed in trans-**32** and **38** was also observed in trans-**39** and **40**, wherein the phenyl group was replaced by a naphthyl group. To understand these emissions, the reaction potentials of the electronic excited states of trans-**32** and **38** were calculated using the state-averaged complete active space self-consistent field



Scheme 7. Mechanism for the stereoselectivity in the denitrogenation of **31**.

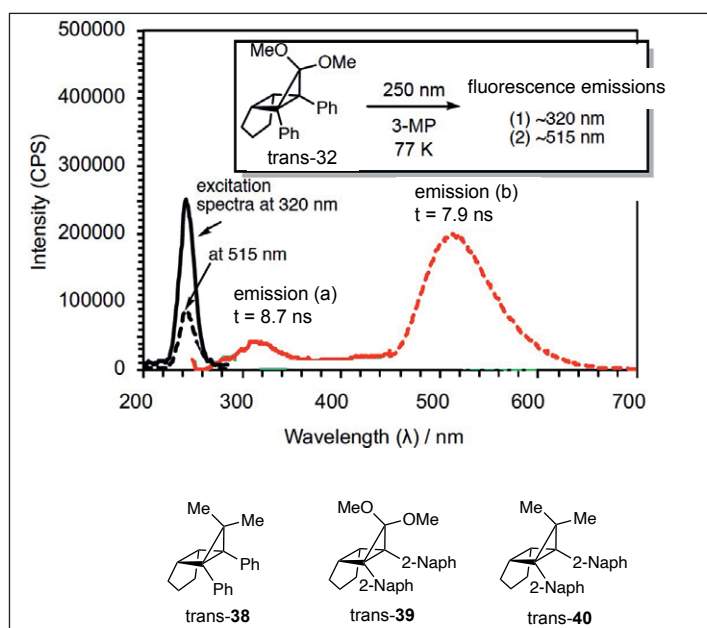


Figure 12 Fluorescence spectra from trans-**32** in 3-MP at 250 nm at 77 K. Short-wavelength emission (a) at around 320 nm and long-wavelength emission (b) at around 520 nm.

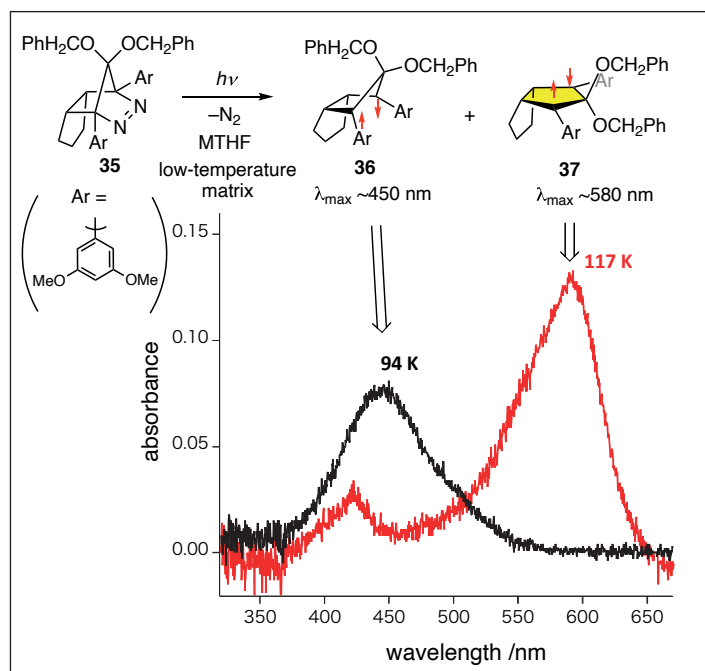


Figure 11. Detection of puckered diradical **36** and planar diradical **37** in the photolysis of **35**.

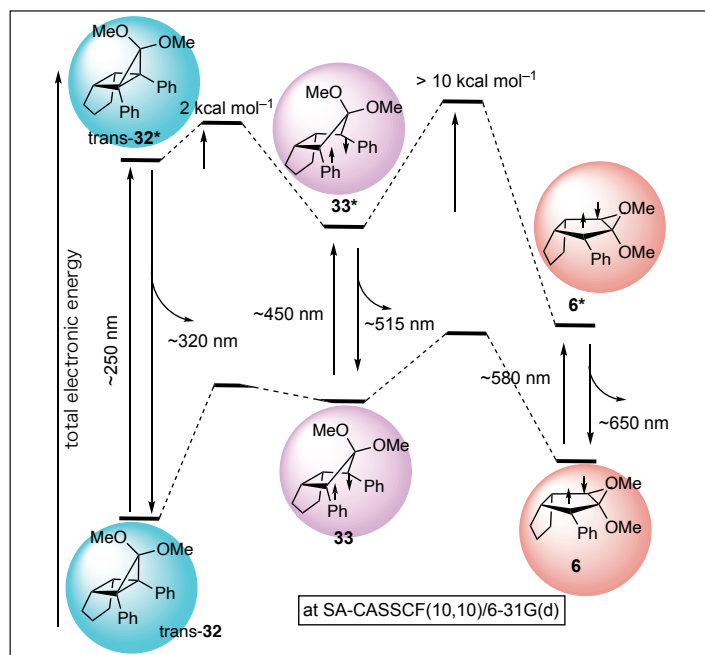


Figure 13. Ground state and excited state potential energy surfaces in trans-**32**, calculated at the SA-CASSCF(10,10)/6-31G(d) level of theory.

(SA-CASSCF) method (Figure 13). Although the SA-CASSCF method entails a large computational cost, it is able to obtain the electronic states and energies of the multiconfigurational singlet diradicals with an open-shell nature more precisely.

As shown in Figure 13, the activation energy of the adiabatic bond-homolysis process to give the puckered-type intermediate **33*** from the electronically excited state trans-**32*** was found to be very small, approximately 2 kcal mol⁻¹, and the two fluorescence peaks observed in the emission spectrum of trans-**32** were from trans-**32*** and **33***. The activation energy from **33*** to **6*** is as high as 10 kcal mol⁻¹, which is consistent with the experimental observation that the emission from **6*** (~650 nm) was not observed. A similar adiabatic excited-state cleavage reaction was performed for trans-**38***, and the energy barrier for the bond homolysis cleavage process was as high as approximately 6 kcal mol⁻¹, consistent with the fact that only phenyl-group-derived fluorescence was observed from trans-**38***. Thus, the existence of a third minimal-energy structure in the bond homolysis process of trans-**32** even in the electronically excited state was revealed.

Conclusion

In this article, we elucidate the kinetic stabilization of localized singlet diradicals entailed in the bond homolysis process to extend their lifetime and investigate their chemical properties. By thoroughly studying the bond homolysis process, which is a fundamental chemical reaction, we propose novel bonding styles and new reaction intermediates. We hope that more research will be conducted using these new chemical concepts in the future.

Finally, since we are often asked about the difference between “diradical” and “biradical,” we will explain the definition of “diradical” used in this paper. According to the IUPAC Gold Book, a diradical is a chemical species with two strongly interacting radicals in a molecule and two spin multiplicities, a singlet (↑↓) and a triplet (↑↑); by contrast, when two radicals are far apart in a molecule, the spin interaction is small, and they are judged to be two doublet species (2 × ↑), they are called biradicals.

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