CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.201300038

# Kinetic Stabilization and Reactivity of π Single-Bonded Species: Effect of the Alkoxy Group on the Lifetime of Singlet 2,2-Dialkoxy-1,3-diphenyloctahydropentalene-1,3-diyls

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*This paper is dedicated to Professor Waldemar Adam on the occasion of his 75th birthday and Professor Herbert Mayr on the occasion of his 65th birthday*

**Abstract:** Kinetic stabilization and reactivity of π single-bonded species have been investigated in detail by generating a series of singlet 2,2-dialkoxy-1,3-diphenyloctahydropentalene-1,3-diyls (**DR**s). The lifetime at 293 K in benzene was found to increase when the carbon chain length of the alkoxy groups was increased; 292 ns (**DRb**; $OR=OR'=OCH_3$) <880 ns (**DRc**; $OR=OR'=OC_2H_5$) <1899 ns (**DRd**; $OR=OR'=OC_3H_7$) ≈2292 ns (**DRe**; $OR=OR'=OC_6H_{13}$) ≈2146 ns (**DRf**; $OR=OR'=OC_{10}H_{21}$). **DRh** ($OR=OC_3H_7$, $OR'=OCH_3$; 935 ns) with the mixed-acetal moiety is a longer-lived species than another diastereomer **DRg** ($OR=OCH_3$, $OR'=OC_3H_7$; 516 ns). Activation parameters determined for the first-order decay process reveal that the enthalpy factor plays a crucial role in determining the energy barrier of the ring-closing reaction, that is, from the π-bonding to the σ-bonding compounds. Computational studies using density functional theory provided more insight into the structures of the singlet species with π single-bonded character and the transition states for the ring-closing reaction, thereby clarifying the role of the alkoxy group on the lifetime and the stereoselectivity of the ring-closing reaction.

**Keywords:** density functional calculations · diradicals · kinetics · pi single bonds · substituent effects

## Introduction

The three-dimensional molecular structure and electronic structure play important roles in molecular functions. The structures are determined by chemical bonds, which are one of the most important concepts in chemistry. There are two types of carbon–carbon covalent bonds, that is, σ bonds and π bonds (Figure 1); π bonds are weaker than σ bonds, $\Delta E\sigma > \Delta E\sigma\pi$. Thus, the π-bonding system is believed to exist only together with a strong σ bond. The typical example is a π bond in ethylene. Is it possible to make a π single bond without a σ bond? The π single-bonded compounds possess planar four-coordinate carbon atoms[1] (Figure 1).

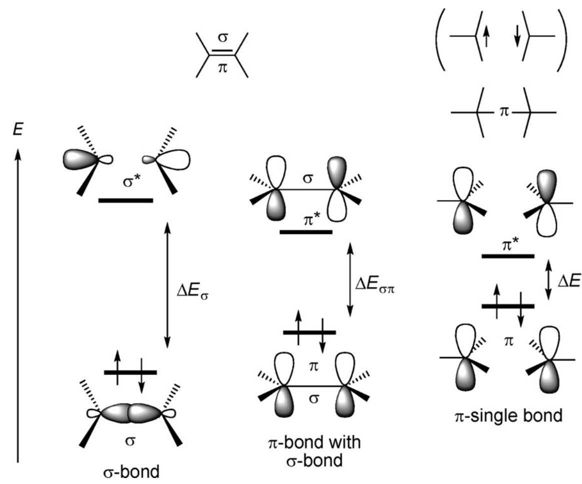

Figure 1. Chemical bonds: σ bonds and π bonds in ethylene, and π single bond.

The generation and the molecular functions derived from such an unusual bonding system are worth investigating. The HOMO–LUMO energy gap ($\Delta E\pi$) should be smaller than the normal π-bonding system ($\Delta E\sigma\pi$) in multiple bonds.

To make such a π single-bonding system, the singlet ground state of localized diradicals is indispensable. Over the last few decades, a significant development of the local-

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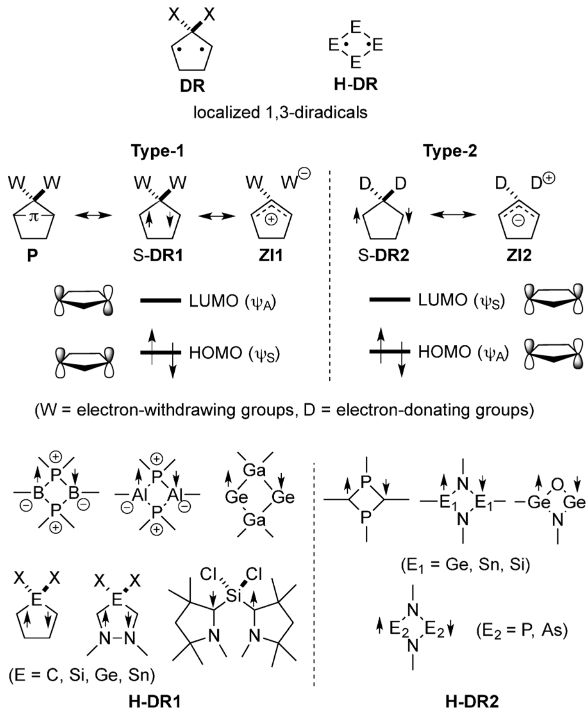
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201300038.

ized singlet diradical chemistry has been achieved after the pioneering studies by Borden et al.,[2] Niecke et al.,[3] Bertrand et al.,[4] and this laboratory[1g–j] on the ground-state spin multiplicity of propane-1,3-diyls such as cyclopentane-1,3-diyls **DR** and heterocyclic butane-1,3-diyls **H-DR** (Scheme 1).[5]



Scheme 1. Localized singlet 1,3-diradicals of Type-1 and Type-2.

The localized singlet 1,3-diradicals can be categorized as Type-1 and Type-2 on the basis of the most stable electronic configuration of the singlet state.[1j,6] Diradicals **DR1** with a substituted electron-withdrawing group (W = F, OR, and so forth) at C(2) are typically classified as Type-1 diradicals, whereas diradicals **DR2** with a substituted electron-donating group (D = H, $SiR_3$, and so on) belong to Type-2. In the Type-1 molecules, two electrons preferentially occupy the symmetric molecular orbital (MO) $\psi_S$. Thus, the singlet states S-**DR1** possess a π single-bonding character between the two radical sites and the zwitterionic character. The characters can be represented in the resonance structures **P** and **ZI1**.[1g–j,7] In the Type-2 molecules, however, the antisymmetric MO $\psi_A$ is selectively occupied by the two electrons. The Type-2 molecules S-**DR2** possess the zwitterionic character of **ZI2**. The reactivity of singlet diradicals is largely dependent on the most stable electronic configuration, Type-1 versus Type-2.[2,8] For example, a disrotatory ring closure is an energetically favored process for Type-1 molecules to give σ-bonded compounds. In contrast, the conrotatory ring closure is required for Type-2 singlet state.

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## Abstract in Japanese:

要旨：本研究では，π単結合化合物である一重項 2,2–ジアルコキシ–1,3–ジフェニルオクタヒドロペンタレン–1,3–ジイル **DR** を発生し，その速度論的安定化と反応性に関する研究を実施した．その結果，293K のベンゼン中において，2 位のアルコキシ基のアルキル鎖長が長くなるに連れてπ単結合化合物 **DR** の寿命が謙著に増加する事が明らかになった．つまり，292 ns (**DRb**; OR = OR’ = $OCH_3$) < 880 ns (**DRc**; OR = OR’ = $OC_2H_5$) < 1899 ns (**DRd**; OR = OR’ = $OC_3H_7$) ~ 2292 ns (**DRe**; OR = OR’ = $OC_6H_{13}$) ~ 2146 ns (**DRf**; OR = OR’ = $OC_{10}H_{21}$)の結果が得られた．混合アセタールが置換したジラジカル **DRg,h** の寿命と量子化学計算の結果から，π単結合化合物が失活する過程は，トランス環化体へではなくシス環化体への閉環反応である事が明らかになった．

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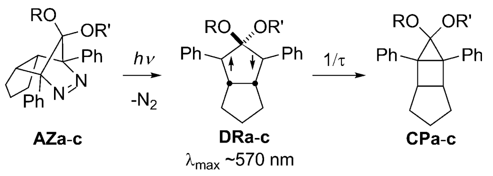
1,3-Diradicals **H-DR** in heterocycles are also classified as Type-1 and Type-2. Diradicals **H-DR1**[4,9] are Type-1 molecules because the low-lying σ* orbital (pseudo-π orbital) exists between the two p orbitals. Thus, 2-silapropane-1,3-diyls and 1,2-diaazacyclopentane-3,5-dilys belong to Type-1 molecules. Very recently, Fischer and Frenking et al. reported a π single bond in a $Ge_2Ga_2$ four-membered molecule.[10] Diradicals **H-DR2**[3,6a,11,12] belong to Type-2 molecules because the n orbital of the lone-pair electrons of N, O, and P interact with $\psi_S$.

This laboratory has reported so far the generation and detection of 2,2-dialkoxyoctahydropentalene-1,3-diyls **DRa–c**,[1g–j,13] which are categorized as Type-1 molecules, in the photochemical denitrogenation of the corresponding azoalkanes **AZa–c** (Scheme 2). Ring-closing compounds **CPa–c** were quantitatively formed in the denitrogenation reactions. The singlet species with $\lambda_{max} \approx 570$ nm were persistent at liquid-nitrogen temperature ($\approx 77$ K) and detected on the nanosecond (ns) timescale at room temperature. The strong absorption band in the visible region is due to the HOMO($\psi_S$)–LUMO($\psi_A$) electronic excitation of the π single-bonding system between the two radical sites. The lifetime at 293 K ($\tau_{293}$) was found to be largely dependent upon the alkoxy group (OR/OR′) as shown in Scheme 2. Thus, the diethoxy-substituted compound **DRc** (OR/OR′ = $OC_2H_5/OC_2H_5$, $\tau_{293} = 880$ ns in benzene and 1010 ns in acetonitrile)[1h] was a longer-lived species than both the dimethoxy-substituted compound **DRb** (OR/OR′ = $OCH_3/OCH_3$, 302 ns in benzene)[1i] and the ethylene–ketal-substituted compound **DRa** (OR/OR′ = $-O(CH_2)_2O-$, approximately 2 ns in acetonitrile).[13]

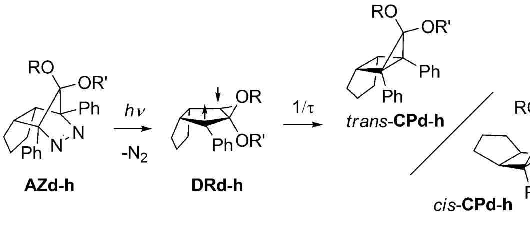


| | **a** | **b** | **c** |
|---|---|---|---|
| OR,OR' | $O(CH_2)_2O$ | $OCH_3$,$OCH_3$ | $OC_2H_5$,$OC_2H_5$ |
| $\tau_{293}$ | -[a]<br>(2 ns)[b] | 302 ns[a]<br>(-)[b] | 880 ns[a]<br>(1010 ns)[b] |

[a] in $C_6H_6$, [b] in $CH_3CN$

Scheme 2. Alkoxy-group effect on the lifetime of **DR**s.

In the present study, azoalkanes **AZd–f** with a series of alkyl chains (R/R′) of $C_3H_7$, $C_6H_{13}$, and $C_{10}H_{21}$ were synthesized to clarify the effect of the alkoxy group (OR = OR′) on the lifetime of the Type-1 molecules with $\pi$ single bonds (Scheme 3). Furthermore, compounds **DRg**,**h** with mixed-acetal moieties (OR ≠ OR′) were designed and generated from **AZg**,**h** to gain more insight into the role of the alkoxy group on the reactivity of S-**DR**. Quantum chemical calculations clarified the structure of the singlet diradical with $\pi$ single-bonded character, the role of the alkoxy group on the lifetime, and the stereoselectivity of the conrotatory ring-closing reaction. The combined experimental and computational study made a significant contribution to research on the kinetic stabilization of $\pi$ single-bonded molecules and understanding their reactivity.

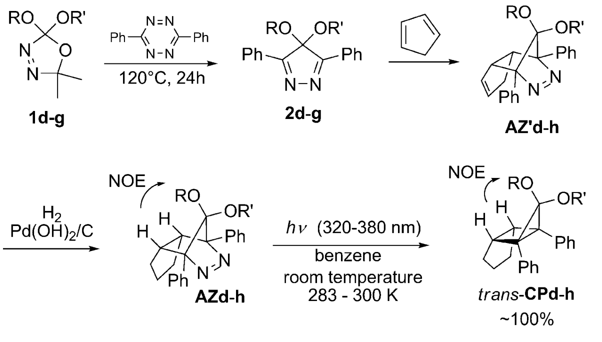


| | d | e | f | g | h |
|---|---|---|---|---|---|
| OR | $OC_3H_7$ | $OC_6H_{13}$ | $OC_{10}H_{21}$ | $OCH_3$ | $OC_3H_7$ |
| OR' | $OC_3H_7$ | $OC_6H_{13}$ | $OC_{10}H_{21}$ | $OC_3H_7$ | $OCH_3$ |

Scheme 3. Present study: generation and reactivity of **DRd–h** in the denitrogenation of **AZd–h**.

## Results and Discussion

**Synthesis of azoalkanes AZd–h and their denitrogenation reaction**: The synthesis of azoalkanes **AZd–h** is shown in Scheme 4. Oxadiazole derivatives **1d–g** were prepared according to the method reported by Warkentin and co-workers.[14] 4,4-Dialkoxypyrazoles **2d–g** were obtained by the [4+1] cycloaddition reaction of the thermally generated dialkoxycarbene with diphenyltetrazine and the following [4+2] cycloreversion, that is, the denitrogenation reaction. The cycloaddition reaction of **2d–g** with cyclopentadienes followed by the hydrogenation reaction of the resulting cycloadducts **AZ′d–h** gave azoalkanes **AZd–h**.[15]



Scheme 4. Synthesis of azoalkanes **AZd–h** and their photodenitrogenation reaction.

The maximum absorption of the azo chromophore (n,$\pi^*$) was found at the typical position of approximately 360 nm with low molar absorption coefficients ($\varepsilon \approx 100\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$). The structural determination of **AZd–h** was performed on the basis of the spectroscopic analyses, in particular by NMR spectroscopic measurements. The nuclear Overhauser effect (NOE) in conjunction with $^1H$ NMR spectroscopic experiments was used to determine the stereochemical configuration of the azoalkanes. The configurational assignment for **AZ′g** (OR/OR′ = $OCH_3/OC_3H_7$) was unequivocally confirmed by X-ray crystallographic analysis (see Figure S1 in the Supporting Information). The stereochemical determination was consistent with the structure determined by the NOE measurements.

Product analysis was performed in the photochemical denitrogenation of azoalkanes **AZd–h** (0.2 M in [$D_6$]benzene) by using a Xe lamp through a band-path filter ($h\nu$ = 320–380 nm) for 12 h at room temperature (≈295 K). The photolysates were directly analyzed by $^1H$ and $^{13}C$ NMR spectroscopic measurements. As shown in Scheme 4, *trans*-configured ring-closed compounds **CPd–h** were quantitatively obtained. The results clearly indicate that intermediates **DRd–h** are generated in the photochemical reaction. The formation of *trans*-configured ring-closing compounds was determined by the NOE measurements, for example, 2.2% NOE for *trans*-**CPe**.

**Steady-state absorption spectroscopy at 80 K**: Photochemical irradiation of the corresponding azoalkanes **AZd–h** was examined to directly observe the singlet-state molecules **DRd–h** in a 2-methyltetrahydrofuran (MTHF) glass matrix at 80 K using an Xe lamp through a band-path filter (320–380 nm; Figure 2 and Table 1). For comparison, 2,2-dimethoxycyclopentane-1,3-diyl **DRb** (OR/OR′ = $OCH_3$)[13b] was also generated under the same irradiation conditions. As shown in Figure 2, strong absorption spectra at $\lambda_{max} \approx 570$ nm were detected under the photochemical irradiation conditions. The species were persistent at 80 K at least for one night. The persistent species were electron-spin-resonance (ESR) silent under the similar photoirradiation conditions at 79 K in an ESR cavity resonator. The strong absorption signals in the visible region are characteristic of the singlet 2,2-dialkoxy-1,3-diphenylcyclopentane-1,3-diyls.[1h,i] The absorption band was assigned to the HOMO($\psi_S$)–LUMO($\psi_A$) electronic excitation of the $\pi$ single-bonding system (Figures 1 and 2, and Scheme 1). The assignment was confirmed by time-dependent (TD) DFT calculations.[10] As shown in Figure 2 and Table 1, the absorption maxima were not significantly dependent on the alkoxy group. Thus, the HOMO–LUMO energy spacing in **DRb**,**d–h** was not dependent upon the chain length. The energy gap affects the

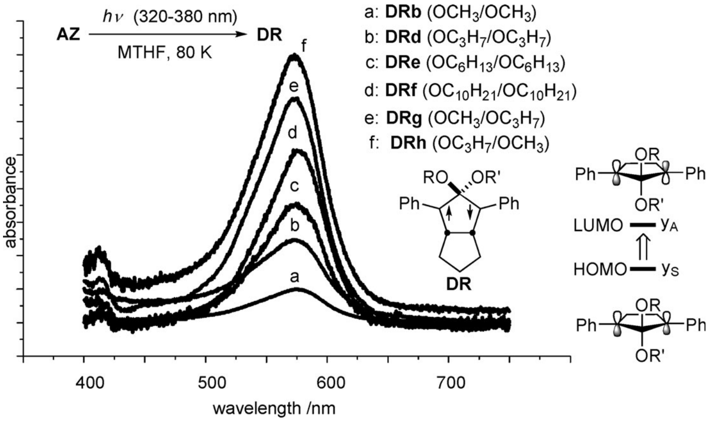


Figure 2. Electronic absorption spectra of singlet diradicals S-**DRb**,**d-h** in MTHF glass at 80 K. To see the respective spectra for **DRb**,**d–h** clearly, the original intensity of the signals were modified, that is: **DRb** × 1.0, **DRd** × 1.8, **DRe** × 2.5, **DRf** × 4.5, **DRg** × 6.5, and **DRh** × 8.2.

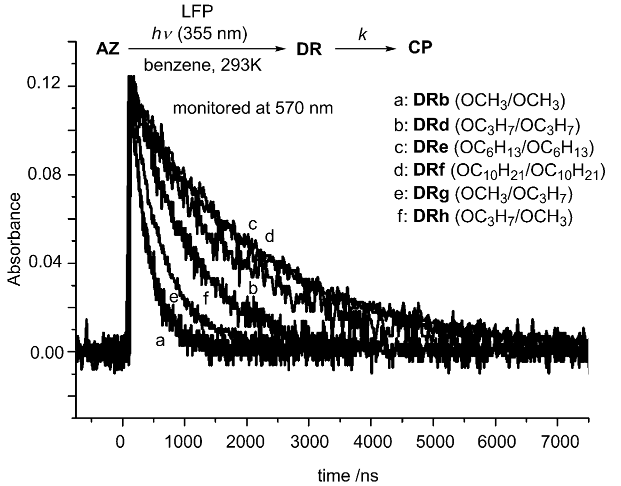


Figure 3. Transient decay trace of the singlet diradicals **DRb**,**d–h** ($\lambda_{obs}$ = 570 nm), generated by photolysis of **AZb**,**d–h** ($\lambda_{exc}$ = 355 nm) in benzene at 293 K.

Table 1. Maximum absorption ($\lambda_{max}$) and lifetime ($\tau_{293}$) of singlet diradicals **DRb**,**d–h**; and activation parameters ($E_a$, log$A$, $\Delta H^{\&\#8225;}$; $\Delta S^{\&\#8225;}$) for the first-order decay process of the singlet diradicals.

| Entry | S-**DR** (OR/OR′) | $\lambda_{max}$ [nm][a] | $\tau_{293}$ [ns][b] | $E_a$ [kJ mol$^{-1}$][c] | log($A$ [s$^{-1}$])[c] | $\Delta H^{\ddagger}$ [kJ mol$^{-1}$][d] | $\Delta S^{\ddagger}$ [J mol$^{-1}$ K$^{-1}$][d] |
|---|---|---|---|---|---|---|---|
| 1 | S-**DRb** ($OCH_3/OCH_3$) | 574 | 292 | 33.4 | 12.5 | 30.7 | −15.0 |
| 2 | S-**DRd** ($OC_3H_7/OC_3H_7$) | 571 | 1899 | 39.3 | 12.7 | 36.7 | −10.0 |
| 3 | S-**DRe** ($OC_6H_{13}/OC_6H_{13}$) | 572 | 2292 | 38.8 | 12.6 | 36.5 | −14.6 |
| 4 | S-**DRf** ($OC_{10}H_{21}/OC_{10}H_{21}$) | 572 | 2146 | 38.2 | 12.5 | 36.1 | −13.1 |
| 5 | S-**DRg** ($OCH_3/OC_3H_7$) | 568 | 516 | 36.4 | 12.8 | 33.8 | −9.0 |
| 6 | S-**DRh** ($OC_3H_7/OCH_3$) | 568 | 935 | 37.8 | 12.8 | 35.2 | −9.2 |

[a] The maximum absorption was determined by the absorption spectra of **DRb**,**d–h** measured in MTHF glass at 80 K (Figure 2). [b] In benzene at 293 K; errors of approximately 5 % are standard deviations of the mean (five data points). [c] Determined from Arrhenius plots of the lifetimes of the singlet diradical at ten temperatures between 20 and 60 °C. Error in the data is less than approximately 0.4 kJ mol$^{-1}$ for $E_a$ and approximately 0.1 for log$A$. [d] Determined from Eyring plots of the lifetimes of the singlet diradical at five temperatures between 20 and 60 °C. Error in the data is less than approximately 0.4 kJ mol$^{-1}$ for $\Delta H^{\ddagger}$ and approximately 1.1 for $\Delta S^{\ddagger}$ (Figure S2 in Supporting Information).

thermodynamic stability of the π single-bonded species, for example, the π-bonding strength of C(1)−C(3).[1i,j]

**Time-resolved absorption spectroscopy**: The transient absorption spectra and decay traces in the photolysis of azoalkanes **AZd–f** were measured in degassed benzene by means of laser-flash photolysis ($\lambda_{exc}$ = 355 nm, 5 ns pulse). The measurements were expected to provide valuable information about the alkoxy-group effect on the reactivity of the π single-bonded species (Table 1). The spectroscopic data were compared with those observed for **AZb** (OR/OR′ = $OCH_3/OCH_3$). As found under the low-temperature matrix conditions, the strong transient absorption bands were observed at around 570 nm, which decayed with clean first-order kinetics (Figure 3) and displayed linear Eyring temperature dependencies (see Figure S2 in the Supporting Information). The first-order process corresponds to the ring-closing reaction that produces the ring-closed compounds **CP**, because the quantitative formation of **CP** was found with high quantum yields (≈0.90). The quantum yields for the denitrogenation of **AZd–f** were determined by comparison with that reported for a similar azoalkane.[16] All of the transient species derived from **AZb**,**d–f** were not quenched by molecular oxygen. The results clearly support the theory that the transient species at approximately 570 nm are the singlet species **DRb**,**d–f** because the triplet diradicals, $\lambda_{max} \approx 330$ nm, were known to be quenched by molecular oxygen with diffusion-controlled rate constants.[17]

The lifetime was found to be largely dependent upon the alkoxy groups (OR/OR′) of the acetal moiety, although the absorption maximum was not dependent upon the alkoxy group. Thus, the propoxy-substituted compound **DRd** (OR/OR′ = $OC_3H_7/OC_3H_7$, 1899 ns at 293 K in benzene; Table 1, entry 2) was a longer-lived species by one order of magnitude than the methoxy-substituted compound **DRb** (OR/OR′ = $OCH_3/OCH_3$, 292 ns; Table 1, entry 1). The lifetime of **DRe** (OR/OR′ = $OC_6H_{13}/OC_6H_{13}$, 2292 ns; Table 1, entry 3) was found to be only a little bit longer than that of **DRd**. The lifetime of **DRf** (OR/OR′ = $OC_{10}H_{21}/OC_{10}H_{21}$, 2146 ns; Table 1, entry 4) was nearly the same as that of **DRe**. The activation parameters ($E_a$, log$A$, $\Delta H^{\ddagger}$, and $\Delta S^{\ddagger}$) were determined for the ring-closing reaction by measuring the temperature-dependent change of the decay rate constant ($k$) of the singlet diradicals (Table 1 and Figure S2 in the Supporting Information).

The large preexponential Arrhenius factor (log$A$ ≈ 12–13) for all compounds **DRb**,**d–h** clearly indicates that the first-order decay process is spin-allowed, which is consistent with the intramolecular cyclization from **DRd–h** to **CPd–h**.[2b,18] The negative activation entropy of $\Delta S^{\ddagger} \approx 10\,\mathrm{J\,mol^{-1}\,K^{-1}}$ is reasonable for the intramolecular ring-closing reaction. The values were not significantly different among **DRb**,**d–h** (Table 1, entries 1–5). Thus, the alkoxy-group-dependent change of the Gibbs energy barrier in the ring-closing reaction was mainly controlled by the enthalpy factor ($\Delta H^{\ddagger}$). The nonbonded repulsive interaction, that is, steric hindrance of the alkoxy group, plays an important role in determining the energy barrier of the ring-closing reaction.

The chain-length effect over C3 of the alkoxy group on the lifetime of the singlet diradicals was found to be quite small: **DRd** ($OC_3H_7$, 1899 ns) ≈ **DRe** ($OC_6H_{13}$, 2292 ns) ≈ **DRf** ($OC_{10}H_{21}$, 2146 ns). The small effect of the alkoxy group over the C3 chain length suggests that the alkyl-chain moiety over C3 locates far from the nonbonded interaction site during the ring-closing reaction. The details will be discussed in the computational studies on the structures of the singlet species and the transition states for the disrotatory ring-closing reaction.

**Computational studies on S-DRb**: To obtain insight into the effect of the alkoxy group on the lifetime of the singlet species, structural analysis was first carried out for the dimethoxy-substituted singlet species S-**DRb** at the UB3LYP/6-31G(d) level[19] with the broken-symmetry (BS)[20] method (Figure 4). The DFT level of theory is known to reproduce the activation parameters determined by the experiment in a ring-opening reaction of 1,4-diphenylbicyclo[2.1.0]pentane to the singlet 1,3-diphenylcyclopentane-1,3-diyl.[21] The geometries of stationary points and transition states were all located, and vibrational analyses were performed with the Gaussian 09[22] suite of programs.

Surprisingly, the most stable conformer was calculated to be not the gauche–gauche conformer S-**DRb**-gg of the acetal moiety, but the in–in conformer of the acetal moiety S-**DRb**-ii (Figure 4). Thus, the in–in conformer S-**DRb**-ii ($S^2 = 0.923$) was calculated to be energetically more stable than the in–gauche isomer S-**DRb**-ig ($S^2 = 0.929$), the gauche–in isomer S-**DRb**-gi ($S^2 = 0.938$), and the gauche–gauche conformer S-**DRb**-gg by 4.6, 12.5, and 27.2 kJ mol$^{-1}$, respectively. The singlet states were computed to be lower in energy than those triplet states by $\Delta E_{ST} = E_S - E_T = -16.4$, $-15.6$, $-15.2$, and $-14.9$ kJ mol$^{-1}$, respectively.

The gauche–gauche conformer was expected to be the most stable structure among the possible conformers because of the stereoelectronic stabilization in the acetal moiety. The conformational preference of the in–in isomer S-**DRb**-ii can be explained by the spiroconjugative stabilization interaction of the lone pair of electrons $n_O$ with $\psi_A$[13,23] and the energetic destabilization of the gauche–gauche isomer due to the repulsive interaction between the methoxy and phenyl group (Figure 4).

The π single-bonding character of S-**DRb**-ii was assessed by calculating the occupation number of electrons in the bonding orbital $\psi_S$ and the antibonding orbital $\psi_A$ at the CASSCF(2/2)/6-31G(d) level of theory (Figure 5). The occupation numbers in the $\psi_S$ and $\psi_A$ orbitals were found to be 1.37 and 0.63, respectively As shown in the molecular orbitals, S-**DRb**-ii thus possesses a significant π single-bonding character.

The transition states for the ring-closing reaction of S-**DRb** were calculated at the same level of theory, that is, BS-(U)B3LYP/6-31G(d) (Figure 5, entry 1 in Table 2). Surprisingly, the transition state *cis*-**TSb** ($\Delta H_{rel} = 43.9$ kJ mol$^{-1}$, $\nu^{\ddagger} = 28.8i$ cm$^{-1}$, $S^2 = 0.00$) that produces the *cis*-configured ring-closed compound *cis*-**CPb** was found to be energetically more stable than the transition state *trans*-**TSb** ($\Delta H_{rel} =$ 65.4 kJ mol$^{-1}$, $\nu^{\ddagger} = 228.8i$ cm$^{-1}$, $S^2 = 0.176$) that produced the *trans*-configured isomer *trans*-**CPb** by $\Delta\Delta H_{rel}$ ($\Delta\Delta E_{zpe}$) = 21.5 (20.2) kJ mol$^{-1}$. The imaginary frequency ($\nu^{\ddagger}$) of the transition state *cis*-**TSb** was found to be very low. The intrinsic reaction coordinate (IRC) calculations confirmed that *cis*-**TSb** and *trans*-**TSb** connected S-**DRb** with the ring-closing compounds *cis*-**CPb** and *trans*-**CPb**, respectively.

The energetic preference for the formation of the *cis* isomer is reasonably explained (Figure 6). The phenyl ring in *trans*-**TSb** has to go downward to the cyclopentane ring during the formation of the *trans* isomer. On the other hand, the phenyl ring goes upward in *cis*-**TSb** during the formation of the *cis* isomer. Thus, the repulsive interaction of "*a*" in *trans*-

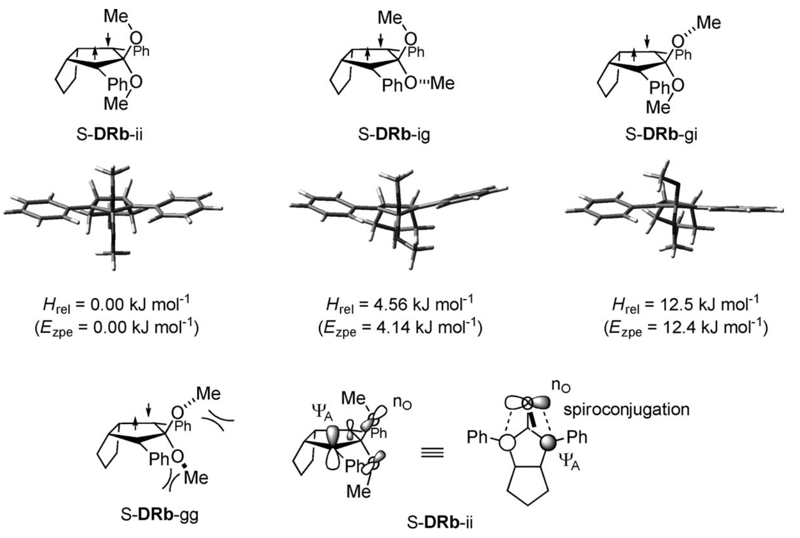


Figure 4. Three equilibrated structures of the singlet diradicals S-**DRb** optimized at the BS-UB3LYP/6-31G(d) level of theory. The value $\Delta H_{rel}$ is the relative thermal enthalpy calculated at 298 K and 1 atm; $\Delta E_{zpe}$ is the electronic energy after zero-point energy corrections.

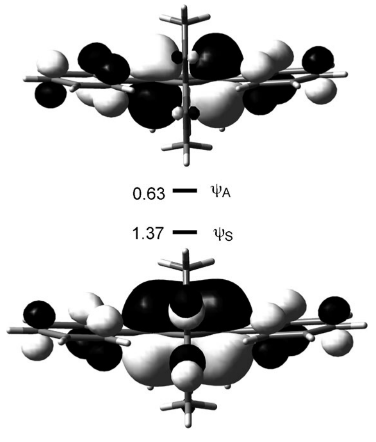


Figure 5. The calculated HOMO ($\psi_S$) and LUMO ($\psi_A$) orbitals of S-**DRb**-ii and the occupation numbers of two electrons in their orbitals at the CASSCF(2/2)/6-31G(d) level of theory.

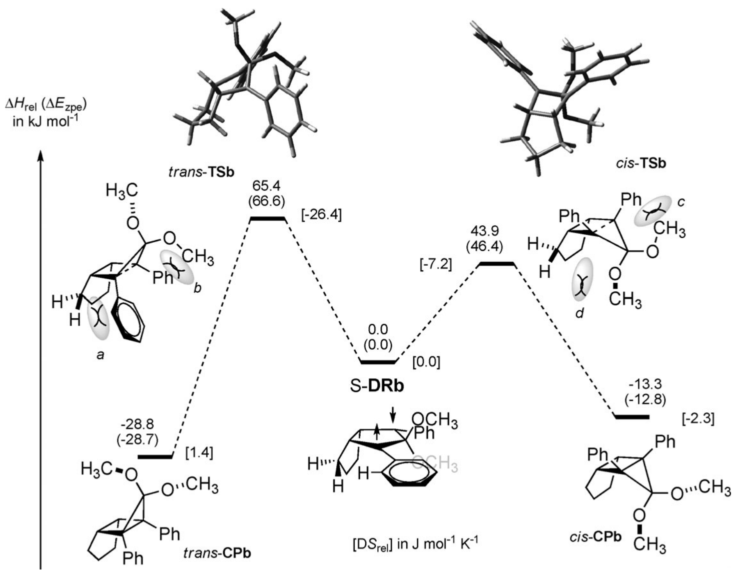


Figure 6. Reaction profiles of S-**DRb** at the BS-UB3LYP/6-31G(d) level of theory. The value $\Delta H_{rel}$ is the relative thermal enthalpy calculated at 298 K and 1 atm; $\Delta E_{zpe}$ is the electronic energy after zero-point energy corrections.

**TSb** increases the energy of the transition state *trans*-**TSb** that produces the *trans* isomer *trans*-**CPb** (see Figure 6 for depictions of "*a*" to "*d*") because the energetic destabilization of the interaction "*b*" in *trans*-**TSb** and "*c*" in *cis*-**TSb** should be similar each other. The repulsive interaction of "*d*" in *cis*-**TSb** also influences the energy of the transition state *cis*-**TSb**, but the effect was found to be smaller than the interaction "*a*." *trans*-**CPb** was calculated to be energetically more stable than *cis*-**CPb** by $\Delta\Delta H_{rel}$ ($\Delta\Delta E_{zpe}$) = 15.5 (15.9) kJ mol$^{-1}$. Thus, *cis*-**CPb** is the kinetically controlled product in the ring-closing reaction of S-**DRb**.

In our experimental studies of the denitrogenation reaction of **AZb**,**d–f** at room temperature, the *trans* isomers of the ring-closing compounds **CP** were quantitatively isolated. At first glance, the computational results, which predict the selective formation of the *cis* isomer, contradict the experimental observation of the exclusive formation of the *trans*-configured **CP**. The transition state *trans*-**TSb** energetically locates above the ring-closing compound *cis*-**CPb** by just $\Delta\Delta H_{rel}$ ($\Delta\Delta E_{zpe}$) = 78.7 (79.4) kJ mol$^{-1}$, which is equal to 18.8 (19.0) kcal mol$^{-1}$ (Figure 6). Thus, the *cis*-configured ring-closing compound *cis*-**CPb** is equilibrated with the *trans* isomer *trans*-**CPb** at room temperature, which is energetically more stable than cis-**CPb** by approximately 15 kJ mol$^{-1}$.

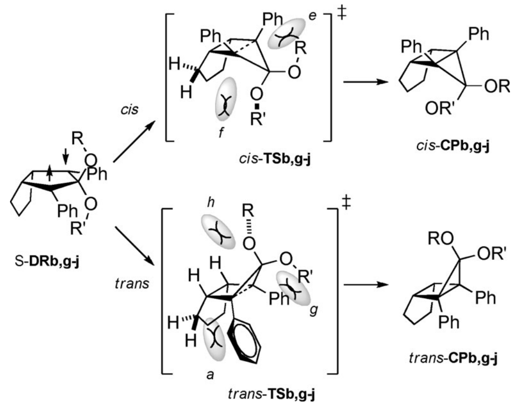
The DFT calculations in the gas phase overestimated the experimentally determined transition-state energy of *cis*-**TSb** by approximately 13 kJ mol$^{-1}$ (entry 1 in Table 1). The transition-state energy of *trans*-**TSb** is also supposed to be overestimated in a similar way. Thus, the isomerization reaction from the *cis* isomer to the *trans* isomer would be faster than that predicted by the computations.

**Computational studies on S-DRg–j**: To clarify in more detail the effect of the alkoxy group on the transition-state energy of the ring-closing reactions, computations on the singlet species S-**DRg–j** with the mixed-acetal moiety were calculated at the same level of theory (Scheme 5, entries 2–5 in Table 2). The transition-state energy of *cis*-**TSi** (OR/OR′ = $OCH_3$/OH) from S-**DRi**, $\Delta H_{rel}$ ($\Delta E_{zpe}$) = 42.0 (45.0) kJ mol$^{-1}$ with $\nu^{\ddagger} = 33.2i$ cm$^{-1}$ (Table 2, entry 2), was calculated to be a little bit smaller than that of *cis*-**TSb** (OR/OR′ = $OCH_3$/$OCH_3$, $\Delta H_{rel}$ ($\Delta E_{zpe}$) = 43.9 (46.4) kJ mol$^{-1}$, Figure 5, entry 1 in Table 2). The results clearly indicate that the energetic destabilization caused by the interaction "*f*" (Scheme 5) is small but not negligible in the transition states for the formation of the *cis* isomers. Indeed, the transition-state energy of *cis*-**TSg** (OR/OR′ = $OCH_3$/$OC_3H_7$) from S-**DRg**, $\Delta H_{rel}$ ($\Delta E_{zpe}$) = 44.7 (47.3) kJ mol$^{-1}$ with $\nu^{\ddagger}$ =

Table 2. Computational results of the ring-closing reaction of S-**DRb**,**g–j** at the BS-UB3LYP/6-31G(d) level of theory.

| Entry | S-**DR** (OR/OR′) | $\Delta H_{rel}$ ($\Delta E_{zpe}$) [kJ mol$^{-1}$][a] | | | |
|---|---|---|---|---|---|
| | | *cis*-**TS** | *trans*-**TS** | *cis*-**CP** | *trans*-**CP** |
| 1 | S-**DRb** ($OCH_3$/$OCH_3$) | 43.9 (46.4) | 65.4 (66.6) | −13.3 (−12.8) | −28.8 (−28.7) |
| 2 | S-**DRi** ($OCH_3$/OH) | 42.0 (45.0) | 35.5 (37.2) | −14.5 (−13.3) | −36.3 (−35.4) |
| 3 | S-**DRj** (OH/$OCH_3$) | 18.3 (20.2) | 62.8 (64.3) | −18.9 (−17.9) | −27.9 (−26.6) |
| 4 | S-**DRg** ($OCH_3$/$OC_3H_7$) | 44.7 (47.3) | 66.9 (68.6) | −13.0 (−12.4) | −40.0 (−41.0) |
| 5 | S-**DRh** ($OC_3H_7$/$OCH_3$) | 48.0 (46.9) | 65.5 (67.1) | −13.6 (−12.6) | −40.7 (−39.8) |

[a] At the BS-(U)B3LYP/6-31G(d) level of theory. The values of the calculated enthalpy ($\Delta H_{rel}$) are relative to those of the singlet diradicals S-**DRb**,**g–j**. The values of the zero-point-energy-corrected electronic energies ($\Delta E_{zpe}$) are relative to those of the singlet diradicals S-**DRb**,**g–j**.



Scheme 5. Computations on the reactivity of S-**DRb**,**g–i** at the BS-UB3LYP/6-31G(d) level of theory.

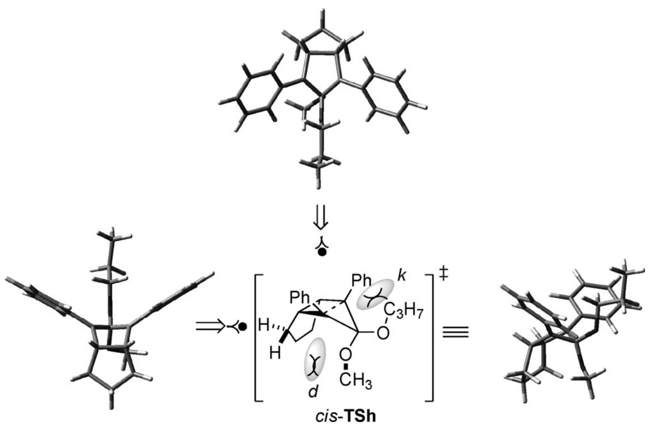


Figure 7. Optimized transition-state structure of *cis*-**TSh** at the BS-UB3LYP/6-31G(d) level of theory.

$29.2i\,cm^{-1}$ (Table 2, entry 4), was found to be larger than that of *cis*-**TSb** (Table 2, entry 1).

The transition-state energy of *cis*-**TSj** (OR/OR′ = OH/$OCH_3$), $\Delta H_{rel}$ ($\Delta E_{zpe}$) = 18.3 (20.2) kJ mol$^{-1}$ with $\nu^{‡} = 278.9i\,cm^{-1}$ (Table 2, entry 3), was found to be significantly smaller than that of *cis*-**TSi** (Table 2, entry 2). Thus, the effect of the repulsive interaction "*e*" between the phenyl ring and the alkoxy group was found to play a crucial role in determining the energy barrier in the formation of the *cis* isomers. Indeed, the transition-state energy of *cis*-**TSh** (OR/OR′ = $OC_3H_7$/$OCH_3$) from S-**DRh**, $\Delta H_{rel}$ ($\Delta E_{zpe}$) = 48.0 (46.9) kJ mol$^{-1}$ with $\nu^{‡} = 38.1i\,cm^{-1}$ (Table 2, entry 5) was calculated to be larger than those of *cis*-**TSb** (Table 2, entry 1).

The transition-state energy of *trans*-**TSj** (OR/OR′ = OH/$OCH_3$), $\Delta H_{rel}$ ($\Delta E_{zpe}$) = 62.8 (64.3) kJ mol$^{-1}$ with $\nu^{‡} = 245.3i\,cm^{-1}$ (Table 2, entry 3), was calculated to be a little bit smaller than that of *trans*-**TSb**, $\Delta H_{rel}$ ($\Delta E_{zpe}$) = 65.4 (66.6) kJ mol$^{-1}$ (Figure 6, entry 1 in Table 2). The results clearly indicate that the energetic destabilization caused by the interaction "*h*" (Scheme 5) is small in determining the transition-state energy for the formation of the *cis* isomers. Thus, interactions "*g*" and "*a*" determine the energy barrier for the formation of the *trans* isomer. Although the similar energy barriers for *trans*-**TSg** and *trans*-**TSh** were obtained at the same level of theory (Table 2, entries 4 and 5), the energy of *trans*-**TSg** was calculated to be a little bit larger than that of *trans*-**TSh** because the interaction of the propoxy group with the phenyl ring is larger than that between the methoxy group and the phenyl ring (Scheme 5).

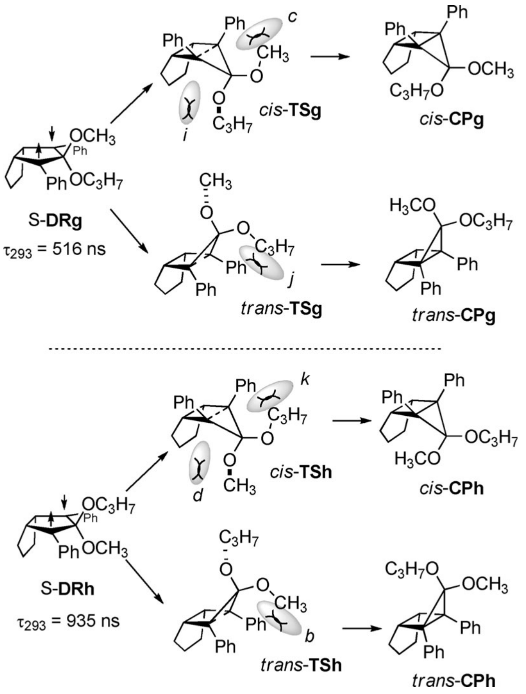
The energy of *trans*-**TSi**, $\Delta H_{rel}$ ($\Delta E_{zpe}$) = 35.5 (37.2) kJ mol$^{-1}$ with $\nu^{‡} = 155.5i\,cm^{-1}$ (Table 2, entry 2), was found to be significantly smaller than those of *trans*-**TSb**,**j** (Table 2, entries 1,3). Thus, the energetic destabilization derived from the interaction "*g*" of the phenyl ring with the alkoxy group was also found to be important in determining the transition-state energy for the formation of the *trans* isomers.

The optimized transition-state structure of *cis*-**TSh** (OR/OR′ = $OC_3H_7$/$OCH_3$) is shown in Figure 7. The methyl group of the propoxy group was found located at the end of the two phenyl rings. Thus, the interaction "*e*" is expected to be quite small, when the alkyl-chain length is greater than C3 (Scheme 5). Indeed, as mentioned above, the chain-length effect over C3 of the alkoxy group on the lifetime of singlet diradicals was found to be quite small: **DRd** ($OC_3H_7$, 1899 ns) ≈ **DRe** ($OC_6H_{13}$, 2292 ns) ≈ **DRf** ($OC_{10}H_{21}$, 2146 ns) (Table 1 and Figure 3).

DFT calculations clearly indicate that the kinetically favored result of the singlet diradicals is to produce the *cis* isomers, except in the case of the reactivity of the diradical S-**DRi** (OR/OR′ = $OCH_3$/OH).

**Low-temperature NMR spectroscopic measurements**: An attempt to detect the kinetically favored *cis* isomer *cis*-**CPb** was examined in the photodenitrogenation of **AZb** in [D$_8$]toluene in a NMR spectroscopy tube at 213 K using an Xe lamp. After 6 h irradiation at 213 K, the photolysate was transferred to the precooled NMR spectrometer, and the $^1$H NMR spectrum was measured at 213 K as quickly as possible. However, only the *trans* isomer *trans*-**CPb** was detected in the photolysate. The conversion of the azoalkane was 12 %. The experimental result suggests that the kinetically favored *cis*-**CPb** is converted into the thermodynamically favored *trans* isomer *trans*-**CPb** during the transfer of the sample to the NMR spectroscopic cavity, or that the lifetime of *cis*-**CPb** is less than 6 h under the NMR spectroscopic measurement conditions. In situ NMR spectroscopic measurements[24] under irradiation conditions that used a high-power light source (such as a laser) would be indispensable in detecting such a short-lived species.

**Photochemical generation of S-DRg and S-DRh and their reactivity**: The singlet diradicals S-**DRg** (OR/OR′ = $OCH_3$/$OC_3H_7$) and S-**DRh** (OR/OR′ = $OC_3H_7$/$OCH_3$) were experimentally generated from the corresponding azoalkanes and the lifetimes were compared with each other (Scheme 6). The experiments were expected to provide experimental evidence for the formation of the kinetically favored *cis* isomer (entries 5 and 6 in Table 1, entries 4 and 5 in



Scheme 6. Generation of S-**DRg**,**h** and their reactivity.

Table 2). When the ring-closing mode, that is, the result of the singlet diradicals, produces the *cis* isomer, the singlet diradical S-**DRh** is predicted to be a longer-lived species than S-**DRg** because the steric interaction "*k*" between the propoxy group ($OC_3H_7$) and the phenyl ring (Ph) in *cis*-**TSh** was calculated to be higher than interaction "*c*" between the methoxy ($OCH_3$) and Ph in *cis*-**TSg** (entries 4 and 5 in Table 2). Actually, the singlet diradical S-**DRh** (935 ns) was found to be a significantly longer-lived species than S-**DRg** (516 ns). If the ring-closing mode produces the *trans* isomers, the lifetime of S-**DRh** should be shorter than S-**DRg** because the interaction "*b*" in *trans*-**TSh** is smaller than the interaction "*j*" in *trans*-**TSg** (Scheme 6). All of the combined experimental and computational results revealed that the ring-closing mode, which determines the lifetime of the singlet diradicals, produces the *cis* isomers.

The lifetime of S-**DRg** ($OR/OR' = OCH_3/OC_3H_7$, 516 ns) was longer than that of S-**DRb** ($OR/OR' = OCH_3/OCH_3$, 292 ns). The results suggest that the effect of interaction "*i*" in *cis*-**TSg** is not negligible in determining the activation energy of the ring-closing mode of the reactions. The energetic destabilization caused by interaction "*i*" between the propoxy group and the cyclopentane ring should be larger than that derived from interaction "*d*" between the methoxy group and the cyclopentane ring in *cis*-**TSb** (Scheme 6, Figure 6). Actually, the transition-state energy of *cis*-**TSg** (Table 2, entry 4) was calculated to be a little bit larger than that in *cis*-**TSb** (Table 2, entry 1). Thus, the experimental results of the longer-lived species S-**DRg** (relative to S-**DRb**) can be reasonably explained by the increase in the repulsive interaction between the alkoxy group and the cyclopentane ring.

On the other hand, the lifetime of S-**DRh** ($OR/OR' = OC_3H_7/OCH_3$, 935 ns) was found to be shorter than S-**DRd** ($OR/OR' = OC_3H_7/OC_3H_7$, 1899 ns). The result is reasonably explained again by the repulsive interaction between the alkoxy group and the cyclopentane ring. Interaction "*d*" of the methoxy group with the cyclopentane ring should be smaller than interaction "*i*" of the propoxy group with the cyclopentane ring.

## Conclusion

A series of singlet 2,2-dialkoxy-1,3-diphenyloctahydropentalene-1,3-diyls was generated using the photochemical denitrogenation of the corresponding azoalkanes to clarify the effect of the alkoxy group of C(OR)(OR′) at the C(2) position on the lifetime of the singlet diradicals with π single-bonding character **DR**. The combined experimental and computational studies clarified the hitherto unknown role of the alkoxy group on the reactivity. The fate of singlet diradicals with π single-bonding character was not to produce the *trans*-configured ring-closed products, but to produce the *cis*-configured ring-closed compounds.[25] The kinetically controlled *cis*-configured products were not directly observed by NMR spectroscopic analyses owing to the short-lived character of the *cis* isomers. The steric interaction between the alkoxy group and the phenyl ring, which determines the energy barrier of the ring-closing reaction, was found to play a crucial role in determining the lifetime of the singlet-state molecules. The present studies provide a concrete strategy to obtain the long-lived π single-bonded molecules.

## Experimental Section

**General procedure for the synthesis of *endo*-2,3-diazo-10,10-dialkoxy-1,4-diphenyltricyclo[5.2.1.0$^{5,9}$]dec-2-ene (AZd–h)**: Trifluoroacetic acid (0.5 equiv) was added dropwise to a solution of cyclopentadiene (20 equiv) and 4,4-dialkoxy-3,5-diphenyl-pyrazole[1i,13] in $CH_2Cl_2$ (1 mL) at 0C° under nitrogen. After stirring for 10 min, the reaction was quenched with $NaHCO_3$ (aq) until the pH of the solution reached 8. After washing the solution with water and brine, and drying by $MgSO_4$, the organic phase was then filtered, concentrated, and purified by column chromatography. The [4+2] cycloadduct **AZ′d–h** was dissolved in ethyl acetate (2 mL), and palladium (5 mg) on a charcoal catalyst was added. The mixture was stirred under a hydrogen gas atmosphere for 24 h at room temperature, the palladium catalyst was removed by filtration over Celite, and the ethyl acetate was evaporated under reduced pressure. Cycloadducts **AZd**–**AZh** were purified by column chromatography and recycling column chromatography. The *endo* configuration was determined by NOE experiments.

***endo*-2,3-Diazo-10,10-dipropoxy-1,4-diphenyltricyclo[5.2.1.0$^{5,9}$]dec-2-ene (AZd)**: Yield: 222 mg (43 % from **2d**) as a viscous oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta = 7.96$–7.92 (m, 4H), 7.48–7.34 (m, 6H), 3.60–3.52 (m, 2H), 3.03 (t, $J = 6.70$ Hz, 2H), 2.75 (t, $J = 6.70$ Hz, 2H), 1.68–1.36 (m, 8H), 1.16 (m, 2H), 0.89 (t, $J = 7.39$ Hz, 3H), 0.61 ppm (t, $J = 7.39$ Hz, 3H); $^{13}$C NMR (68 MHz, $CDCl_3$): $\delta = 136.8$ (C), 128.3 (CH), 128.1 (CH), 127.6 (CH), 118.5 (C), 94.5 (C), 65.3 ($CH_2$), 65.0 ($CH_2$), 49.0 (CH), 27.8 ($CH_2$), 25.7 ($CH_2$), 23.0 ($CH_2$), 22.7 ($CH_2$), 10.8 ($CH_3$), 10.4 ppm ($CH_3$); IR (neat): $\tilde{\nu} = 2962$, 2940, 2876, 1602, 1496, 1446, 1175, 1075 cm$^{-1}$; UV (benzene): $\varepsilon_{365nm}$ = 99.7 L mol$^{-1}$ cm$^{-1}$; HRMS (EI): *m/z* calcd for $C_{26}H_{32}N_2O_2$: 404.2464; found: 404.2473.

***endo*-2,3-Diazo-10,10-dihexoxy-1,4-diphenyltricyclo[5.2.1.0$^{5,9}$]dec-2-ene (AZe)**: Yield: 151 mg (41 % from **2e**) as a viscous oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.86–7.82 (m, 4H), 7.38–7.25 (m, 6H), 3.48–3.43 (m, 2H), 2.95 (t, *J* = 6.40 Hz, 2H), 2.67 (t, *J* = 6.40 Hz, 2H), 1.58–0.76 (m, 22H), 0.80 (t, *J* = 7.23 Hz, 3H), 0.72 ppm (t, *J* = 7.31 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 136.7 (C), 128.2 (CH), 128.0 (H), 127.4 (CH), 118.5 (C), 94.4 (C), 63.7 ($CH_2$), 63.4 ($CH_2$), 48.9 (CH), 31.3 ($CH_2$), 31.2 ($CH_2$), 29.6 ($CH_2$), 29.2 ($CH_2$), 28.7 ($CH_2$), 28.7 ($CH_2$), 25.6 ($CH_2$), 25.5 ($CH_2$), 22.3 ($CH_2$), 22.2 ($CH_2$), 13.8 ($CH_3$), 13.7 ppm ($CH_3$); IR (neat): $\tilde{\nu}$ = 3058, 3028, 2931, 2860, 1742, 1603, 1496, 1447, 1174, 1090, 1027, 748, 699 cm$^{-1}$; UV (MTHF): $\varepsilon_{365nm}$ = 83 L mol$^{-1}$ cm$^{-1}$; ESI-MS: *m/z* calcd for $C_{32}H_{45}O_2N_2$: 489.3476 [$M$+H]$^+$; found: 489.3473.

***endo*-2,3-Diazo-10,10-didecyloxy-1,4-diphenyltricyclo[5.2.1.0$^{5,9}$]dec-2-ene (AZf)**: Yield: 181 mg (39 % from **2f**) as a viscous oil. $R_f$ = 0.63 (hexane/EtOAc = 7:3); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.94 (d, *J* = 7.60 Hz, 4H), 7.45–7.36 (m, 6H), 3.52–3.58 (m, 2H), 3.05 (t, *J* = 6.47 Hz, 2H), 2.77 (t, *J* = 6.47 Hz, 2H), 1.67–1.00 (m, 42H), 0.89 (t, *J* = 6.78 Hz, 3H), 0.88 ppm (t, *J* = 6.93 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 136.9 (C), 128.4 (CH), 128.1 (CH), 127.6 (CH), 118.7 (C), 94.6 (C), 63.9 ($CH_2$), 63.6 ($CH_2$), 49.1 (CH), 31.9 ($CH_2$), 29.9 ($CH_2$), 29.5 ($CH_2$), 29.5 ($CH_2$), 29.3 ($CH_2$), 29.3 ($CH_2$), 29.3 ($CH_2$), 29.2 ($CH_2$), 27.8 ($CH_2$), 26.2 ($CH_2$), 25.8 (CH), 22.7 ($CH_2$), 14.1 ppm ($CH_3$); IR (neat): $\tilde{\nu}$ = 2926, 2855, 1603, 1496, 1466, 1176, 747, 698 cm$^{-1}$; UV (benzene): $\varepsilon_{364nm}$ = 119.3 L mol$^{-1}$ cm$^{-1}$; elemental analysis (%) calcd for $C_{40}H_{60}N_2O_2$: C 79.95, H 10.06, N 4.66; found: C 79.93, H 10.23, N, 4.64.

***endo*-2,3-Diazo-10-methoxy-10-propoxy-1,4-diphenyltricyclo[5.2.1.0$^{5,9}$]dec-2-ene (AZg)**: Yield: 42 mg (23 % from **2g**) as a viscous oil. $R_f$ = 0.70 (hexane/EtOAc = 7:3); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.95–7.91 (m, 4H), 7.48–7.35 (m, 6H), 3.60–3.52 (m, 2H), 2.94 (s, 3H), 2.73 (t, *J* = 6.47 Hz, 2H), 1.70–1.35 (m, 6H), 1.19 (m, 2H), 0.63 ppm (t, *J* = 7.31 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 136.5 (C), 128.2 (CH), 128.0 (CH), 127.5 (CH), 118.7 (C), 94.3 (C), 65.1 ($CH_2$), 51.4 (CH), 48.6 ($CH_3$), 27.6 ($CH_2$), 25.6 ($CH_2$), 22.5 ($CH_2$), 10.2 ppm ($CH_3$); IR (neat): $\tilde{\nu}$ = 2975, 2928, 1601, 1498, 1445, 1382, 1258, 1112, 1044, 700 cm$^{-1}$; UV (benzene): $\varepsilon_{355nm}$ = 110 L mol$^{-1}$ cm$^{-1}$; ESI-MS: *m/z* calcd for $C_{24}H_{28}O_2N_2Na$: 399.2043 [$M$+Na]$^+$; found: 399.2047.

***endo*-2,3-Diazo-10-methoxy-10-propoxy-1,4-diphenyltricyclo[5.2.1.0$^{5,9}$]dec-2-ene (AZh)**: Yield: 51 mg (20 % from **2h**) as a viscous oil. $R_f$ = 0.70 (hexane/EtOAc = 7:3); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.97–7.91 (m, 4H), 7.49–7.35 (m, 6H), 3.65–3.54 (m, 2H), 3.02 (t, *J* = 6.36 Hz, 2H), 2.64 (s, 3H), 1.86–1.36 (m, 8H), 0.89 ppm (t, *J* = 7.39 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 136.5 (C), 128.2 (CH), 128.1 (CH), 127.5 (CH), 118.7 (C), 94.4 (C), 64.9 ($CH_2$), 51.8 (CH), 48.7 ($CH_3$), 27.6 ($CH_2$), 25.5 ($CH_2$), 22.5 ($CH_2$), 10.6 ppm ($CH_3$); IR (neat): $\tilde{\nu}$ = 2975, 2928, 1601, 1498, 1445, 1382, 1257, 1112, 1044, 700 cm$^{-1}$; UV (benzene): $\varepsilon_{355nm}$ = 100 L mol$^{-1}$ cm$^{-1}$; ESI-MS: *m/z* calcd for $C_{24}H_{28}O_2N_2Na$: 399.2043 [$M$+Na]$^+$; found: 399.2046.

**Photodenitrogenation of AZd–AZh**: A solution of *endo*-2,3-diazo-10,10-dialkoxy-1,4-diphenyltricyclo[5.2.1.0$^{5,9}$]dec-2-ene in $C_6D_6$ was added into an NMR spectroscopy tube. After bubbling $N_2$ through it for 5 min, the solution was exposed to light ($\lambda_{exc}$ = 355 nm) for 24 h at room temperature. The quantitative formation of the ring-closing products **CPd–h** was observed by the NMR spectroscopic analysis of the photolysate. The *trans* configuration was determined by NOE experiments.

**3,3-Dipropoxy-2,4-diphenyltricyclo[3.3.1.0$^{2,4}$]octane (*trans*-CPd)**: Yield: 15 mg (100 % from **AZd**) as a viscous oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.41–7.39 (m, 4H), 7.20–7.06 (m, 6H), 3.83 (t, *J* = 6.42 Hz, 2H), 3.15 (t, *J* = 6.53 Hz, 2H), 3.01 (d, *J* = 6.53 Hz, 2H), 1.95–1.89 (m, 3H), 1.73 (sext, *J* = 7.39 Hz, 2H), 1.56–1.36 (m, 3H), 1.14 (sext, *J* = 7.39 Hz, 2H), 1.03 (t, *J* = 7.33 Hz, 3H), 0.57 ppm (t, *J* = 7.39 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 136.4 (C), 131.2 (CH), 128.6 (CH), 127.0 (CH), 97.9 (C), 69.2 ($CH_2$), 66.9 ($CH_2$), 48.3 (C), 42.3 (CH), 29.1 ($CH_2$), 26.0 ($CH_2$), 24.2 ($CH_2$), 23.8 ($CH_2$), 11.9 ($CH_3$), 11.4 ppm ($CH_3$); IR (neat): $\tilde{\nu}$ = 3084, 3056, 3024, 2957, 2875, 1945, 1602, 1498, 1261 cm$^{-1}$; HRMS (EI): *m/z* calcd for $C_{26}H_{32}O_2$: 376.2402; found: 376.2394.

**3,3-Dihexoxy-2,4-diphenyltricyclo[3.3.1.0$^{2,4}$]octane (*trans*-CPe)**: Yield: 16 mg (100 % from **AZe**) as a viscous oil. $^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 7.45–7.41 (m, 4H), 7.24–7.06 (m, 6H), 3.95 (t, *J* = 6.47 Hz, 2H), 3.25 (t, *J* = 6.76 Hz, 2H), 3.07–3.03 (m, 2H), 2.00–0.70 ppm (m, 28H); $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 135.2 (C), 130.0 (CH), 127.4 (CH), 125.8 (CH), 96.9 (C), 66.5 ($CH_2$), 64.5 ($CH_2$), 47.2 (C), 41.2 (CH), 31.7 ($CH_2$), 31.2 ($CH_2$), 29.9 ($CH_2$), 29.3 ($CH_2$), 27.9 ($CH_2$), 26.1 ($CH_2$), 25.5 ($CH_2$), 24.8 ($CH_2$), 22.5 ($CH_2$), 22.3 ($CH_2$), 13.7 ($CH_3$), 13.6 ppm ($CH_3$); ESI-MS: *m/z* calcd for $C_{32}H_{44}O_2Na$ [$M$+Na]$^+$: 483.3234; found: 483.3232.

**3,3-Didecyloxy-2,4-diphenyltricyclo[3.3.1.0$^{2,4}$]octane (*trans*-CPf)**: Yield: 18 mg (100 % from **AZf**) as a viscous oil. $^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 7.44–7.43 (m, 2H), 7.22–7.07 (m, 8H), 3.98 (t, *J* = 6.4 Hz, 2H), 3.27 (t, *J* = 6.7 Hz, 2H), 3.02–3.08 (m, 2H), 1.93–1.81 (m, 4H), 1.58–1.03 (m, 34H), 0.91 (t, *J* = 6.4 Hz, 3H), 0.90 ppm (t, *J* = 6.7 Hz, 3H); $^{13}$C NMR (125 MHz, $C_6D_6$): $\delta$ = 136.4 (C), 131.2 (CH), 128.6 (CH), 127.0 (CH), 98.1 (C), 67.8 ($CH_2$), 65.8 ($CH_2$), 48.4 (C), 42.4 (CH), 33.0 ($CH_2$), 31.2 ($CH_2$), 30.8 ($CH_2$), 30.7 ($CH_2$), 30.6 ($CH_2$), 30.6 ($CH_2$), 30.5 ($CH_2$), 30.4 ($CH_2$), 30.3 ($CH_2$), 29.1 ($CH_2$), 27.7 ($CH_2$), 26.0 ($CH_2$), 23.8 ($CH_2$), 15.0 ppm ($CH_3$); EI-MS: *m/z* calcd for $C_{40}H_{60}O_2$ [$M$]$^+$: 572.4593; found: 572.4588.

**3-Methoxy-3-propoxy-2,4-diphenyltricyclo[3.3.1.0$^{2,4}$]octane (*trans*-CPg)**: Yield: 17 mg (100 % from **AZg**) as a viscous oil. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ = 7.32–7.18 (m, 10H), 3.67 (s, 3H), 2.94 (t, *J* = 6.77 Hz, 2H), 2.89–2.83 (m, 2H), 1.88–1.46 (m, 8H), 1.12 (sext, *J* = 7.05 Hz, 3H), 0.55 ppm (t, *J* = 7.39 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 134.8 (C), 129.9 (CH), 127.3 (CH), 125.6 (CH), 97.6 (C), 66.0 ($CH_2$), 54.0 ($CH_3$), 47.1 (C), 40.9 (CH), 27.8 ($CH_2$), 24.7 ($CH_2$), 22.5 ($CH_2$), 10.2 ppm ($CH_3$); IR (neat): $\tilde{\nu}$ = 2922, 2852, 1738, 1603, 1495, 1447, 748, 698 cm$^{-1}$; APPI-MS: *m/z* calcd for $C_{24}H_{28}O_2$: 348.2080; found: 348.2090.

**3-Methoxy-3-propoxy-2,4-diphenyltricyclo[3.3.1.0$^{2,4}$]octane (*trans*-CPh)**: Yield: 19 mg (100 % from **AZh**) as a viscous oil. $^1$H NMR (500 MHz, $C_6D_6$): $\delta$ = 7.40–7.32 (m, 4H), 7.20–7.02 (m, 6H), 3.78–3.71 (t, *J* = 6.40 Hz, 2H), 2.99–2.91 (m, 2H), 1.96–1.32 (m, 8H), 0.98 ppm (t, *J* = 7.37 Hz, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ = 134.8 (C), 129.8 (CH), 127.4 (CH), 125.7 (CH), 97.4 (C), 68.4 ($CH_2$), 52.2 ($CH_3$), 47.0 (C), 40.9 (CH), 27.8 ($CH_2$), 24.7 ($CH_2$), 22.9 ($CH_2$), 10.9 ppm ($CH_3$); IR (neat): $\tilde{\nu}$ = 2922, 2852, 1738, 1603, 1495, 1447, 748, 698 cm$^{-1}$; IR (neat): $\tilde{\nu}$ = 2929, 2893, 1606, 1496, 1367, 1330, 1184, 752, 711, 559 cm$^{-1}$; APPI-MS: *m/z* calcd for $C_{24}H_{28}O_2$: 348.2080; found: 348.2090.

## Acknowledgements

NMR spectroscopic and MS measurements were performed at N-BARD, Hiroshima University. This work was supported by a Grant-in-Aid for Science Research on Innovative Areas "Stimuli-Responsive Chemical Species" (no. 24109008), "pi-Space" (no. 21108516), and from the Ministry of Education, Culture, Sports, Science and Technology, Japan, and by the Tokuyama Science Foundation (no. 19350021).

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[1] a) R. Hoffmann, R. W. Alder, C. F. Wilcox, *J. Am. Chem. Soc.* **1970**, *92*, 4992; b) O. J. Cooper, A. J. Wooles, J. McMaster, W. Lewis, A. J. Blake, S. T. Liddle, *Angew. Chem.* **2010**, *122*, 5702; *Angew. Chem. Int. Ed.* **2010**, *49*, 5570; c) J. B. Collins, J. D. Dill, E. D. Jemmis, P. v. R. Schleyer, R. Seeger, J. A. Pople, *J. Am. Chem. Soc.* **1976**, *98*, 5419; d) U. D. Priyakumar, G. N. Sastry, *Tetrahedron Lett.* **2004**, *45*, 1515; e) U. Deva Priyakumar, A. S. Reddy, G. N. Sastry, *Tetrahedron Lett.* **2004**, *45*, 2495; f) B. Sateesh, A. S. Reddy, G. N. Sastry, *J. Comput. Chem.* **2007**, *28*, 335; g) M. Abe, W. Adam, W. M. Nau, *J. Am. Chem. Soc.* **1998**, *120*, 11304–11310; h) M. Abe, W. Adam, T. Heidenfelder, W. M. Nau, X. Zhang, *J. Am. Chem. Soc.* **2000**, *122*, 2019; i) M. Abe, W. Adam, M. Hara, M. Hattori, T. Majima, M. Nojima, K. Tachibana, S. Tojo, *J. Am. Chem. Soc.* **2002**, *124*, 6540; j) M. Abe, J. Ye, M. Mishima, *Chem. Soc. Rev.* **2012**, *41*, 3808.

[2] a) J. D. Xu, D. A. Hrovat, W. T. Borden, *J. Am. Chem. Soc.* **1994**, *116*, 5425; b) W. Adam, W. T. Borden, C. Burda, H. Foster, T. Heidenfelder, M. Jeubes, D. A. Hrovat, F. Kita, S. B. Lewis, D. Scheut-

zow, J. Wirz, *J. Am. Chem. Soc.* **1998**, *120*, 593; c) W. T. Borden, *Chem. Commun.* **1998**, 1919.

[3] a) E. Niecke, A. Fuchs, F. Baumeister, M. Nieger, W. W. Schorller, *Angew. Chem.* **1995**, *107*, 640; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 555; b) M. Sebastian, M. Nieger, D. Szieberth, L. Nyulaszi, E. Niecke, *Angew. Chem.* **2004**, *116*, 647; *Angew. Chem. Int. Ed.* **2004**, *43*, 637.

[4] D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2002**, *295*, 1880.

[5] For delocalized diradicals, see: a) W. T. Borden, H. Iwamura, J. A. Berson, *Acc. Chem. Res.* **1994**, *27*, 109; b) J. A. Berson, *Acc. Chem. Res.* **1997**, *30*, 238; c) K. Matsuda, H. Iwamura, *J. Chem. Soc. Perkin Trans. 2* **1998**, 1023; d) T. Kubo, A. Shimizu, M. Sakamoto, M. Uruichi, K. Yakushi, M. Nakano, D. Shiomi, K. Sato, T. Takui, Y. Morita, K. Nakasujii, *Angew. Chem.* **2005**, *117*, 6722; *Angew. Chem. Int. Ed.* **2005**, *44*, 6564; e) Z. Sun, Q. Ye, C. Chi, J. Wu, *Chem. Soc. Rev.* **2012**, *41*, 7857.

[6] a) W. W. Schoeller, A. Rozhenko, D. Bourissou, G. Bertrand, *Chem. Eur. J.* **2003**, *9*, 3611; b) D. A. Dougherty, *Acc. Chem. Res.* **1991**, *24*, 88.

[7] a) D. Y. Zhang, D. A. Hrovat, M. Abe, W. T. Borden, *J. Am. Chem. Soc.* **2003**, *125*, 12823; b) D. M. Lemal, *J. Org. Chem.* **2009**, *74*, 2413; c) D. M. Lemal, *J. Org. Chem.* **2010**, *75*, 6411.

[8] a) W. T. G. Johnson, D. A. Hrovat, A. Skancke, W. T. Borden, *Theor. Chem. Acc.* **1999**, *102*, 207; b) M. Abe, S. Kawanami, C. Ishihara, M. Nojima, *J. Org. Chem.* **2004**, *69*, 5622; c) M. Abe, C. Ishihara, S. Kawanami, A. Masuyama, *J. Am. Chem. Soc.* **2005**, *127*, 10.

[9] a) D. Scheschkewitz, H. Amii, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Angew. Chem.* **2004**, *116*, 595; *Angew. Chem. Int. Ed.* **2004**, *43*, 585; b) A. Rodriguez, R. A. Olsen, N. Ghaderi, D. Scheschkewitz, F. Tham, L. J. Mueller, G. Bertrand, *Angew. Chem.* **2004**, *116*, 4988; *Angew. Chem. Int. Ed.* **2004**, *43*, 4880; c) G. Fuks, N. Saffon, L. Maron, G. Bertrand, D. Bourissou, *J. Am. Chem. Soc.* **2009**, *131*, 13681; d) P. Henke, T. Pankewitz, W. Klopper, F. Breher, H. Schnöckel, *Angew. Chem.* **2009**, *121*, 8285; *Angew. Chem. Int. Ed.* **2009**, *48*, 8141; e) J. Ma, Y. Ding, K. Hattori, S. Inagaki, *J. Org. Chem.* **2004**, *69*, 4245; f) M. Abe, C. Ishihara, A. Takegami, *J. Org. Chem.* **2004**, *69*, 7250; g) M. Abe, E. Kubo, K. Nozaki, T. Matsuo, T. Hayashi, *Angew. Chem.* **2006**, *118*, 7992; *Angew. Chem. Int. Ed.* **2006**, *45*, 7828; h) T. Nakamura, L. Gagliardi, M. Abe, *J. Phys. Org. Chem.* **2010**, *23*, 300; i) T. Nakamura, A. Takegami, M. Abe, *J. Org. Chem.* **2010**, *75*, 1956; j) K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter, D. Stalke, *Angew. Chem.* **2013**, *125*, 1845; *Angew. Chem. Int. Ed.* **2013**, *52*, 1801.

[10] A. Doddi, C. Gemel, M. Winter, R. A. Fischer, C. Goedecke, H. S. Rzepa, G. Frenking, *Angew. Chem.* **2013**, *125*, 468; *Angew. Chem. Int. Ed.* **2013**, *52*, 450.

[11] F. Breher, *Coord. Chem. Rev.* **2007**, *251*, 1007.

[12] a) H. Sugiyama, S. Ito, M. Yoshifuji, *Angew. Chem.* **2003**, *115*, 3932; *Angew. Chem. Int. Ed.* **2003**, *42*, 3802; b) S. Ito, J. Miura, N. Morita, M. Yoshifuji, A. J. Arduengo III, *Angew. Chem.* **2008**, *120*, 6518; *Angew. Chem. Int. Ed.* **2008**, *47*, 6418; c) M. Yoshifuji, Y. Hirano, G. Schnakenburg, R. Streubel, E. Niecke, S. Ito, *Helv. Chim. Acta* **2012**, *95*, 1723; d) C. Cui, M. Brynda, M. M. Olmstead, P. P. Power, *J. Am. Chem. Soc.* **2004**, *126*, 6510; e) H. Cox, P. B. Hitchcock, M. Lappert, L. J.-M. Peirssens, *Angew. Chem.* **2004**, *116*, 4600; *Angew. Chem. Int. Ed.* **2004**, *43*, 4500; f) D. A. Dickie, P. T. K. Lee, O. A. Labeodan, G. Schatte, N. Weinberg, A. R. Lewis, G. M. Bernard, R. E. Wasylishen, J. A. C. Clyburne, *Dalton Trans.* **2007**, 2862; g) X. Wang, Y. Peng, M. M. Olmstead, J. C. Fettinger, P. P. Power, *J. Am. Chem. Soc.* **2009**, *131*, 14164; h) T. Beweries, R. Kuzora, U. Rosenthal, A. Schulz, A. Villinger, *Angew. Chem.* **2011**, *123*, 9136; *Angew. Chem. Int. Ed.* **2011**, *50*, 8974; i) K. Takeuchi, M. Ichinohe, A. Sekiguchi, *J. Am. Chem. Soc.* **2011**, *133*, 12478; j) W. W. Schoeller, E. Niecke, *Phys. Chem. Chem. Phys.* **2012**, *14*, 2015; k) S. Demeshko, C. Godemann, R. Kuzora, A. Shultz, A. Villinger, *Angew. Chem.* **2013**, *125*, 2159; *Angew. Chem. Int. Ed.* **2013**, *52*, 2105.

[13] M. Abe, W. Adam, W. T. Borden, M. Hattori, D. A. Hrovat, M. Nojima, K. Nozak, J. Wirz, *J. Am. Chem. Soc.* **2004**, *126*, 574.

[14] X. Lu, D. Reid, J. Warkentin, *Can. J. Chem.* **2001**, *79*, 319.

[15] a) K. Beck, S. Huenig, *Chem. Ber.* **1987**, *120*, 477; b) W. Adam, T. Heidenfelder, C. Sahin, *Synthesis* **1995**, 1163.

[16] a) W. D. Clark, C. Steel, *J. Am. Chem. Soc.* **1971**, *93*, 6347; b) M. Abe, S. Watanabe, H. Tamura, S. Boinapally, K. Kanahara, Y. Fujiwara, *J. Org. Chem.* in press, DOI: 10.1021/jo3019472.

[17] F. Kita, W. Adam, P. Jordan, W. M. Nau, J. Wirz, *J. Am. Chem. Soc.* **1999**, *121*, 9265.

[18] S. L. Buchwalter, G. L. Closs, *J. Am. Chem. Soc.* **1979**, *101*, 4688–4694.

[19] a) P. C. Hariharan, J. A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; d) P. C. Harihara, A. Pople, *Theor. Chim. Acta* **1973**, *28*, 213.

[20] K. Yamaguchi, F. Jensen, A. Dorigo, K. N. Houk, *Chem. Phys. Lett.* **1988**, *149*, 537.

[21] M. Abe, H. Furunaga, D. Ma, L. Gagliardi, G. J. Bodwell, *J. Org. Chem.* **2012**, *77*, 7612.

[22] M. J. Frisch, et al., Gaussian 09, Revision B.01, Gaussian Inc., Wallingford, CT, **2009**.

[23] H. E. Simmons, T. Fukunaga, *J. Am. Chem. Soc.* **1967**, *89*, 5208.

[24] G. E. Ball, *Spectrosc. Prop. Inorg. Organomet. Compd.* **2010**, *41*, 262.

[25] For the stereoselectivity during the thermal and photochemical denitrogenation reaction of azoalkanes, see: a) M. Abe, I. Iwakura, A. Yabushita, S. Yagi, J. Liu, K. Okamura, T. Kobayashi, *Chem. Phys. Lett.* **2012**, *527*, 79; b) S. Yagi, Y. Hiraga, R. Yakagi, *J. Phys. Org. Chem.* **2011**, *24*, 894; c) E. L. Allred, R. L. Smith, *J. Am. Chem. Soc.* **1969**, *91*, 6766; d) M. B. Reyes, B. K. Carpenter, *J. Am. Chem. Soc.* **2000**, *122*, 10163; e) W. R. Roth, M. Martin, *Liebigs Ann. Chem.* **1967**, *702*, 1; f) W. Adam, M. Diedering, A. Trofimov, *J. Phys. Org. Chem.* **2004**, *17*, 643; g) W. Adam, H. Garcia, M. Diedering, V. Marti, M. Olivucci, E. Palomares, *J. Am. Chem. Soc.* **2002**, *124*, 12192; h) M. Hamaguchi, M. Nakaishi, T. Nagai, T. Nakamura, M. Abe, *J. Am. Chem. Soc.* **2007**, *129*, 12981.

Received: January 5, 2013
Revised: April 22, 2013