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# Extremely Long-lived Localized Singlet Diradicals in a Macrocyclic Structure: A Case Study of the Stretch Effect

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Abstract: Localized singlet diradicals have attracted much attention not only in the field of bond-homolysis chemistry, but also in nonlinear optical materials. In this study, an extremely long-lived localized singlet diradical emerged using a new molecular design-a macrocyclic structural effect-that is kinetically stabilized by increasing the molecular strain of the corresponding  $\sigma$ -bonded product. Notably, the lifetime of this diradical (14 µs) is two-orders of magnitude longer than that of a standard singlet diradical without a macrocyclic structure (~0.2 µs) at 293 K. The species is persistent at below the temperature of 100 K. In addition to the kinetic stabilization of the singlet diradical, the spontaneous oxidation of its corresponding ring-closed compound at 298 K produced oxygenated products under atmospheric conditions. Apparently, the "stretch effect" induced by the macrocyclic structure plays a crucial role in extending the lifetime of localized singlet diradicals and increasing the reactivity of their corresponding  $\sigma$ -bonded products.

**DR2a-f** have been intensively investigated for over a decade (Chart 1).<sup>[11]</sup> The lifetime in benzene at 293 K has been reported to range from  $T_{293} = 2$  ns to ~5500 ns depending on the substituents around the radical sites, which kinetically and/or thermodynamically stabilize the localized singlet diradicals. A unique nonlinear optical property has been also discovered for species with diradicaloid character.<sup>[12]</sup>

A new kinetic stabilization effect, termed the "stretch effect",<sup>[13]</sup> on the reactivity of the localized singlet diradical S-**DR2g,h** was designed and examined in the present study. Notably, laser flash photolysis (LFP) experiments of the precursor azoalkanes **AZ2g,h** (Scheme 1) revealed that the lifetimes of S-**DR2g,h** are roughly two orders of magnitude longer (T<sub>293</sub> = ~14 µs) than S-**DR2e**<sup>[14]</sup> (T<sub>293</sub> = ~0.2 µs). The intermolecular reactivity of the extremely long-lived singlet diradical S-**DR2h** was also investigated in this study.

#### Introduction

Open-shell molecules with unpaired electrons have attracted considerable attention not only in the field of reactive intermediate chemistry<sup>[1]</sup> but also in other chemical sciences such as non-linear optical materials,<sup>[2]</sup> organic magnets,<sup>[3]</sup> luminescent materials,<sup>[4]</sup> and biological studies.<sup>[5]</sup> The three dimensional and electronic structures of such high-energy molecules play a crucial role in their functionality. In general, however, the structure and reactivity of such species are experimentally elusive because of their short-lived character. Studies aimed at extending the lifetime of such reactive species is worthwhile to fully characterize their structure and reactivity, which give rise to their unique properties. Several studies on the isolation of highly energetic species such as carbenes,<sup>[6]</sup> radicals,<sup>[7]</sup> and delocalized diradicals,<sup>[8]</sup> have been reported using kinetic and thermodynamic stabilization.

Localized diradicals are key intermediates in bondhomolysis processes.<sup>[9]</sup> The isolation of singlet diradicals has been reported in the four-membered heterocyclic systems  $(E_2E_2)$ .<sup>[10]</sup> The ground state spin-multiplicity of propane-1,3-diyl diradicals **DR1** and the direct observation of singlet diradicals S-

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 $\label{eq:scheme-1} \begin{array}{l} \mbox{Scheme-1.} \ \mbox{This study: Macrocyclic effect on the reactivity of localized singlet diradicals.} \end{array}$ 

#### **Results and Discussion**

Synthesis of azoalkane AZ2g,h. The synthesis of azoalkanes AZ2g,h, the precursors of DR2g,h, were achieved by the Hünig<sup>[15]</sup> and the inter- and intramolecular Sonogashira cross-coupling<sup>[16]</sup> reactions as the key steps (Scheme S1). The  $n,\pi^*$  electronic transition of the azo chromophore was observed at 359 nm ( $\epsilon$  = 183 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) and 358 nm ( $\epsilon$  = 171 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>) in benzene for AZ2g and AZ2h, respectively (Figure S1). The molar extinction coefficients (ɛ) at ~360 nm were somewhat larger than that of a typical azo chromophore. For example, the  $\varepsilon$  of AZ2b in benzene, which is the precursor of DR2b, has been reported to be ~112 at 367 nm, indicating that the ε values of AZ2g,h contain a contribution from the 1,3diacetylphenyl chromophore. A high-quality single crystal of AZ2g was obtained by recrystallization, and the macrocyclic structure of AZ2g was confirmed by single-crystal X-ray crystallographic analysis (Figure 1). Table 1 summarizes the C9-C13 distance in AZ2g, which becomes the radical center after denitrogenation, and selected bond angles. Slightly bent structures were observed in the four triple bonds: C10-C16-C25 = 175.68° (entry 3), C16-C25-C15 = 175.36° (entry 4), C18-C21-C29 = 176.63°(entry 7), and C21-C29-C2 = 174.61°(entry 8). The experimentally obtained values were well reproduced by optimizing the geometry of AZ2g at the B3LYP/6-31G(d)^{[17]} level of theory (Table 1). For instance, the experimentally obtained and calculated C9-C13 bond distances were found to be very similar (2.264 and 2.269 Å, respectively; Table 1, entry 1). The slightly bent triple bonding ~175° was also well reproduced by the calculations.

Macrocyclic effect on the molecular structures. The singlet diradical S-DR2g and its ring-closed compound trans-CP2g were also computed at (R,U)B3LYP/6-31G(d) (Table 1). The distance between the radical centers at C9 and C13 was calculated to be 2.389 Å in S-DR2g, which was longer than that in AZ2g (entry 1). The C9-C6-C13 angle in the propane-1,3-diyl moiety was larger than that of AZ2g (entry 2), which is in consistent with the longer distance between C9 and C13 (entry 1). The triple bonds in S-DR2g were found to be more linear than those in AZ2g (entries 3-10). For example, the C10-C16-C25 and C16-C25-C15 angles in S-DR2g were 179.12° and 178.32°, respectively, whereas they were 175.20° and 174.47° in AZ2g (entries 3,4). In contrast to the linear triple bonding in S-DR2g, relatively distorted triple bonds were computed in the ring-closed compound trans-CP2g (entries 3-10). For example, the angles C5-C22-C8, C22-C8-C7, and C18-C21-C29 were found to be 169.76°, 167.56°, and 173.38° in CP2g (entries 5-7).

To examine the macrocyclic effect more fully, the structures of AZ2e, S-DR2e, and trans-CP2e, which have no macrocyclic ring, were compared with those of AZ2g, S-DR2g, and trans-CP2g (Table 1, entries 1,2). As expected, the distance between the two azocarbons C9 and C13 in AZ2g (2.264 Å) was slightly longer than that of the related azocarbons in AZ2e (2.255 Å). The single-crystal X-ray structure of AZ2e is shown in Figure S2. In addition to the effect on the carbon-carbon distance, the C9-C6-C13 bond angle in AZ2e (91.73°) was smaller than that in AZ2g (92.51°), indicating that the macrocyclic ring system stretches C9 and C13 in opposite



Figure 1. Top and side views of X-ray crystallographic structures of AZ2g.

Table 1. Experimental and computed structural data<sup>*e*</sup> for AZ2e,g, <sup>*b*</sup> DR2e,g, <sup>*c*</sup> trans-CP2e,g<sup>*b*</sup>



eı	ntry		AZ2e <sub>exp</sub> AZ2g <sub>ex</sub>	AZ2e <sub>cal</sub> AZ2g <sub>cal</sub>	S- <b>DR2e</b> cal S- <b>DR2g</b> cal	trans- <b>CP2e</b> cal trans- <b>CP2g</b> cal
	1	C9–C13	2.255 2.264	2.269 2.269	2.389 2.389	1.547 1.583
	2	C9–C6–C13	91.73 92.51	91.92 91.75	103.93 103.78	61.57 63.15
	3	C10-C16-C25	_ 175.68	_ 175.20	_ 179.12	_ 176.06
	4	C16-C25-C15	_ 175.36	_ 174.47	_ 178.32	_ 169.37
	5	C5-C22-C8	_ 176.44	_ 175.82	_ 176.25	_ 169.76
	6	C22–C8–C7	_ 175.38	_ 176.58	_ 174.84	_ 169.56
	7	C18-C21-C29	_ 176.63	_ 177.02	_ 174.87	_ 173.38
	8	C21-C29-C2	_ 174.61	_ 177.10	_ 176.34	_ 177.75
	9	C20-C23-C17	_ 175.81	_ 176.48	_ 178.30	_ 178.35
	10	C23-C17-C3	_ 177 19	- 176 30	- 170 17	_ 176.27

<sup>a</sup> Bond lengths in Å, angles in °. <sup>b</sup> and <sup>c</sup>Optimized at (R)B3LYP/6-31G(d) and (U)B3LYP/6-31G(d), respectively.

directions in **AZ2g** (Figure 2). This macrocyclic effect was also observed more significant in the computed ring-closed structure trans-**CP2**, although the distance in S-**DR2** was calculated to be nearly identical for S-**DR2e** and S-**DR2g** (Table 1, entries 1,2). The distance in **CP2g** (1.583 Å) was found to be longer than that in **CP2e** (1.547 Å), indicating that the two carbons in **CP2g** are pulled in opposite directions because of the macrocyclic ring strain (Figure 2). This new kinetic stabilization effect induced by the macrocyclic ring is expected to extend the lifetime of the singlet diradical S-**DR2g** and the reactivity of the ring-closed compound **CP2g** relative to S-**DR2e** and **CP2e**.



Figure 2. Stretch effect induced by a macrocyclic system.

The bending effect ( $\theta$ ) of the triple bonds on the destabilization energy was estimated by the angle-dependent energy change of 1,2-diphenylethyne at the B3LYP/6-31G(d) level of theory (Figure 3). The total electronic energy at 175° was 2 kJ mol<sup>-1</sup> higher than that at 180°. Energetic destabilizations of 8, 18, and 33 kJ mol<sup>-1</sup> were computed for angles of 170°, 165°, and 160°, respectively, for one diphenylethyne moiety.



Figure 3. Bending effect on the energetic destabilization of the 1,2-diphenylethyne moiety.

To further investigate the macrocyclic effect on the energetic destabilization of CP2g, the energy difference between the singlet diradicals S-DR2g and CP2g was computed at the B3LYP/6-31G(d) level of theory and compared with that of S-DR2e and CP2e (Table 2). As expected by the stretch effect, as induced by the strain of bending the triple bond within the system (Table 1, Figure 3) the enthalpy differences for S-DR2g and CP2g with macrocyclic structures (i.e., -20.9 (trans isomer) and -0.5 (cis isomer)) were found to be much smaller than those of S-DR2e and CP2e (i.e., -36.9 (trans isomer) and -13.7 (cis isomer)). Consistent with the destabilization of the ring-closed compound CP2g, the transition state energies from the singlet diradical S-DR2g to trans- and cis-CP2g (68.5 and 50.3 kJ mol<sup>-1</sup>, respectively) were larger than those for the reaction from DR2e without the macrocyclic ring to trans- and cis-CP2e (63.6 and 44.2 kJ mol<sup>-1</sup>, respectively), indicating that S-DR2g is kinetically stabilized by the macrocyclic ring. As previously found for S-DR2b, formation of cis-CP2e and cis-CP2g was predicted to be energetically more favorable than formation of the trans isomers.9n Thermal isomerization from the cis- to the transisomer appears to be possible for cis-**CP2g** at 298 K; indeed, the activation enthalpy for the transition from S-**DR2g** to trans-**CP2g** is computed to be 68.5 kJ mol<sup>-1</sup>, as observed for the thermal isomerization from cis-**CP2b** to trans-**CP2b**.<sup>[9n]</sup> The singlet ground states of **DR2e** and **DR2g** were also confirmed by the computations as  $\Delta E_{\text{ST}} = E_{\text{S}} - E_{\text{T}} = \sim -17$  kJ mol<sup>-1</sup> (Table 2).



$\Delta H_{\rm rel}$ ( $\Delta E_{\rm rel}$ ) /kJ mol <sup>-1</sup>							
	S-DR	T-DR	trans-CP	cis-CP	TS <sub>trans</sub> / v <sup>i, b</sup>	TScis/v <sup>i, b</sup>	
2e	0.00 (0.00)	17.5 (17.2)	–36.87 (–36.53)	–13.74 (–9.67)	63.58 (66.18) / –329.33	44.18 (45.96) / –371.65	
2g	0.00 (0.00)	17.1 (16.7)	–20.85 (–19.89)	–0.53 (0.38)	68.54 (71.23) /45.09	50.31 (53.07) / –36.32	

<sup>a</sup>Optimized at the (R,U)B3LYP/6-31G(d) level of theory. <sup>b</sup>The values of v<sup>i</sup> are imaginary frequencies computed at the same level of theory.

UV-vis and EPR studies on Photolysis of AZ2e,g,h and 16. Transient absorption spectroscopic analyses were conducted following the LFP of AZ2g (5 mg, 2.5 mM, Abs<sub>355</sub> = 0.46) and AZ2h (6 mg, 2.4 mM, Abs<sub>355</sub> = 0.48) in benzene with a Nd-YAG laser ( $\lambda_{exc}$  = 355 nm, 5 ns pulse, 7 mJ) at 293 ± 0.1 K (Figure 4). Under a N2 atmosphere, two transient species were observed at ~480 and ~580 nm for AZ2g and decayed with first order kinetics (Figure 4a). The lifetimes of each species were determined as 2.1  $\pm$  0.1  $\mu s$  and 12.7  $\pm$  1.1  $\mu s$  using single exponential kinetic fitting. Under air conditions, only the transient species at ~580 nm was observed with a small band at ~460 nm (Figure 4b) and also decayed with first-order kinetics, giving a lifetime of 14.0  $\pm$  1.1 µs and 13.8  $\pm$  1.2 µs, respectively. The nearly the same lifetime of the 580 and 460 nm clearly indicates that the two bands are derived from the same species. This lifetime is nearly identical under a N<sub>2</sub> atmosphere, indicating that the species at 480 nm is a triplet and that at 580 nm is a singlet. The absorption maximum of localized singlet diradicals DR2 typically occur at ~500-600 nm (Chart 1).[11] The absorption band corresponds to a  $\pi$ -to- $\pi^*$  electronic transition of the  $\pi$ single bonding system  $(C-\pi-C)$ .<sup>[18]</sup> All the experimental evidence suggests that the transient species at 580 nm is the singlet diradical S-DR2g. The lifetime of S-DR2g (~14 µs at 293

K) was almost two-orders of magnitude longer than the parent S-**DR2e** compound (209 ns at 293 K).<sup>[14]</sup> As expected by the stretch effect induced by the macrocyclic system (Figure 2), S-**DR2g** is highly kinetically stabilized as an extremely long-lived localized singlet diradical.



Figure 4. Transient absorption spectra for the LFP (293 K, benzene) of (a) AZ2g (5 mg, 2.5 mM, Abs<sub>355</sub> = 0.46) under N<sub>2</sub> conditions. Insert: time profiles of the 480 and 580 nm species. (b) AZ2g (5 mg, 2.5 mM, Abs<sub>355</sub> = 0.46) under atmospheric conditions. Insert: time profile of the 580 nm species.

To gain additional insight into the triplet species observed at ~480 nm in the LFP experiment (Figure 4a), the UV-vis absorption spectrum for the photolysis of **AZ2g** was recorded under low-temperature glassy matrix conditions using a solution of **AZ2g** in degassed 2-methyltetrahydrofuran (MTHF). As shown in Figure 5a, two bands were observed at ~470 nm and ~580 nm during the photolysis of **AZ2g** in the MTHF-glassy matrix at 90 K. After 3 min of photolysis, the ~470 nm species decayed under dark conditions while the 580 nm species having the low-intensity band at ~460 nm persisted. These phenomena clearly indicate that the 470 nm species is an electronically excited state that has a T-T absorption at ~470 nm, and the 580 nm species with 460 nm is a reactive intermediate (i.e., S-DR2g), which is existent at low temperature.

To confirm the spin multiplicity of the 470 nm and 580 nm species, low-temperature electron paramagnetic resonance



(EPR) spectroscopic and phosphorescence analyses were

**Figure 5.** (a) UV-vis spectroscopic analysis of the photolysis of **AZ2g** using a Xe lamp (360 ± 10 nm) in a MTHF matrix at 90 K. (b) EPR spectroscopic analysis during the photolysis of **AZ2g** in a MTHF matrix at 80 K. (c) (1) Fluorescence spectrum of **AZ2g** (0.12 mM,  $\lambda_{exc}$  = 360 nm) in MTHF at 77 K; (2) Phosphorescence spectrum of **AZ2g** (0.12 mM,  $\lambda_{exc}$  = 360 nm) in MTHF at 77 K.

absorption measurements (Figures 5b). During the photolysis of **AZ2g** using a 365 nm LED, triplet EPR signals were observed at 1512, 2049, 2682, 3944, and 4676 G. The high-intensity signal at 1512 G corresponds to the half-field transition ( $m_s = \pm 2$ ) of the allowed transitions ( $m_s = \pm 1$ ) at 2049 (z), 2682 (x,y), 3944 (x,y), and 4676 (z), from which the zero-field splitting parameters *D*/hc and *E*/hc were determined as 0.123 and < 0.001 cm<sup>-1</sup>, respectively. An accurate *E* value was difficult to obtain owing to the broad x and y signals. The large *D* value suggests that the

triplet state is not derived from the 1,3-diradical moiety but from a benzene moiety. The typical D value for triplet 1,3diphenylpropane-1,3-diyl diradical species is known to be ~0.05 cm<sup>-1</sup>.<sup>[19]</sup> D values of ~0.12–0.15 cm<sup>-1</sup> have been reported for the triplet state of benzene derivatives such as benzene itself<sup>[20]</sup> and 1,3-dicyanobenzene.<sup>[21]</sup> The typical triplet signals disappeared under dark conditions, indicating that they were derived from the 470 nm species. In fact, structured phosphorescence was observed at  $\lambda_{0.0}$  = ~470 nm following the 360 nm excitation of AZ2h (0.12 mM) in MTHF at 77 K together with fluorescence at  $\lambda_{0-0}$  ~370 nm (Figure 5c). The concomitant generation of the triplet state of the di-meta-substituted benzene moiety at ~470 nm with the singlet diradical DR2g at 580 nm is reasonable, because the absorbance at ~360 nm occurs viz. the mixture of azo and 1,3-diacetylphenyl chromophores (cf. the ε values for AZ2g,h). After 5 min of irradiation at 365 nm using a LED, no triplet EPR signals were observed under dark conditions, although purple-colored 580 nm species were clearly observed by UV-vis spectroscopy (Figure 5a). This observation provides evidence that the 580 nm species is the singlet state of the localized diradical S-DR2g.

A similar transient absorption spectrum was also observed for the LFP study of AZ2h (R =  $C_8H_{14}$ , Figure S3) under air conditions. The lifetime of the 580 nm species. DR2h. was determined as 14.2 ± 0.8 µs at 293 K in benzene, which is nearly identical to that of DR2g, indicating a negligible alkyl chain effect on the lifetime. The temperature-dependent change of the lifetime of S-DR2g,h (Figures S3,S4) gave activation parameters (E<sub>a</sub>, logA,  $\Delta H^{\ddagger}$ ,  $\Delta S^{\ddagger}$ ,  $\Delta G_{293}^{\ddagger}$ ) for the ring-closing process of the singlet diradicals S-DR2g,h to CP2g,h using Eyring and Arrhenius plots at temperatures between 283 and 313 K (Table 3). The activation energy and enthalpy of the decay process of S-DR2g,h were found to be ~20 kJ mol-1 higher than that for DR2e, indicating that the singlet diradicals are kinetically stabilized by the macrocyclic ring. To understand the substituent effect at the meta-positions in S-DR2g,h on the lifetime, a LFP study on compound 16 with two arylacetyl substituents at the meta-position, which is the byproduct in the synthesis of AZ2h, was also performed (Scheme S1, Scheme 2, Table 3). The lifetime of the singlet diradical S-DR16 was found to be 620 ± 12 ns at 293 K (Figure S5), which is much shorter than that of S-DR2g,h with the macrocyclic system (Table 3). As judged by the large logA values of ~12, the decay of 580 nm species is spin-allowed process to give the corresponding singlet products (Scheme 2).<sup>[22]</sup> The activation energies of the first-order decay process of DR2g,h were found to be ~52-55 kJ mol<sup>-1</sup>, which are close to the computed values for the ringclosing reaction to the cis-isomer of the ring-closing product, cis-CP2g (Table 2). The negligible substituent effect of the metasubstituents on the thermodynamic stabilization of the diradical was realized by the similar absorption maxima of S-DR2e, S-DR2g, and S-DR16, which were found to be 575 nm, 575 nm, and 576 nm. Furthermore, the computed spin-density of 0.735 at the benzylic position of the triplet state of DR2e was also similar to that of 0.736 in T-DR2g at the UB3LYP/6-31G(d) level of theory, indicating the negligible meta-substituent effect on the thermodynamic stability of DR2.

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Product Analysis in Photolysis of AZ2e,h, and 16 and Intermolecular Reactivity of CPe,h, and 17. Product analysis of the photochemical reaction of AZ2e, AZ2h, and 16 was conducted at 365 nm using a LED in a sealed degassed NMR tube in a C<sub>6</sub>D<sub>6</sub> solution of azoalkanes at 298 K. The photolysate was directly analyzed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy (Scheme 2, Figures 6, S6, S7). The NMR analysis of the photochemical denitrogenation of AZ2g was difficult due to its low solubility. A clean photochemical denitrogenation AZ2e, AZ2h, and 16,  $\Phi_{-N2} \sim 0.9$ ,<sup>[23]</sup> was observed to quantitatively produce the corresponding ring-closed compounds trans-CP2e, trans-CP2h, and trans-17, respectively (Scheme 2). The transselective formation of CP2 was observed at ~298 K as final products, as observed for S-DR2b<sup>[9n]</sup>.

**Table 3.** Lifetime (T<sub>293</sub>) and Activation Parameters ( $E_a$ , logA,  $\Delta H^{\ddagger}$ ,  $\Delta S^{\ddagger}$ ,  $\Delta G_{293}^{\ddagger}$ ) of S-**DR2e.g.h.** and S-**DR16.** 

DR	т <sub>293</sub> /µs <sup>a</sup>	Ea <sup>b</sup> /kJ mol <sup>-1</sup>	log(A /s <sup>-1</sup> ) <sup>b</sup>	Δ <i>H</i> <sup>‡ c</sup> /kJ mol <sup>−1</sup>	∆S <sup>‡ c</sup> /J K <sup>-1</sup> mol <sup>-1</sup>	∆G <sub>293</sub> ‡ <sup>c</sup> /kJ mol <sup>_1</sup>
DB2a	0.209	30.5	12.1	28.0	-21.5	24 2+0 9
DRZe	±0.012	±0.4	±0.1	±0.4	±0.8	34.2±0.0
DR2a	14.0	55.4	14.7	52.9	28.4	<i>11</i> 6+0 9
DIVES	±1.1	±0.7	±0.2	±0.7	±3.2	44.010.3
DR2h	14.2	52.3	14.1	49.7	17.1	<i>11</i> 7+0 <i>1</i>
DIVEN	±0.8	±0.4	±0.1	±0.4	±1.2	44.7±0.4
DP16	0.620	31.2	11.7	28.7	-28.9	37 2+0 8
DIVIO	±0.012	±0.8	±0.1	±0.8	±2.7	57.210.0

<sup>a</sup> In benzene at 293 K; errors are standard derivation from five data points. <sup>b,c</sup> Determined by Arrhenius plots and Eyring plots, respectively, of the lifetimes of singlet diradicals monitored at 580 nm at five temperatures between 283 and 313 K.

Compounds trans-CP2e and trans-17 with no macrocyclic ring were stable under air conditions and also on silica gel, as confirmed by <sup>1</sup>H NMR spectroscopy after isolation of trans-CP2e and trans-17, see the experimental section in supporting information. Interestingly, however, trans-CP2h with the macrocyclic system was highly air sensitive even at 298 K and gave the oxygenated products 18, 19, and 20 with isolated yields of 25%, 38%, and 15%, respectively (Figure 6, Scheme 3). The structures of 18-20 are guite similar to the oxygenated products of compound 21 under air at benzene reflux conditions,<sup>[24]</sup> and their formation suggests that the endoperoxide 22 is the intermediate for product formation. The high reactivity of trans-CP2h clearly indicates that the C9–C13  $\sigma$ bond is weaken by the stretched effect induced by the macrocyclic system.

In-situ NMR analysis of the photochemical denitrogenation of AZ2h at 188 K. As shown in Table 2, the gas-phase DFT calculations suggest that S-DR2g is nearly the same in energy with cis-CP2g. The computational study clarified that the cis-isomers cis-CP2g,h are the photo-primary product of AZ2g,h. Low-temperature in situ NMR analysis at 188 K was conducted for the reaction of AZ2h (3.4 mg, 9.5 mM) in  $d_{8}$ -toluene under N<sub>2</sub> using a 355 nm YAG laser (Figure 7), which was guided into the NMR cavity using a quartz rod.<sup>[9n],[25]</sup> At 188 K, thermally labile species (signals a-d) were observed with trans-CP2h (signals e-l) and unreacted AZ2h (signals m-p).

After 15 min under dark conditions, the signals a-d disappeared with a concomitant increase of signals e-I (Figure 7), suggesting that the signals a-d are derived from cis-CP2h and/or S-DR2h. From the activation parameter found for the decay process of S-DR2h (Table 3), the lifetime of S-DR2h should be ~1 s at 188 K; thus, the signals a-d do not correspond to S-DR2h but to cis-CP2h. These observations suggest that the DFT calculations overestimate the destabilization energy of CP2g and/or the stability of S-DR2g. The formation of cis-CP2h and its thermal isomerization to trans-CP2h indicate that the primary photoproduct from AZ2h included cis-CP2h. Consistent with the experimental observations, the experimentally determined activation energy of the S-DR2g decay process,  $E_a$  = 55.4 kJ mol<sup>-1</sup> and  $\Delta H^{\ddagger}$  = 52.9 kJ mol<sup>-1</sup> (Table 3), was close to the computed energy barrier of  $\Delta E_{ZPE}$  = 53.1 kJ mol<sup>-1</sup> and  $\Delta H^{\ddagger}$  = 50.3 kJ mol<sup>-1</sup> involving S-DR2g and cis-CP2g (Table 2).



Scheme 2. Product analysis of azoalkanes AZ2e, AZ2h, and 16 in the photochemical denitrogenation in benzene at 298 K.



denitrogenation of **AZ2h** (10.6 mg, 30 mM) in a scaled NMR tube in de-benzene under degassing conditions with a LED lamp (365 nm) at 298 K. (a) <sup>1</sup>HNMR spectrum of AZ2h before irradiation. (b) <sup>1</sup>HNMR spectrum of trans-CP2h after 15 min of irradiation. (c) <sup>1</sup>HNMR spectrum of trans-CP2h after 67 h under atmospheric conditions at 298 K.

O<sub>2</sub>

MeO

OMe

OMe



Scheme 3. Intermolecular reaction of DR2h with molecular oxygen (O2).



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**Figure 7.** In situ NMR (400 MHz, 2–6 ppm) analysis of the photochemical denitrogenation of (a) **AZ2h** (3.4 mg, 9.5 mM) in  $d_8$ -toluene under N<sub>2</sub> conditions with a YAG laser (355 nm, 30 mJ) at 188 K; (b) after 60 min; (c) after 15 min under dark; (d) trans-**CP2h** at 188 K in  $d_8$ -toluene.

#### Conclusions

In the present study, a new kinetic stabilization (stretch) effect, which is induced by the presence of a macrocyclic ring, has been examined in the context of affecting the reactivity of localized singlet diradicals and their corresponding ring-closed compounds. Extremely long-lived singlet diradicals S-DR2g,h  $(T_{293} = ~14 \mu s)$  emerged in this study. The experimental and computational studies clarified that the distorted triple bonding system in the ring-closed compounds CP2g,h is central to activating the stretch effect, which kinetically stabilizes the intermediary singlet diradicals DR2g,h. The high reactivity of CP2h, which was induced by the stretch effect, was confirmed by the spontaneous intermolecular reaction with molecular oxygen at 298 K to give the oxidation products 18-20. The observed stretch effect may spread into other bond activation chemistry<sup>[26]</sup> generation such as radical reactions. denitrogenations, and photochromism.

#### **Experimental Section**

Full experimental methods including detailed synthetic procedure and characterization data, NMR, MS, UV-vis, X-ray crystallographic details, and DFT calculations (PDF) are available in the supporting information.

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**Keywords:** localized singlet diradical • kinetic stabilization • stretch effect • macrocyclic effect • oxidation

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## FULL PAPER

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