

Impacts of Solvent and Alkyl Chain Length on the Lifetime of Singlet Cyclopentane-1,3-diyl Diradicaloids with π -Single Bonding

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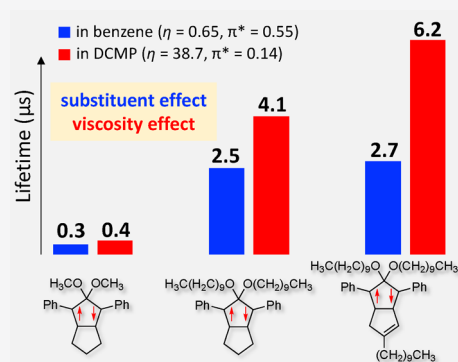


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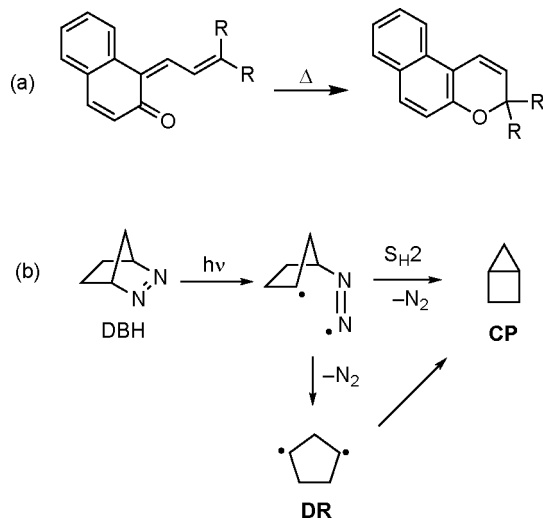
ABSTRACT: The singlet 2,2-dialkoxycyclopentane-1,3-diyl diradicaloids are not only the important key intermediates in the process of bond homolysis but are also attracting attention as π -single bonding compounds. In the present study, the effects of solvent viscosity η (0.24–125.4 mPa s) and polarity π^* (−0.11 to 1.00 kcal mol^{−1}) on the reactivity of localized singlet diradicaloids were thoroughly investigated using 18 different solvents including binary mixed solvent systems containing ionic liquids. In low- η solvents ($\eta < 1$ mPa s), the lifetimes of singlet diradicaloids, which are determined by the rate constant for the isomerization of π -single-bonded singlet diradicaloids to the σ -bonded isomer, were substantially dependent on π^* . Slower isomerization was observed in more polar solvents. In high- η solvents ($\eta > 2$ mPa s), the rate of isomerization was largely influenced by η in addition to π^* . Slower isomerization was observed in more viscous solvents. Experimental results demonstrated the crucial roles of both solvent polarity and viscosity in the reactivity of singlet diradicaloids and thus clarified the characters of singlet diradicaloids and molecular motions during the chemical transformation. The dynamic solvent effect was further proved by a long alkyl chain introduced at a remote position of the reaction site.



INTRODUCTION

By studying the polarity and viscosity effects of solvents on chemical reactions such as isomerization,^{1–10} we can

Scheme 1. Effect of Viscosity Effect (Dynamic Solvent Effect) on the (a) Isomerization of 1-Prop-2-enyldenaphthalen-2-one Derivatives to 3H-Naphtho[2,1-b]pyrans^{31–34} and (b) Photochemical Denitrogenation of 2,3-Diazabicyclo[2.2.1.]hept-2-ene (DBH)^{35–38}



investigate the mechanism of chemical reactions and the nature of reaction intermediates. For example, in the past few decades, considerable efforts have been devoted to understanding the mechanisms of thermal and light-induced isomerization by studying the effect of the solvent on the dynamics of molecular transformations.^{5,11–22} Comprehensive studies on the polarity effect have clarified the dipolar character of the transition state in the photoisomerization of stilbene.²³ It should be noted that the photoisomerization rate was also found to be strongly affected by solvent viscosity; thus, the isomerization rate of stilbenes decreases with an increase in viscosity.^{24–27} The so-called dynamic solvent effect is understood in terms of an increase in friction between molecules. Thus, transition state theory cannot be applied to molecular transformations in highly viscous solvents.^{28–30}

A typical example of the dynamic solvent effect has been reported for the thermal cyclization of 1-prop-2-enyldenaphthalen-2-one derivatives (Scheme 1a). Thermal ring-closing has been described by a two-dimensional model composed of medium and chemical coordinates.³¹ Note that

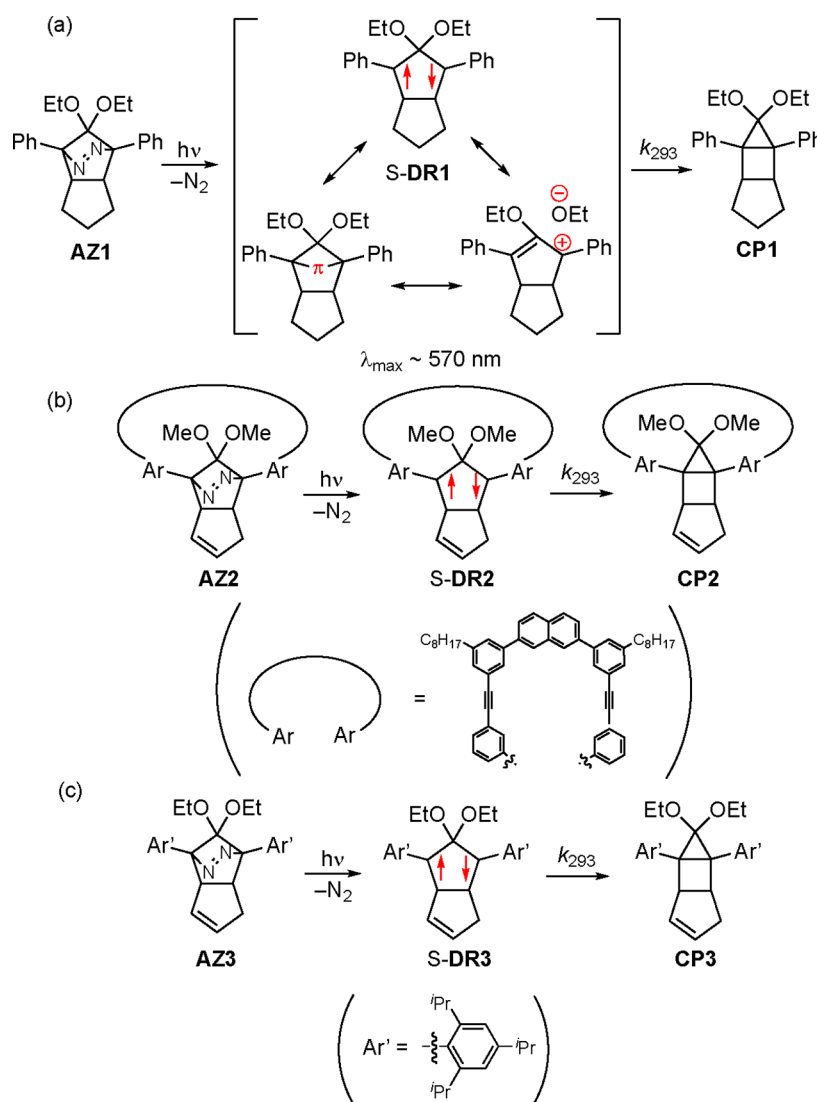
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Scheme 2. (a) Generation of the Singlet Diradicaloid S-DR1 in the Photolysis of the Azoalkane AZ1 and the Isomerization of S-DR1 to the Ring-Closing Compound CP1;^{46,49,50} (b) Generation and Isomerization of S-DR2 Having a Macrocyclic Structure;⁵¹ (c) Generation and Isomerization of S-DR3 Having Bulky Substituents⁵²

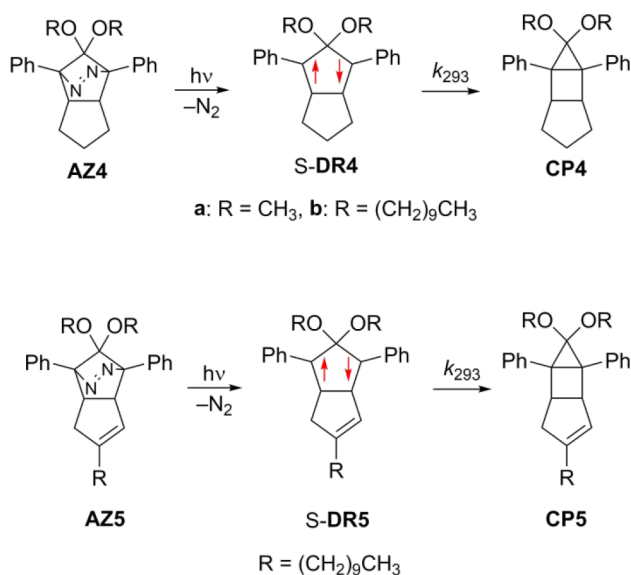


dynamic solvent effects can be used to identify the moving moieties of molecules inside solvent shells during molecular transformation.^{32,33} Asano and Ohga et al. revealed that the relative mobility of the ethenyl moiety dominated cyclization instead of the naphthalenone moiety in the isomerization of 1-prop-2-enylidenenaphthalen-2-one derivatives.³³ In 2016, the dynamic solvent effect was also reported for thermal isomerization for R = Ph in an ionic liquid.³⁴ Adam et al. used the dynamic solvent (viscosity) effect as an experimental tool to investigate the photochemical denitrogenation mechanism of 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) (Scheme 1b), in which the ring-closing product CP is produced by either a concerted reaction via homolytic substitution (S_H2) or a stepwise reaction via 1,3-diradical (DR).^{35–38}

We have been focusing our attention on investigating the reactivity and nature of cyclopentane-1,3-diyl diradicaloids that not only are the important key intermediates in the process of bond homolysis but also are attracting attention as π -single bonding compounds.^{39–46} We have shown so far that (1) a singlet ground state was achieved by introducing an electron-

withdrawing group at the C2 position of 1,3-diradicaloids,^{47,48} (2) the singlet diradicaloid S-DR1 (Scheme 2a) was experimentally detected by submicrosecond time-resolved spectroscopy during the denitrogenation of the azoalkane AZ1; (3) S-DR1 exhibited strong absorption bands at ~ 570 nm, which corresponded to the $\pi \rightarrow \pi^*$ electronic transition in the π -single bonding moiety;^{46,49} and (4) a moderately linear correlation was observed between the lifetime ($\tau_{293} = 1/k_{293}$) of S-DR1 and solvent polarity, suggesting the zwitterionic character of the singlet state.⁵⁰ Very recently, the dynamic solvent effects on the rates of isomerization of localized singlet diradicaloids having macrocyclic structures and bulky aryl groups to σ -single-bonded isomers were investigated in our laboratory (Scheme 2b,c).^{51,52} Both solvent polarity (π^* in kcal mol⁻¹)⁵³ and viscosity (η in mPa s) were found to play crucial roles in structural transformation. For example, both π^* and η substantially influence the τ_{293} of S-DR2, whereas π^* is dominant for a parent singlet diradicaloid lacking a macrocyclic structure.⁵¹ Most notably, the τ_{293} of the singlet diradicaloid S-DR3 reached 2 s at room temperature in the highly viscous

Scheme 3. Generation and Isomerization of the Localized Singlet Diradicaloids S-DR4 and S-DR5 from AZ4 and AZ5, Respectively



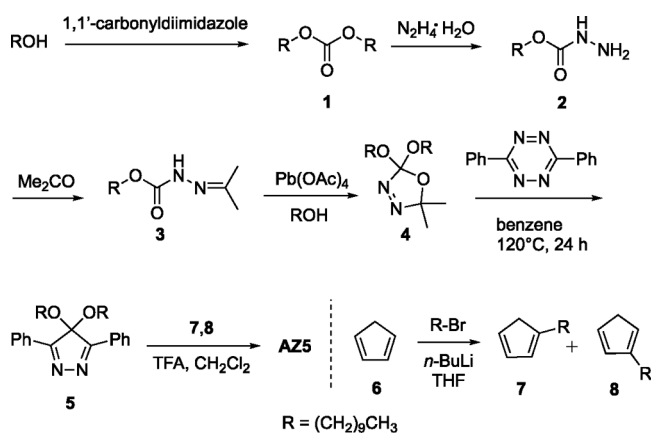
solvent 2,4-dicyclohexyl-2-methyl pentane (DCMP) under high-pressure conditions.⁵²

In this study, we examined the solvent polarity and viscosity effects on the τ_{293} values of the singlet diradicaloids S-DR4a (R = CH₃) and S-DR4b (R = (CH₂)₉CH₃) to determine the effects of alkyl chain length on the dynamic solvent effect (Scheme 3). The influence of the alkyl chain length of the alkoxy group on the reactivity has been previously analyzed in low viscous solvents such as benzene.^{46,54,55} Furthermore, the singlet diradicaloid S-DR5 with a long alkyl chain at the remote position from the reaction center was generated from the corresponding azoalkane AZ5, and the solvent effect on the reactivity of S-DR5 was compared with that in the case of S-DR4b. The difference in the reactivities of S-DR4b and S-DR5 would clarify molecular motion during the isomerization of the planar S-DR4b and S-DR5 to CP4b and CP5 having puckered structures, respectively. To comprehensively investigate the solvent effect, herein, we used 18 different solvents including binary mixed solvent systems containing the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF₆] and the organic solvents glycerin triacetate (GTA) and dimethyl sulfoxide (DMSO), which enabled sufficiently broad changes in η and π^* .

RESULTS AND DISCUSSION

Synthesis of the Azoalkanes AZ4 and AZ5. The azoalkanes AZ4a (R = CH₃) and AZ4b (R = (CH₂)₉CH₃) were synthesized according to the methods reported in literatures.^{54,56,57} A new azoalkane, AZ5 (R = (CH₂)₉CH₃), was prepared using the method described in Scheme 4. The didecyl carbonate **1** was obtained by treating 1,1'-carbonyldiimidazole with 1-decanol. Then, hydrazinolysis of **1** and condensation of **2** with acetone were conducted, followed by oxidative cyclization to produce **4**. [4 + 1] Cycloaddition of **4** with diphenyltetrazine and subsequent denitrogenation afforded 4,4-dialkoxy pyrazole (**5**). Diels–Alder cycloaddition of **5** with 10 equiv of a mixture of 1-decylcyclopenta-1,3-diene (**7**) and 2-decylcyclopenta-1,3-diene (**8**) provided AZ5.⁵⁸ Hydrogenation of the cyclopentene moiety could not be

Scheme 4. Synthesis of the Azoalkane AZ5



achieved under standard hydrogenation conditions, that is, under a H₂ atmosphere in the presence of Pd/C. The molecular structure of AZ5 was examined by several techniques including nuclear magnetic resonance spectroscopies (¹H and ¹³C NMR, Figures S1 and S2), nuclear Overhauser effect measurements (NOE, Figure S3), and electrospray ionization–mass spectrometry (MS, Figure S4).

Solvent Polarity and Viscosity Effects on the τ_{293} Values of S-DR4a, S-DR4b, and S-DR5. S-DR4a and S-DR4b were generated in the laser flash photolysis (LFP) of AZ4a and AZ4b, respectively, at 293 K with 355 nm laser (~5 mJ/pulse, 5 ns pulse width) in various solvent systems (Figures 1 and S12–15, Table 1).^{51,52} Figure 1 shows the transient absorption spectra and decay traces of S-DR4 and S-DR5 at 293 K in 2,4-dicyclohexyl-2-methyl pentane (DCMP, η = 38.7 mPa s). The τ_{293} values were determined by single exponential fitting of the first-order decay (k_{293}) signals at 560 (S-DR4a) and 570 nm (S-DR4b) (Figures 1 and S14 and 15, Table 1). As previously reported, τ_{293} of S-DR4b was one-order of magnitude longer than that of S-DR4a. The substituent effect was explained by the steric interaction between the Ph and OR groups in the transition state of σ -bond formation.⁵⁴ In low- η solvents such as *n*-hexane and acetone (η < 1.0 mPa s, entries 1–7, Table 1), the τ_{293} values of S-DR4a and S-DR4b at 293 K increased with an increase of the solvent polarity (π^*). The dependence of the τ_{293} of S-DR4a on π^* can be clearly noticed in the plot of τ_{293} versus π^* (Figure 2a) as the multiple correlation coefficient R^2 was 0.89. A similar correlation was observed for S-DR4b (Figure 2a); nevertheless, R^2 (0.73) for S-DR4b was lower than that for S-DR4a. However, the τ_{293} values of S-DR4a and S-DR4b did not show any significant linear correlation with η as the R^2 values were very low (0.36 and 0.27, respectively) in the cases of low- η solvents (Figure 2b).

To examine the effects of η on the isomerization of S-DR4a and S-DR4b to σ -bonded CP4a and CP4b, respectively, the highly viscous solvents DMSO (η = 2.24 mPa s), GTA (η = 23.00 mPa s), and DCMP (η = 38.7 mPa s) were used for the LFP experiments (Figure 1, entries 8–10 in Table 1). Interestingly, although the π^* of GTA (0.63 kcal mol⁻¹) is significantly lower than that of DMSO (π^* = 1.00 kcal mol⁻¹, entry 10 in Table 1), the longest τ_{293} values of S-DR4a (0.76 μ s) and S-DR4b (5.96 μ s) were obtained in GTA (entry 8). Particularly, the τ_{293} values acquired in GTA were approximately 2.5-fold those achieved in acetone (π^* = 0.62 kcal mol⁻¹) with π^* similar to that of GTA, indicating that the

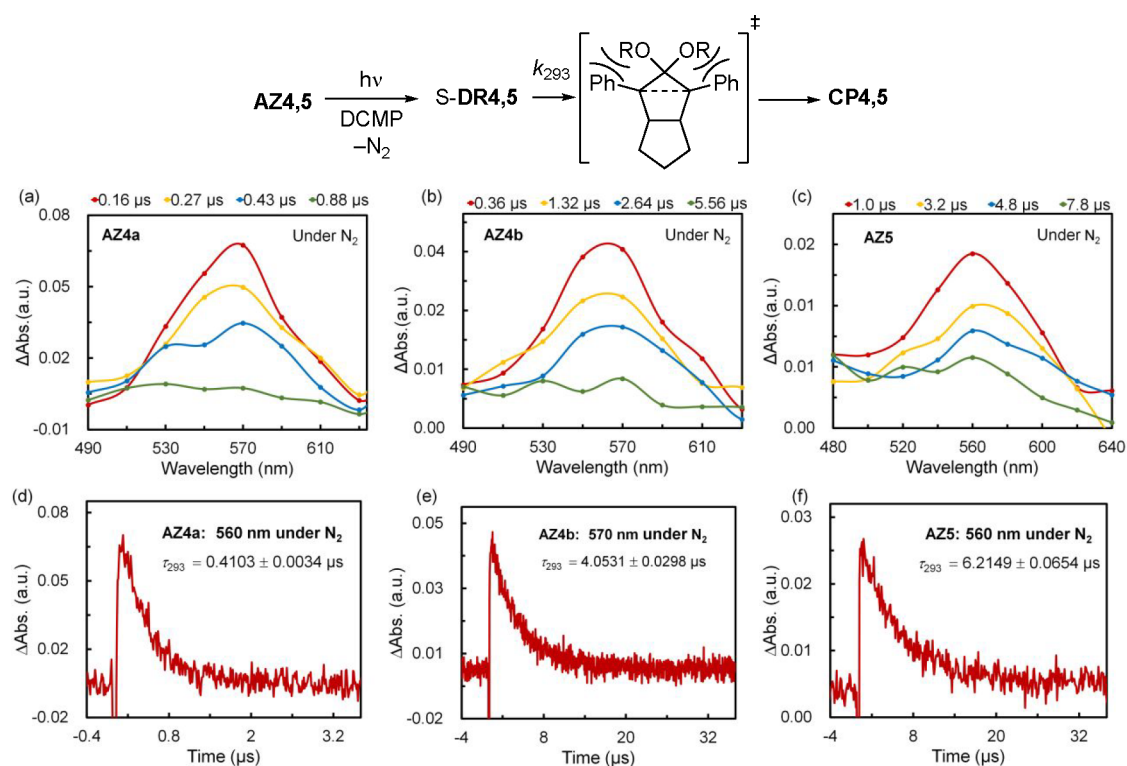


Figure 1. Submicrosecond transient absorption spectra during the laser flash photolysis of (a) AZ4a, (b) AZ4b, and (c) AZ5 at 293 K in 2,4-dicyclohexyl-2-methyl pentane (DCMP, $\eta = 38.7$ mPa s) under a N_2 atmosphere (entry 9, Table 1). (d) Time profile of S-DR4a at 560 nm under a N_2 atmosphere, (e) Time profile of S-DR4b at 570 nm under a N_2 atmosphere, (f) Time profile of S-DR5 at 560 nm under a N_2 atmosphere.

Table 1. Lifetimes (τ_{293}) of the Singlet Diradicaloids S-DR4a, S-DR4b, and S-DR5 at 293 K in Different Solvents

entry	solvent	polarity (π^*)/ kcal mol ⁻¹	viscosity (η)/mPa s	S-DR4a $\tau_{293}/\mu\text{s}^a$	S-DR4b $\tau_{293}/\mu\text{s}^a$	S-DR5 $\tau_{293}/\mu\text{s}^a$
1	<i>n</i> -hexane	-0.11	0.31	0.1444 ± 0.0010	1.4465 ± 0.0109	1.3545 ± 0.0004
2	diethyl ether	0.24	0.24	0.1754 ± 0.0013	1.6499 ± 0.0149	1.4438 ± 0.0150
3	ethyl acetate	0.45	0.46	0.2675 ± 0.0023	2.1855 ± 0.0067	2.1673 ± 0.0128
4	toluene	0.49	0.59	0.3031 ± 0.0037	2.5722 ± 0.0061	2.8108 ± 0.0340
5	benzene	0.55	0.65	0.3145 ± 0.0021	2.5161 ± 0.0063	2.7391 ± 0.0308
6	acetone	0.62	0.32	0.3001 ± 0.0050	2.3251 ± 0.0439	2.4325 ± 0.0092
7	dichloromethane	0.73	0.44	0.4983 ± 0.0030	4.7714 ± 0.0381	4.7606 ± 0.0177
8	glycerin triacetate (GTA)	0.63	23.00	0.7626 ± 0.0025	5.9599 ± 0.0491	8.7210 ± 0.1607
9	2,4-dicyclohexyl-2-methyl pentane (DCMP)	0.14	38.7	0.4103 ± 0.0034	4.0531 ± 0.0298	6.2149 ± 0.0654
10	dimethyl sulfoxide (DMSO)	1.00	2.24	0.6451 ± 0.0034	4.8613 ± 0.0121	nd ^b

^aAverage value of three experimental lifetimes. The error value was the standard deviation of the lifetime. ^bNot detected.

solvent viscosity plays an important role in determining the rates of isomerization of localized singlet diradicaloids to σ -bonded compounds. When the τ_{293} values of S-DR4a and S-DR4b were plotted for all ten sets π^* and η values (Figure 3a,b), the correlation of the τ_{293} of S-DR4a ($R^2 = 0.57$) with π^* was found to be better than that in the case of S-DR4b ($R^2 = 0.43$) (Figure 3a). In contrast, the correlation of the τ_{293} of S-DR4b ($R^2 = 0.51$) with η was better than that for S-DR4a ($R^2 = 0.45$) (Figure 3b). These results demonstrate that (1) the influences of solvent on the τ_{293} of singlet diradicaloids cannot be explained only with respect to the changes in π^* or η and (2) the response of S-DR4b to the changes in η is higher than that of S-DR4a.

Effects of Substituents at Remote Positions. As mentioned before, the τ_{293} values of singlet 2,2-dialkoxycyclopentane-1,3-diyl diradicaloids considerably depend on the

alkoxy group (OR) near the reaction site. During σ -bond formation of singlet diradicaloids, substantial molecular motion is expected to occur from the planar structure to the puckered structure. This prompted us to investigate the effects of substituents at a remote position from the reaction site. The effect of the substituent at the remote position on the τ_{293} of S-DR5 was examined in various solvents in the photochemical denitrogenation of AZ5 (Table 1). Both the acetal moiety and cyclopentene ring must move during the isomerization of planar S-DR5 to puckered CP5 (Scheme 3). In contrast, during the isomerization of S-DR4a and S-DR4b, either the acetal moiety or cyclopentane can move for σ -bond formation. The inferior solubility of AZ5 in DMSO prohibited the measurement of τ_{293} of S-DR5 in DMSO (entry 10, Table 1).

The τ_{293} values of S-DR4b and S-DR5 in low- η solvents ($\eta < 1$ mPa s) were very similar (entries 1–7, Table 1). This is

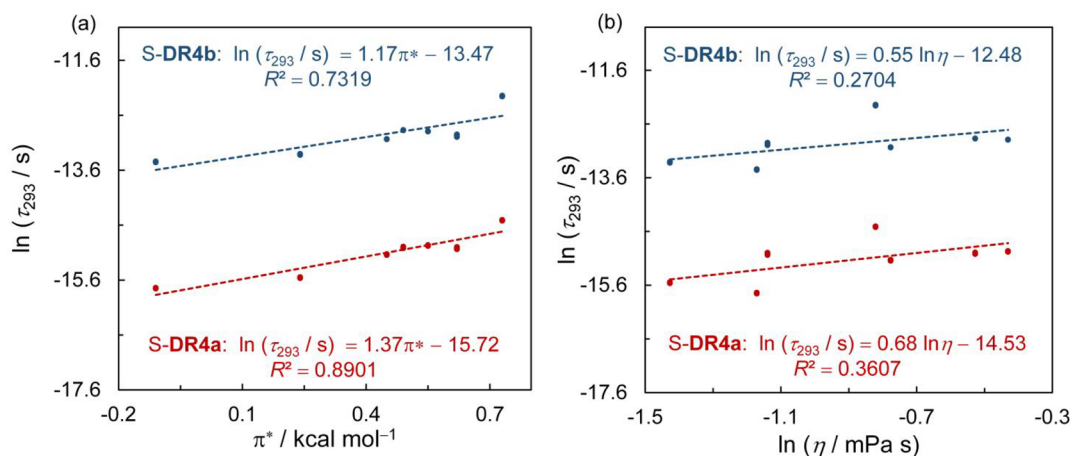


Figure 2. Correlations between (a) the lifetimes (τ_{293}) of S-DR4a and S-DR4b and polarity (π^*), and (b) viscosity (η) at 293 K in low- η ($\eta < 1$ mPa s) organic solvents.

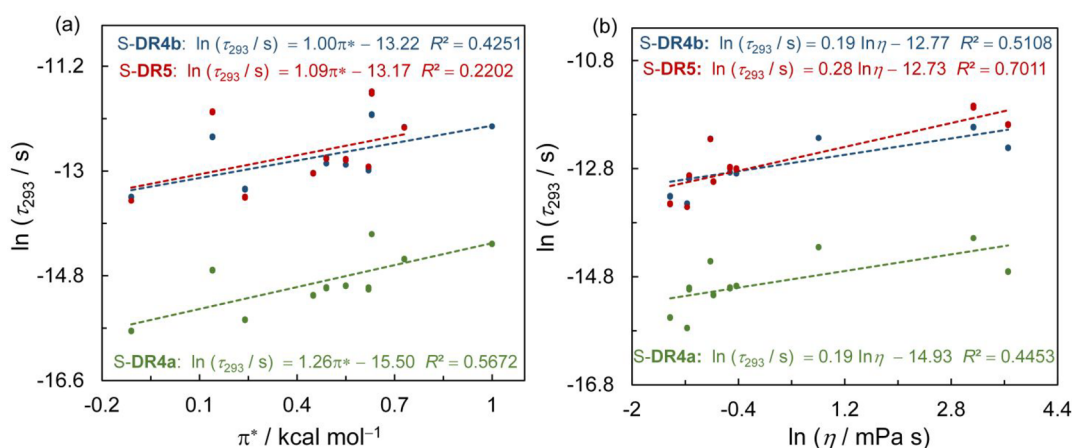


Figure 3. Correlations of the τ_{293} values of S-DR4a, S-DR4b, and S-DR5 with (a) π^* and (b) η of different pure organic solvents.

Table 2. Regression Analysis for Fitting the Observed $\ln(\tau_{293})$ to Equation 1 for S-DR4a, S-DR4b, and S-DR5 in Different Pure Organic Solvents

coefficient	S-DR4a	S-DR4b	S-DR5
A	1.4812	1.2265	1.4518
B	0.0248	0.0252	0.0384
C	-15.7681	-13.4965	-13.5919

reasonable because the steric hindrance between the acetal moiety and the phenyl ring in S-DR4b and S-DR5 should be similar in the corresponding transition states. Interestingly, in the highly viscous solvents GTA and DCMP, the τ_{293} values of S-DR5 were significantly high, which were approximately 1.5 times those of S-DR4b (entries 8 and 9, respectively, in Table 1). These results clearly imply that the effect of η caused by the friction between molecules plays a crucial role in molecular transformation, for which the transition state theory cannot be applied. The substantial effect of η on the τ_{293} of S-DR5, when

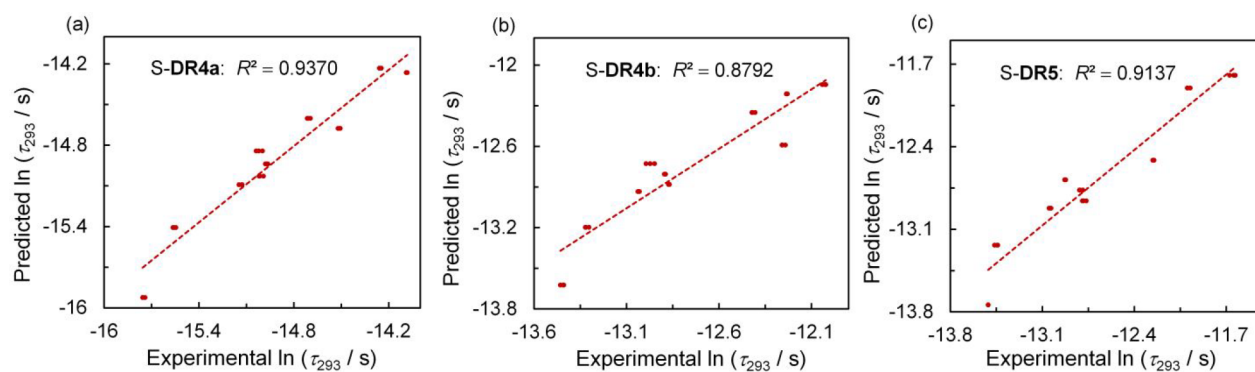


Figure 4. Correlation between the experimental and predicted $\ln(\tau_{293})$ for S-DR4a, S-DR4b, and S-DR5 in different pure organic solvents.

Table 3. η (20 °C) and π^* (23 °C) of the Binary Mixed Systems of [BMIM][PF₆] + GTA/DMSO

GTA mole fraction	λ_{\max}/nm	$\pi^*/\text{kcal mol}^{-1}$	$\rho/\text{g mL}^{-1}$ (calcd) ^a	$\eta/\text{mPa s}$
0	nd ^b	0.9 ^c	nc ^d	312 ^e
0.3571	312.11	0.88	1.29	177.3
0.5263	311.73	0.87	1.26	125.4
0.6249	311.27	0.85	1.24	93.44
0.6896	310.70	0.82	1.23	81.13
0.8474	309.76	0.78	1.19	45.18
1	nd	0.63	1.16	23.00
DMSO mole fraction	λ_{\max}/nm	$\pi^*/\text{kcal mol}^{-1}$	$\rho/\text{g mL}^{-1}$ (calcd) ^a	$\eta/\text{mPa s}$
0	nd ^b	0.9 ^c	nc ^d	312 ^e
0.1640	313.00	0.92	1.34	158.2
0.3704	313.21	0.93	1.32	57.35
0.5953	313.68	0.95	1.27	23.37
0.7463	314.25	0.97	1.23	10.84
0.9363	314.73	0.99	1.14	3.44
1	nd ^b	1.00	1.10	2.24

^aCalculated density. ^bNot detected. ^cThe polarity of [BMIM][PF₆].⁶¹
^dNot calculated. ^eThe viscosity of [BMIM][PF₆].⁶²

compared with that in the case of S-DR4b, supports the hypothesis that the cyclopentene moiety moves during isomerization in a solvent matrix.

To further understand the correlation of π^* and η with τ_{293} , we conducted a regression analysis according to eq 1, where A and B are the π^* and η coefficients, respectively, and C is a constant term. All terms are compound-dependent. A, B, and C calculated

$$\ln(\tau_{293}) = A\pi^* + B\eta + C \quad (1)$$

via the regression analysis are presented in Table 2. The predicted τ_{293} determined by eq 1 was appropriately consistent with the experimentally obtained τ_{293} . The B/A ratio for S-DR5 (0.0264) was higher than those for S-DR4a (0.0167) and S-DR4b (0.0205). Thus, the τ_{293} of S-DR5 was more sensitive to η . Moreover, via regression analysis, the τ_{293} values of S-DR4a, S-DR4b, and S-DR5 in the gas phases ($A = 0, B = 0$) at 293 K were determined to be 0.142, 1.376, and 1.251 μs , respectively. These values are nearly consistent with those acquired in *n*-hexane (0.144, 1.447, and 1.355 μs for S-DR4a, S-DR4b, and S-DR5, respectively). Thus, τ_{293} can be appropriately predicted using eq 1 (Figure 4).

Table 5. Regression Analysis for Fitting the Observed $\ln(\tau_{293})$ to Equation 1 for S-DR4a and S-DR4b in Different Solvents and Solvent Mixtures

coefficient	S-DR4a	S-DR4b
A	1.6273	1.3753
B	0.0101	0.0089
C	-15.6907	-13.4097

To further assess the influences of π^* and η on the isomerization of localized singlet diradicaloids, transient absorption spectroscopy was performed for S-DR4a and S-DR4b in binary mixed systems of [BMIM][PF₆] with GTA or DMSO (Table 4). Azoalkanes did not dissolve in pure [BMIM][PF₆]. The experiments for S-DR5 were hampered by the insolubility of AZ5 in binary-mixed solvents. The Kamlet–Taft polarizability parameters π^* of binary systems containing [BMIM][PF₆] and GTA/DMSO were determined by measuring the wavelength of maximum absorption (λ_{\max}) of 4-nitroanisole in these solvents. The unknown π^* values were calculated according to eq 2, and the results are provided in Table 3.⁵³ Contrary to the increase in π^* with a decrease in the GTA molar fraction, π^* decreased with a concomitant decrease in the DMSO molar fraction.

$$10^4/\lambda_{\max} = 34.17 - 2.41\pi^* \quad (2)$$

To measure the η of the binary mixed systems containing [BMIM][PF₆] and GTA/DMSO, we speculated that the total volume of the binary systems comprising [BMIM][PF₆] and GTA/DMSO was equal to the sum of the volumes of the pure components. Indeed, when the DMSO molar fractions were 0.5953 and 0.9363, the predicted densities (ρ) were 1.27 and 1.14 g mL^{-1} (20 °C), which were analogous to the previously reported results obtained at 25 °C (experimental ρ : 1.2752 and 1.1319 g mL^{-1} for the DMSO molar fractions of 0.6001 and 0.9491), respectively.⁵⁹ The η values of the binary mixed solvents were evaluated using a microviscometer at 20 °C (Table 3). The η of [BMIM][PF₆] + DMSO (molar fraction: 0.3704) (that is, 57.35 mPa s) was similar to the previously reported value measured by Zafarani-Moattar et al. (56.306 mPa s for the DMSO molar fraction of 0.4020) at 298.15 K.⁶⁰ The η values of the binary mixed systems decreased with an increase in the molar fractions of GTA and DMSO.

The longest τ_{293} values of S-DR4a and S-DR4b were obtained in the mixed solvent of [BMIM][PF₆] and DMSO in

Table 4. τ_{293} of the Singlet Diradicaloids S-DR4a and S-DR4b at 293 K in the Binary Systems of [BMIM][PF₆] with GTA or DMSO

entry	GTA molar fraction	$\pi^*/\text{kcal mol}^{-1}$	$\eta/\text{mPa s}$	S-DR4a $\tau_{293}/\mu\text{s}^a$	S-DR4b $\tau_{293}/\mu\text{s}^a$
1	0.5263	0.87	125.4	1.5625 \pm 0.0088	10.7003 \pm 0.1059
2	0.6249	0.85	93.44	1.2927 \pm 0.0025	9.3426 \pm 0.0355
3	0.6896	0.82	81.13	1.2313 \pm 0.0065	8.4704 \pm 0.1442
4	0.8474	0.78	45.18	0.9968 \pm 0.0126	7.1144 \pm 0.0572
5	1	0.63	23.00	0.7626 \pm 0.0025	5.9599 \pm 0.0491
entry	DMSO molar fraction	$\pi^*/\text{kcal mol}^{-1}$	$\eta/\text{mPa s}$	S-DR4a $\tau_{293}/\mu\text{s}^a$	S-DR4b $\tau_{293}/\mu\text{s}^a$
6	0.3704	0.93	57.35	2.0775 \pm 0.0270	15.0033 \pm 0.1182
7	0.5953	0.95	23.37	1.4364 \pm 0.0023	11.2203 \pm 0.1547
8	0.7463	0.97	10.84	1.0022 \pm 0.0007	7.8891 \pm 0.0544
9	0.9363	0.99	3.44	0.6682 \pm 0.0016	5.0925 \pm 0.0994
10	1	1.00	2.24	0.6451 \pm 0.0034	4.8613 \pm 0.0121

^aAverage value of three experimental lifetimes. The error value was the standard deviation of the lifetime.

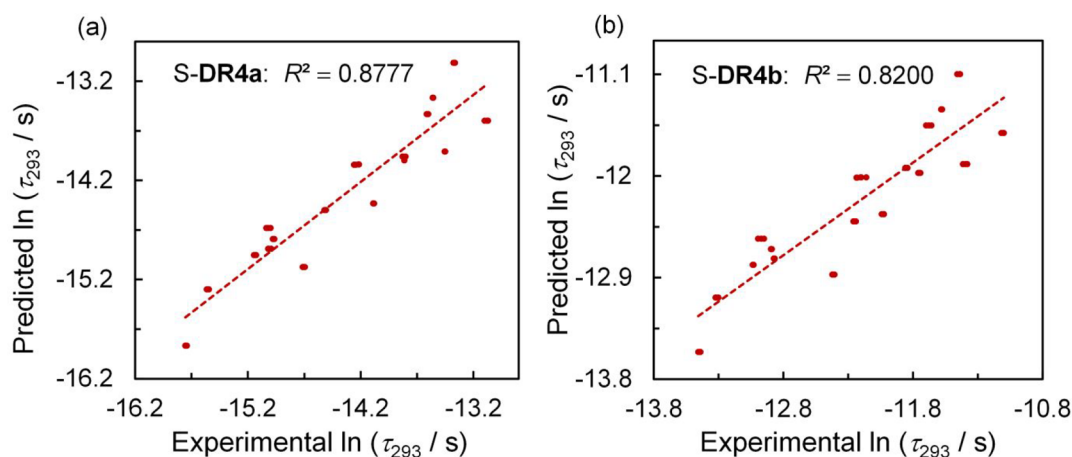


Figure 5. Correlation between the experimental and predicted $\ln(\tau_{293})$ of S-DR4a (a) and S-DR4b (b) in different solvents and solvent mixtures.

a molar ratio of 0.6296/0.3704 (entry 6, Table 4), where the π^* and η were determined to be 0.93 kcal mol⁻¹ and 57.35 mPa s, respectively. Although π^* slightly decreased from 1 (for pure DMSO) to 0.93 kcal mol⁻¹ (for [BMIM][PF₆] + DMSO) (entries 6–10, Table 4), the τ_{293} values achieved under the above-mentioned conditions were ~ 3 times those acquired for S-DR4a and S-DR4b in pure DMSO. AZ4a and AZ4b did not dissolve when the molar ratio of DMSO was lower (0.3704). For the mixed solvent system of [BMIM][PF₆] and GTA (entries 1–5, Table 4), an increase in τ_{293} was also observed with an increase in the molar ratio of [BMIM][PF₆], for which both π^* and η increased. Although the η of [BMIM][PF₆]/GTA = 0.4737/0.5263 (125.4 mPa s) (entry 1, Table 4) was higher than that of [BMIM][PF₆]/DMSO = 0.6296/0.3704 (57.35 mPa s) (entry 6, Table 4), the τ_{293} values of S-DR4a (2.08 μ s) and S-DR4b (15.0 μ s) in [BMIM][PF₆]/DMSO were longer than those in [BMIM][PF₆]/GTA. The τ_{293} values of S-DR4a and S-DR4b were considerably dependent on both π^* and η (Table 1). The longer τ_{293} values were attributed to the higher π^* of [BMIM][PF₆]/DMSO than that of [BMIM][PF₆]/GTA. A similar effect of π^* on the τ_{293} values of S-DR4a and S-DR4b was also noticed in 100% GTA and [BMIM][PF₆]/DMSO = 0.4047/0.5953 with nearly same η and different π^* . Thus, the τ_{293} values of S-DR4a and S-DR4b at [BMIM][PF₆]/DMSO = 0.4047/0.5953 were approximately twice those in 100% GTA.

Finally, a regression analysis was conducted for the τ_{293} values observed for S-DR4a and S-DR4b in all 18 solvents used herein (Table 5 and Figure 5). The B/A ratios were nearly the same for S-DR4a (0.0062) and S-DR4b (0.0065), suggesting that the motion of the cyclopentane moiety was important for the molecular transformation of planar singlet diradicaloids to puckered σ -bonded compounds. The τ_{293} values of S-DR4a and S-DR4b in gas phases ($A = 0$, $B = 0$) at 293 K were calculated to be 0.15 and 1.50 μ s, respectively, which were very similar to those observed in *n*-hexane (entry 1, Table 1). The suitable linear relationships between the predicted and experimental $\ln(\tau_{293})$ values are depicted in Figure 5.

CONCLUSIONS

Herein, the τ_{293} values of S-DR4a and S-DR4b, corresponding to the rate constants of the isomerization of planar cyclopentane-1,3-diyl diradicaloids to ring-closed puckered compounds, were measured in 18 solvent systems with wide ranges

of π^* and η . τ_{293} increased with an increase in π^* and η . A relatively appropriate correlation between π^* and τ_{293} of S-DR4a and S-DR4b was noticed in solvents with relatively low η ($\eta < 1$ mPa s). In high- η solvents, specifically in a binary mixed solvent system of [BMIM][PF₆] and GTA or DMSO, suitable correlations of τ_{293} with η were observed. The regression analysis clarified that τ_{293} was determined by the effects of both π^* and η . Notable effects of substituents at the remote position on the τ_{293} of S-DR5 were noticed in viscous solvents, suggesting that η plays a crucial role in determining the τ_{293} . Thus, the molecular friction increased with an increase in the size of the substituent during molecular motion from the planar structure to the puckered structure. The present study provides insight into the nature of singlet diradicaloids and guidelines for further extending the lifetime of π -single-bonded compounds.

EXPERIMENTAL SECTION

Synthesis of Azoalkanes AZ4a (R = CH₃)⁵⁴ and AZ4b (R = (CH₂)₉CH₃). Azoalkanes AZ4a (R = CH₃)⁵⁴ and AZ4b (R = (CH₂)₉CH₃)⁵⁴ were synthesized according to the reported method via compounds 2⁵⁴ and 3⁵⁴ (Scheme 4, Scheme S1).

General Procedure for the Synthesis of New Azoalkane, AZ5 (R = (CH₂)₉CH₃). Under dark conditions, to a solution of decylcyclopenta-1,3-diene (7/8) (1.55 g, 10 equiv) and 5 (0.40 g, 0.74 mmol) in CH₂Cl₂ (7 mL) was added dropwise trifluoroacetic acid (11 μ L, 0.2 equiv) at 0 °C under a nitrogen atmosphere. After stirring for 1 h, the reaction was quenched by aqueous NaHCO₃, and then the organic layer was washed by brine and extracted with CH₂Cl₂. Next, the mixture was dried, filtrated, and concentrated, and AZ5 (0.44 g, 0.60 mmol, 62%) as a yellow oil was prepared by purification via column chromatography on silica gel (hexane/EtOAc = 15:1). ¹H NMR (400 MHz, CDCl₃): δ 8.00–7.88 (m, 4H), 7.47–7.35 (m, 6H), 5.14 (s, 1H), 4.13–4.07 (m, 1H), 3.74–3.66 (m, 1H), 3.10–3.01 (m, 2H), 2.84–2.73 (m, 2H), 2.31–2.10 (m, 2H), 1.90–1.80 (m, 2H), 1.47–0.96 (m, 48H), 0.92–0.84 (m, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 149.0, 137.1, 136.8, 128.9, 128.4, 128.1, 128.0, 127.7, 119.5, 117.9, 94.8, 93.1, 64.2, 63.9, 57.5, 43.1, 34.8, 32.1, 31.2, 30.0, 29.7, 29.5, 29.4, 27.6, 26.4, 26.0, 22.8, 14.3. HRMS (ESI): calcd for C₅₀H₇₈N₂O₂Na [M + Na]⁺, 761.59555; found, 761.59589.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.joc.1c02895>.

Detailed synthetic procedures, characterization data (NMR and MS), photoproduct analysis, determination

of polarity, regression statistics, and transient absorption spectra (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) Dugave, C.; Demange, L. Cis–Trans Isomerization of Organic Molecules and Biomolecules: Implications and Applications. *Chem. Rev.* **2003**, *103*, 2475–2532.
- (2) Hassam, M.; Taher, A.; Arnott, G. E.; Green, I. R.; van Otterlo, W. A. L. Isomerization of Allylbenzenes. *Chem. Rev.* **2015**, *115*, 5462–5569.
- (3) Tomatsu, I.; Hashidzume, A.; Harada, A. Contrast Viscosity Changes upon Photoirradiation for Mixtures of Poly(Acrylic Acid)-Based α -Cyclodextrin and Azobenzene Polymers. *J. Am. Chem. Soc.* **2006**, *128*, 2226–2227.
- (4) Nevesely, T.; Wienhold, M.; Molloy, J. J.; Gilmour, R. Advances in the $E \rightarrow Z$ Isomerization of Alkenes Using Small Molecule Photocatalysts. *Chem. Rev.* **2021**, DOI: [10.1021/acs.chemrev.1c00324](https://doi.org/10.1021/acs.chemrev.1c00324).
- (5) Gulam, R. M.; Takahashi, T.; Ohga, Y. Dynamic Solvent Effects on the Thermal Isomerization of Zinc Dithizonate. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5170–5174.
- (6) Hirao, Y.; Hamamoto, Y.; Nagamachi, N.; Kubo, T. Solvent Viscosity-Dependent Isomerization Equilibrium of Tetramethoxy-Substituted Bianthrone. *Phys. Chem. Chem. Phys.* **2019**, *21*, 12209–12216.
- (7) Ye, S.; Zhang, H.; Fei, J.; Wolstenholme, C. H.; Zhang, X. A General Strategy to Control Viscosity Sensitivity of Molecular Rotor-Based Fluorophores. *Angew. Chem., Int. Ed.* **2021**, *60*, 1339–1346.
- (8) Roy, P.; Sardjan, A. S.; Danowski, W.; Browne, W. R.; Feringa, B. L.; Meech, S. R. Photophysics of First-Generation Photomolecular Motors: Resolving Roles of Temperature, Friction, and Medium Polarity. *J. Phys. Chem. A* **2021**, *125*, 1711–1719.
- (9) Zhu, C.; Zeng, X. C.; Francisco, J. S.; Gladich, I. Hydration, Solvation, and Isomerization of Methylglyoxal at the Air/Water Interface: New Mechanistic Pathways. *J. Am. Chem. Soc.* **2020**, *142*, 5574–5582.
- (10) Adam, W.; Librera, C.; Trofimov, A. V. Viscosity-Controlled, Product-Selective Rearrangement of the Cyclopentane-1,3-Diyl Radical Cation Derived from an Annelated Housane by Electron Transfer: A Case of Curtin–Hammett Behavior. *J. Am. Chem. Soc.* **2002**, *124*, 11936–11939.
- (11) Asano, T.; Matsuo, K.; Sumi, H. Effects of Solvent Fluctuations on the Rate of the Thermal Z/E Isomerization of N -Benzylideneanilines in a Highly Viscous Liquid Hydrocarbon. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 239–244.
- (12) Quant, M.; Hamrin, A.; Lennartson, A.; Erhart, P.; Moth-Poulsen, K. Solvent Effects on the Absorption Profile, Kinetic Stability, and Photoisomerization Process of the Norbornadiene–Quadracyclanes System. *J. Phys. Chem. C* **2019**, *123*, 7081–7087.
- (13) Rothenberger, G.; Negus, D. K.; Hochstrasser, R. M. Solvent Influence on Photoisomerization Dynamics. *J. Chem. Phys.* **1983**, *79*, 5360–5367.
- (14) Bortolus, P.; Monti, S. Cis-Trans Photoisomerization of Azobenzene. Solvent and Triplet Donors Effects. *J. Phys. Chem.* **1979**, *83*, 648–652.
- (15) Zeglinski, D. M.; Waldeck, D. H. Evidence for Dynamical Solvent Effects on the Photoisomerization of 4,4'-Dimethoxystilbene. *J. Phys. Chem.* **1988**, *92*, 692–701.
- (16) Horbury, M. D.; Quan, W. D.; Flourat, A. L.; Allais, F.; Stavros, V. G. Elucidating Nuclear Motions in a Plant Sunscreen during Photoisomerization through Solvent Viscosity Effects. *Phys. Chem. Chem. Phys.* **2017**, *19*, 21127–21131.
- (17) Quick, M. T.; Quick, M.; Ioffe, I. N.; Richter, C.; Mahrwald, R.; Druzhinin, S.; Kovalenko, S. A. Transient Rotamerism and Photoisomerization Dynamics of *trans*- and *cis*-Naphthylstilbene. *J. Phys. Chem. B* **2020**, *124*, 1049–1064.
- (18) Onganer, Y.; Yin, M.; Bessire, D. R.; Quitevis, E. L. Dynamical Solvation Effects on the Cis-Trans Isomerization Reaction: Photoisomerization of Merocyanine 540 in Polar Solvents. *J. Phys. Chem.* **1993**, *97*, 2344–2354.
- (19) Asano, T.; Okada, T. Thermal $Z-E$ Isomerization of Azobenzenes. The Pressure, Solvent, and Substituent Effects. *J. Org. Chem.* **1984**, *49*, 4387–4391.
- (20) Rice, J. K.; Baronavski, A. P. Ultrafast Studies of Solvent Effects in the Isomerization of *cis*-Stilbene. *J. Phys. Chem.* **1992**, *96*, 3359–3366.
- (21) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; Wiley, 2003.
- (22) Asano, T.; Furuta, H.; Sumi, H. “Two-Step” Mechanism in Single-Step Isomerizations. Kinetics in Highly Viscous Liquid Phase. *J. Am. Chem. Soc.* **1994**, *116*, 5545–5550.
- (23) Hicks, J. M.; Vandarsall, M. T.; Sitzmann, E. V.; Eisenthal, K. B. Polarity-Dependent Barriers and the Photoisomerization Dynamics of Molecules in Solution. *Chem. Phys. Lett.* **1987**, *135*, 413–420.
- (24) Waldeck, D. H. Photoisomerization Dynamics of Stilbenes. *Chem. Rev.* **1991**, *91*, 415–436.
- (25) Nikowa, L.; Schwarzer, D.; Troe, J.; Schroeder, J. Viscosity and Solvent Dependence of Low-barrier Processes: Photoisomerization of *Cis*-stilbene in Compressed Liquid Solvents. *J. Chem. Phys.* **1992**, *97*, 4827–4835.
- (26) Gegiou, D.; Muszkat, K. A.; Fischer, E. Temperature Dependence of Photoisomerization. VI. The Viscosity Effect. *J. Am. Chem. Soc.* **1968**, *90*, 12–18.
- (27) Salties, J.; D’Agostino, J. T. Separation of Viscosity and Temperature Effects on the Singlet Pathway to Stilbene Photoisomerization. *J. Am. Chem. Soc.* **1972**, *94*, 6445–6456.
- (28) Heitele, H. Dynamic Solvent Effects on Electron-Transfer Reaction. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 359–377.
- (29) Kramers, H. A. Brownian Motion in a Field of Force and the Diffusion Model of Chemical Reactions. *Physica*. **1940**, *7*, 284–304.
- (30) Sumi, H. Theory on Reaction Rates in Nonthermalized Steady States during Conformational Fluctuations in Viscous Solvents. *J. Phys. Chem.* **1991**, *95*, 3334–3350.
- (31) Goto, Y.; Takahashi, T.; Ohga, Y.; Asano, T.; Hildebrand, M.; Weinberg, N. Dynamic Solvent Effects on the Thermal Cyclization of a Hexadienone Formed from a Diphenylnaphthopyran: An Example of a System with Distinctly Separate Medium and Chemical

Contributions to the Overall Reaction Coordinate. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1825–1830.

(32) Goto, Y.; Sugita, K.; Takahashi, T.; Ohga, Y.; Asano, T. An Experimental Attempt to Identify a Moving Molecular Moiety in a Solvent Matrix. *Chem. Lett.* **2003**, *32*, 618–619.

(33) Sugita, K.; Goto, Y.; Ono, M.; Yamashita, K.; Hayase, K.; Takahashi, T.; Ohga, Y.; Asano, T. A New Application of High-Viscosity Kinetics. An Attempt to Identify a Site of Solvent Reorganizations around a Reactant. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 1803–1806.

(34) Kitaoka, S.; Nobuoka, K.; Miura, J.; Ohga, Y.; Ishikawa, Y. First Observation for Dynamic Solvent Effect in Ionic Liquids. *Chem. Lett.* **2016**, *45*, 385–387.

(35) Adam, W.; Grüne, M.; Diederling, M.; Trofimov, A. V. Temperature and Viscosity Dependence in the Stereoselective Formation of the Inverted Housane for the Photochemical Nitrogen Loss from the Deuterium-Stereolabeled Parent Diazabicyclo[2.2.1]-hept-2-ene. *J. Am. Chem. Soc.* **2001**, *123*, 7109–7112.

(36) Adam, W.; Corley, D. A.; Trofimov, A. V.; White, R. C. Viscosity Dependence of the Denitrogenation Quantum Yield in Azoalkane Photolysis: Experimental Evidence for Reversible Formation of the Diazenyl Diradical. *Org. Lett.* **2002**, *4*, 4277–4280.

(37) Adam, W.; Trofimov, A. V. Viscosity as an Experimental Tool in Studying the Mechanism of Stereoselective and Product-Selective Chemical Transformations through Frictional Impositions. *Acc. Chem. Res.* **2003**, *36*, 571–579.

(38) Adam, W.; Diederling, M.; Trofimov, A. V. Solvent Effects in the Photodenitrogenation of the Azoalkane Diazabicyclo[2.2.1]hept-2-ene: Viscosity- and Polarity-Controlled Stereoselectivity in Housane Formation from the Diazenyl Diradical. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1036–1039.

(39) Ebner, F.; Greb, L. An Isolable, Crystalline Complex of Square-Planar Silicon(IV). *Chem.* **2021**, *7*, 2151–2159.

(40) Kyushin, S.; Kurosaki, Y.; Otsuka, K.; Imai, H.; Ishida, S.; Kyomen, T.; Hanaya, M.; Matsumoto, H. Silicon–Silicon π Single Bond. *Nat. Commun.* **2020**, *11*, 4009.

(41) Yildiz, C. B.; Leszczyńska, K. I.; González-Gallardo, S.; Zimmer, M.; Azizoglu, A.; Biskup, T.; Kay, C. W. M.; Huch, V.; Rzepa, H. S.; Scheschkewitz, D. Equilibrium Formation of Stable All-Silicon Versions of 1,3-Cyclobutanediyl. *Angew. Chem., Int. Ed.* **2020**, *59*, 15087–15092.

(42) Nukazawa, T.; Iwamoto, T. An Isolable Tetrasilicon Analogue of a Planar Bicyclo[1.1.0]Butane with π -Type Single-Bonding Character. *J. Am. Chem. Soc.* **2020**, *142*, 9920–9924.

(43) Majhi, P. K.; Zimmer, M.; Morgenstern, B.; Scheschkewitz, D. Transition-Metal Complexes of Heavier Cyclopropenes: Non-Dewar–Chatt–Duncanson Coordination and Facile Si = Ge Functionalization. *J. Am. Chem. Soc.* **2021**, *143*, 8981–8986.

(44) Nukazawa, T.; Iwamoto, T. π -Conjugated Species with an Unsupported Si–Si π -Bond Obtained from Direct π -Extension. *Chem. Commun.* **2021**, *57*, 9692–9695.

(45) Wang, Z.; Yadav, P.; Abe, M. Long-Lived Localised Singlet Diradicaloids with Carbon–Carbon π -Single Bonding (C– π -C). *Chem. Commun.* **2021**, *57*, 11301–11309.

(46) Abe, M.; Akisaka, R. Is π -Single Bonding (C– π -C) Possible? A Challenge in Organic Chemistry. *Chem. Lett.* **2017**, *46*, 1586–1592.

(47) Abe, M. Diradicals. *Chem. Rev.* **2013**, *113*, 7011–7088.

(48) Abe, M.; Adam, W.; Hara, M.; Hattori, M.; Majima, T.; Nojima, M.; Tachibana, K.; Tojo, S. On the Electronic Character of Localized Singlet 2,2-Dimethoxycyclopentane-1,3-Diyl Diradicals: Substituent Effects on the Lifetime. *J. Am. Chem. Soc.* **2002**, *124*, 6540–6541.

(49) Abe, M.; Ye, J.; Mishima, M. The Chemistry of Localized Singlet 1,3-Diradicals (Biradicals): from Putative Intermediates to Persistent Species and Unusual Molecules with a π -Single bonded character. *Chem. Soc. Rev.* **2012**, *41*, 3808–3820.

(50) Abe, M.; Adam, W.; Heidenfelder, T.; Nau, W. M.; Zhang, X. Intramolecular and Intermolecular Reactivity of Localized Singlet Diradicals: The Exceedingly Long-Lived 2,2-Diethoxy-1,3-Diphenylcyclopentane-1,3-Diyl. *J. Am. Chem. Soc.* **2000**, *122*, 2019–2026.

(51) Wang, Z.; Akisaka, R.; Yabumoto, S.; Nakagawa, T.; Hatano, S.; Abe, M. Impact of the Macrocyclic Structure and Dynamic Solvent Effect on the Reactivity of a Localised Singlet Diradicaloid with π -Single Bonding Character. *Chem. Sci.* **2021**, *12*, 613–625.

(52) Akisaka, R.; Ohga, Y.; Abe, M. Dynamic Solvent Effects in Radical–Radical Coupling Reactions: An Almost Bottleable Localised Singlet Diradical. *Phys. Chem. Chem. Phys.* **2020**, *22*, 27949–27954.

(53) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. The Solvatochromic Comparison Method. 6. The π^* Scale of Solvent Polarities. *J. Am. Chem. Soc.* **1977**, *99*, 6027–6038.

(54) Nakagaki, T.; Sakai, T.; Mizuta, T.; Fujiwara, Y.; Abe, M. 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. *Chem. – Eur. J.* **2013**, *19*, 10395–10404.

(55) Ye, J.; Fujiwara, Y.; Abe, M. Substituent Effect on the Energy Barrier for σ -Bond Formation from π -Single-Bonded Species, Singlet 2,2-Dialkoxycyclopentane-1,3-Diyls. *Beilstein. J. Org. Chem.* **2013**, *9*, 925–933.

(56) Lu, X.; Reid, D. L.; Warkentin, J. Diaryloxycarbenes from Oxadiazolines. *Can. J. Chem.* **2001**, *79*, 319–327.

(57) Gao, Y.; Wu, Z.; Yu, L.; Wang, Y.; Pan, Y. Alkyl Carbazates for Electrochemical Deoxygenative Functionalization of Heteroarenes. *Angew. Chem., Int. Ed.* **2020**, *59*, 10859–10863.

(58) Hatano, M.; Sakamoto, T.; Mizuno, T.; Goto, Y.; Ishihara, K. Chiral Supramolecular U-Shaped Catalysts Induce the Multiselective Diels–Alder Reaction of Propargyl Aldehyde. *J. Am. Chem. Soc.* **2018**, *140*, 16253–16263.

(59) Hoga, H. E.; Olivieri, G. V.; Torres, R. B. Experimental Measurements of Volumetric and Acoustic Properties of Binary Mixtures of 1-Butyl-3-Methylimidazolium Hexafluorophosphate with Molecular Solvents. *J. Chem. Eng. Data* **2020**, *65*, 3406–3419.

(60) Zafarani-Moattar, M. T.; Majdan-Cegincara, R. Viscosity, Density, Speed of Sound, and Refractive Index of Binary Mixtures of Organic Solvent + Ionic Liquid, 1-Butyl-3-Methylimidazolium Hexafluorophosphate at 298.15 K. *J. Chem. Eng. Data* **2007**, *52*, 2359–2364.

(61) Spange, S.; Lungwitz, R.; Schade, A. Correlation of Molecular Structure and Polarity of Ionic Liquids. *J. Mol. Liq.* **2014**, *192*, 137–143.

(62) Carda–Broch, S.; Berthod, A.; Armstrong, D. W. Solvent Properties of the 1-Butyl-3-Methylimidazolium Hexafluorophosphate Ionic Liquid. *Anal. Bioanal. Chem.* **2003**, *375*, 191–199.