Long-lived localised singlet diradicaloids with carbon–carbon \(\pi\)-single bonding (C–\(\pi\)–C)

Zhe Wang, Pinky Yadav and Manabu Abe*

Localised singlet cyclopentane-1,3-diyl diradicaloids have been considered promising candidates for constructing carbon–carbon \(\pi\)-single bonds (C–\(\pi\)–C). However, the high reactivity during formation of the \(\sigma\)-bond has limited a deeper investigation of its unique chemical properties. In this feature article, recent progress in kinetic stabilisation based on the “stretch effect” and the “solvent dynamic effect” induced by the macrocyclic system is summarised. Singlet diradicaloids S-DR4a/b and S-DR4d containing macrocyclic rings showed much longer lifetimes at 293 K (14 \(\mu\)s for S-DR4a and 156 \(\mu\)s for S-DR4b in benzene) compared to the parent singlet diradicaloid S-DR2 having no macrocyclic ring (209 ns in benzene). Furthermore, the dynamic solvent effect in viscous solvents was observed for the first time in intramolecular \(\sigma\)-bond formation, the lifetime of S-DR4d increased to 400 \(\mu\)s in the viscous solvent glycerin triacetin at 293 K. The experimental results proved the validity of the “stretch effect” and the “solvent dynamic effect” on the kinetic stabilisation of singlet cyclopentane-1,3-diyl diradicaloids, and provided a strategy for isolating the carbon–carbon \(\pi\)-single bonded species (C–\(\pi\)–C), and towards a deeper understanding of the nature of chemical bonding.

Introduction

The molecular structures and reactivities of compounds are largely dependent on their bonding styles and electronic structures, respectively. In this context, both the \(\sigma\) and \(\pi\) bonds are well-known fundamental bonds in carbon–carbon bonding systems (Fig. 1a), wherein \(\sigma\)-bonds are energetically stronger than \(\pi\)-bonds. As a result, \(\pi\)-electronic systems play important roles in various molecular functions, such as light absorption and redox processes. As in ethylene, \(\pi\)-bonding is generally possible with a strong \(\sigma\)-bond framework. Molecules containing \(\pi\)-single bond (C–\(\pi\)–C) systems, in which carbon atoms are not connected by \(\sigma\)-bonding, are expected to show unique molecular properties due to small HOMO–LUMO energy gaps and planar four-coordinated carbon atoms (Fig. 1a).1–7

Zhe Wang was born in Qingdao, P. R. China. He received his bachelor’s degree (BEng) from the China University of Petroleum (East China) in 2017. He then joined the research group of Professor Dr Abe at Hiroshima University. He received his master’s degree (MSc) from the Hiroshima University in 2019 under the supervision of Professor Dr Manabu Abe. He is currently a PhD student at Hiroshima University. His research focuses on the kinetic stabilisation of singlet 2,2-dimethoxycyclopentane-1,3-diyl diradicals.

Pinky Yadav received her PhD in chemistry from the Indian Institute of Technology, Roorkee, India in 2017 under the guidance of Prof. M. Sankar. After a post-doctoral stint at the Technion-Israel Institute of Technology, Haifa, Israel under the supervision of Prof. Z. Gross (2017–2020), she moved to Hiroshima University to work with Prof. M. Abe as an Assistant Professor (specially appointed) in 2021. Her research interest focuses on the study of cyclopentane-1,3-diyl and porphyrinoid diradical systems.
In the period 1998–2000, our research group, in collaboration with Adam and Borden, reported that the ground state of cyclopentane-1,3-diyl diradicals DR1 and their most stable electronic configurations (i.e., the singlet and triplet state of spin multiplicity, indicated by the prefix “S-” and “T-”) can be controlled by the substituent X effect at the C2 carbon atom (Fig. 2a).8–10 In the case of cyclopentane-1,3-diyl species the singlet state has, in principle, a chance to possess the \( p \)-single bond (C–p–C).

The most stable ground state electronic configuration of the diradicaloids can be determined by through-space and through-bond interactions.11–16 As shown in Fig. 2b, the through-space interaction between the two \( p \) orbitals at the C1 and C3 positions produces two molecular orbitals, namely the bonding orbital \( \psi_S \) and the antibonding orbital \( \psi_A \). The through-bond interaction between the resulting bonding orbital \( \psi_S \) and the pseudo-\( p \)/\( p^* \) orbitals \( s/s^* \) of the C2 substituent determine the ground state spin multiplicity and the most stable electronic configuration. Thus, the low-lying \( s^* \) (in Fig. 2, X = an electron-withdrawing group, such as F or OR) can stabilise \( \psi_S \) to increase the energy spacing between \( \psi_S \) and \( \psi_A \), ultimately leading to the singlet ground state of DR1 with \( p \)-single bonding. On the other hand, the interaction with the high-lying \( \sigma (X = an electron-donating group such as H, CH3, or SiR3) destabilises \( \psi_S \), which results in \( \psi_A^* \) being higher in energy than \( \psi_S^* \) (Fig. 2c).17 In this case, singlet diradical species does not show \( \pi \)-single bonding between the radical–radical carbon centres. Thus, electron-withdrawing C2-substituents play a crucial role in the formation of \( \pi \)-single bonds in cyclopentane-1,3-diyl radicals DR1 and their most stable electronic configurations (i.e., the singlet and triplet state of spin multiplicity, indicated by the prefix “S-” and “T-”) can be controlled by the substituent X effect at the C2 carbon atom (Fig. 2a).8–10 In the case of cyclopentane-1,3-diyl species the singlet state has, in principle, a chance to possess the \( p \)-single bond (C–p–C).

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cyclopentane-1,3-diyl diradicals. Recently, singlet diradicaloids exhibiting B–B, Ge–Ge, and Si–Si π-single bonding have been experimental examined by Bertrand, Frenking, Iwamoto, Kyushin, and Scheschkewitz, and cyclobutane-1,3-diyls with C–C π-single bonding have been computationally predicted by Abe (Fig. 1b).

The thermodynamic stabilisation of the highly reactive singlet cyclopentane-1,3-diyl radical S-DR1 has been achieved by introducing aryl groups at the 1,3-positions to extend the spin-delocalisation. However, the thermodynamic stabilisation decreases the π-single bonding. The kinetic stabilisation of reactive species is a useful method for increasing the energy barrier of their chemical reactions to prolong their lifetimes (Fig. 3a). Previously, we have succeeded in the kinetic stabilisation of singlet diradicaloids exhibiting π-single bonding through the steric hindrance originating from the steric repulsion between the bulky aryl groups (Ar) at the C1 and C3 position, and the alkoxy groups (OR) at the C2 position (Fig. 3b). For example, the lifetime of S-DR3d (singlet diradical 3d, R1 = Tipp) was found to be 23.8 μs at 293 K, which is approximately 45 times longer than that of the parent S-DR3a (Fig. 4).

In 2012, a new concept of the “stretch effect” was computationally proposed by our research group for the kinetic stabilisation of singlet diradicaloids (S-DR) embedded in macrocyclic structures. The strain energies induced by the macrocyclic skeletons are proposed to increase during the σ-bond formation process. The σ-bond is expected to be stretched by the macrocyclic structure (Fig. 3bii). The increased molecular strain in the σ-bonded product (CP) energetically destabilises the transition states (TS) for the σ-bond formation. Thus, the singlet diradicaloids can be kinetically stabilised to increase their lifetimes. Experimental proof of the stretch effect was first reported in 2018 for S-DR4a and its dioctyl-substituted derivative S-DR4b with lifetimes of 14.0 and 14.2 μs, respectively at 293 K in benzene (Fig. 4). In 2021, S-DR4d in a smaller macrocycle with a naphthyl moiety was reported for the first time with a significantly longer lifetime (t_{293} = 155.9 μs in benzene at 293 K, Fig. 4) and the dynamic solvent effect in the σ-bond formation processes.

In this feature article, our focus will be on recent studies of the influence of the stretch effect and the solvent dynamic effect on kinetic stabilisation of localised singlet diradicaloids with π-single bond.

1. Molecular design of the stretch effect using quantum chemical calculations

The molecular design of the stretch effect should induce strain in σ-bonds that will lead to increases in the energy of the σ-bonded CP species. To gain such an effect, macrocyclic skeletons with planar structures were designed as shown in S-DR4a and S-DR4c. According to the computational results, the formation of cis-configured σ-bonded products (cis-CP) was kinetically favoured over the thermodynamically favoured trans-configured σ-bonded products (trans-CP). The stretch effect in
both molecules have been well proven by quantum chemical calculations using the (R/U)O97X-D/6-31G(d)31–33 level of theory, which suggests that the σ-bonded products, cis-CP4a/c and trans-CP4a/c, were destabilised by energies (ΔH_{DR-CP}) of 15.16/15.71 and 35.15/37.00 kJ mol\(^{-1}\), respectively, compared to cis-/trans-CP2 (Fig. 5 and Table 1). The increase of the molecular strain in the σ-bonded products was proven by computing the strain energies (SE) of macrocyclic species using isodesmotic reactions. As listed in Table 1, the destabilisation energies of the σ-bonded products CP4 (ΔH_{DR-CP}) were close to the strain energy relative to S-DR2 and S-DR4c, indicating that the increase of the energy of CP4 is mainly derived from the strained structures induced by the macrocyclic skeletons. The molecular strain is the key factor in achieving the energetic destabilisation of σ-bonded products. In addition, the energy barriers for the σ-bonded compounds in S-DR4 slightly increased compared to those in S-DR2, indicating destabilisation of the transition states TS4. These results suggest that S-DR4a and S-DR4c were kinetically stabilised by the stretch effect and were expected to be longer-lived than S-DR2.

The thermodynamic stabilisation derived from the macrocyclic structure in S-DR4c was compared with the parent S-DR2 (Scheme 1). The reaction enthalpy (ΔH) was calculated to be 1.45 kJ mol\(^{-1}\) at the O97X-D/6-31G(d) level of theory, indicating that the macrocyclic skeleton with the meta-connection of the phenyl ring has a negligible influence on thermodynamic stabilisation of the singlet state in comparison with S-DR2. Thus, introduction of the macrocyclic skeleton kinetically stabilises the singlet diradicals.

### Table 1 Strain energies calculated at the (R/U)O97X-D/6-31G(d) level of theory

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>SE</th>
<th>SE_{rel}</th>
<th>ΔH_{DR-CP}</th>
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<tr>
<td>1</td>
<td>S-DR2</td>
<td>a</td>
<td>5.11</td>
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<td>2</td>
<td>S-DR4a</td>
<td>a</td>
<td>8.92</td>
<td>0.00</td>
</tr>
<tr>
<td>3</td>
<td>cis-CP4</td>
<td>a</td>
<td>19.63</td>
<td>14.52</td>
</tr>
<tr>
<td>4</td>
<td>trans-CP4</td>
<td>a</td>
<td>43.66</td>
<td>34.74</td>
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<tr>
<td>5</td>
<td>c</td>
<td>19.97</td>
<td>14.87</td>
<td>15.71</td>
</tr>
<tr>
<td>6</td>
<td>c</td>
<td>45.08</td>
<td>36.16</td>
<td>37.00</td>
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293 K (Fig. 8, Table 2).\textsuperscript{29,30} During the flash photolysis of AZ4a and AZ4d, two transient species were observed at approximately 470 and 580 nm under a nitrogen atmosphere (Fig. 8a and b). It was found that these species show absorptions at \(\lambda_{470}\) nm, which were quenched by oxygen under air, while the species exhibiting 580 nm bands show identical decay rate constants under both nitrogen and air. In addition, the 470 nm species have similar lifetimes during the photolysis of AZ4a (\(\tau_{293} = 2.1\) ms, Fig. 8c) and AZ4d (\(\tau_{293} = 3.1\) ms, Fig. 8d) under a nitrogen atmosphere, indicating that this transient species is derived from the triplet excited state of the aromatic ring in the macrocyclic skeleton, as found in Fig. 7.\textsuperscript{29} The absorption band located at the 500–600 nm region was assigned to the \(p-p^*\) electronic transition of the \(p\)-single bond (C–\(p\)–C) of S-DR4. The lifetime of S-DR4a was found to be 14.0 ms in benzene at 293 K (Fig. 8e, entry 2 in Table 2), which was approximately 70 times longer compared to the non-cyclic S-DR2 (\(\tau_{293} = 209\) ns).\textsuperscript{35} A similar TA was also observed for S-DR4b bearing an alkyl chain (Table 2, entry 3). Furthermore, the lifetime of S-DR4b was determined to be 14.2 ms in benzene at 293 K, which was nearly identical to S-DR4a (entry 2), while the singlet diradicaloid S-DR4d exhibited a much longer lifetime of 155.9 ms under the same experimental conditions (Fig. 8f, entry 4 in Table 2),\textsuperscript{30} thereby it is demonstrated that the kinetic stabilisation induced by the macrocyclic ring plays a crucial role in increasing the lifetime.

Variable temperature TA (VT-TA) measurements were conducted to determine the activation parameters of the \(\sigma\)-bond formation process (i.e., \(E_a\), \(\log A\), \(\Delta H^\ddagger\), \(\Delta S^\ddagger\), and \(\Delta G^\ddagger\))\textsuperscript{29,30} As predicted by computational calculations, the activation energies and enthalpies of the ring-closing processes of S-DR4a, S-DR4b, and S-DR4d were increased by approximately 20, 20, and 30 kJ mol\(^{-1}\), respectively, compared to the corresponding values of S-DR2, and this was attributed to kinetic stabilisation of the singlet diradicals by the macrocyclic ring effect (Table 2, entries 1–4). In addition, the large \(\log A\) value (>12) suggests that the spin-allowed decay of the singlet diradicaloids took place. Although the activation entropies showed positive values for the various S-DR4 species, a negative value was found for the decay process of S-DR2.

TA analysis of AZ5 in Fig. 4, which is a byproduct of the synthesis of AZ4b, was conducted to understand the macrocyclic effect. As expected, the lifetime of S-DR5 was 620 ns, which is significantly shorter than that of S-DR4b (entry 5 in Table 2).\textsuperscript{29} The VT-TA experiments also revealed that the activation parameters of the decay process of S-DR5 were
similar to those of S-DR2. Thus, the stretch effect induced by the macrocyclic structure is the key factor in enhancing the lifetimes of singlet diradicaloids.

3. Influence of the stretch effect on the reactivity of CP4

To investigate the influence of the stretch effect on the reactivity of CP4b/d, benzene-d6 solutions of azoalkanes AZ4b and AZ4d were degassed and sealed under a nitrogen atmosphere in NMR tubes, and the photoreactions were directly monitored using 1H NMR spectroscopy (Fig. 9). The clean denitrogenation ($\Phi > 0.9$) of azoalkanes AZ4b and AZ4d quantitatively yielded the $\sigma$-bonded compounds trans-CP4b and trans-CP4d. The stereochernistry of the products was determined using Nuclear Overhauser effect measurements (NOE). Formation of the thermodynamically stable trans-CP2 was confirmed in the photolysis of AZ2, although a higher energy barrier was computed for the formation of the trans isomers compared to the cis isomers (Fig. 5). This contradiction was solved by conducting low-temperature NMR analysis, which shows the selective formation of the cis isomers was observed in the photolysis ($h\nu = 355$ nm) while their isomerisation to the trans isomers was detected under thermal conditions (vide infra in Fig. 10).

The $\sigma$-bonded compounds trans-CP4b and trans-CP4d show high reactivity towards oxygen at room temperature (i.e., 298 K) which results in the formation of oxygenated products 6–8. However, trans-CP2 was not decomposed under the same reaction conditions, but it was observed upon heating up to...
353 K in air. The structures of the oxygenated products obtained from \textit{trans}-CP4a and \textit{trans}-CP4b were similar to those obtained from \textit{trans}-CP2. All these products were derived from the endoperoxide intermediates (Scheme 2).

4. Product analyses at low temperatures

According to the computational studies (Fig. 5), \textit{cis}-CP4b/d should be the major photoproduct in the photochemical denitrogenation of AZ4b/d, as smaller energy barriers were computed for the \textit{cis} isomer compared to those of the \textit{trans} isomer. However, the exclusive formation of \textit{trans}-CP4b and \textit{trans}-CP4d at 298 K suggests that fast isomerisation took place from \textit{cis}-CP4b/d to \textit{trans}-CP4b/d via S-DR4b/d. This isomerisation should be suppressed at low temperatures owing to the relatively large energy barrier between S-DR4b/d and \textit{trans}-CP4b/d. To observe the kinetically favoured compound \textit{cis}-CP4b/d, low-temperature \textit{in situ} \textsuperscript{1}H NMR analyses of the photolysis of AZ4b and AZ4d were conducted in a degassed toluene-\textit{d}_8 solution in sealed NMR tubes (Fig. 10).

Interestingly, during the photolysis of AZ4b thermally labile species (signals a–d) were observed along with \textit{trans}-CP4b and unreacted AZ4b at 188 K using a 355 nm Nd:YAG laser. Signals a–d started to disappear with a concomitant increase in the signals corresponding to \textit{trans}-CP4b after a 15 min reaction in dark conditions (Fig. 10a). The photolysis reaction of AZ4d does not produce any new signals under direct irradiation at 199 K except those originating from \textit{trans}-CP4d (Fig. 10b). New signals (e–f) were observed during the irradiation of AZ4d at 199 K in the presence of the triplet sensitizer, benzophenone, which further converted into \textit{trans}-CP4d under dark conditions over 55 minutes (Fig. 10c). According to the activation energies determined using the VT-LFP experiments (Table 2), the lifetime of S-DR4b at 188 K is approximately 1 second while the lifetime of S-DR4d at 199 K is close to 13 seconds. The new signals observed during the low-temperature photolysis of AZ4b and AZ4d are relatively long-lived over approximately 6 minutes and possibly correspond to \textit{cis}-CP4b and \textit{cis}-CP4d, rather than S-DR4b and S-DR4d. Interestingly, after irradiation, the formation of \textit{trans}-CP4d at 199 K without a triplet sensitizer could be explained by the existence of the puckered-type diradical \textit{puc}-S-DR4d (Path A in Scheme 3), while the benzophenone-sensitisation gives \textit{cis}-CP4d, which involved the formation of a more stable planar \textit{pl}-S-DR4d (Path B in Scheme 3).

5. Solvent dynamic effect\textsuperscript{36} on the reactivity of singlet diradicaloids exhibiting the stretch effect

The influence of the solvent effect on the reactivities of singlet cyclopentane-1,3-diyli diradicaloids was examined in 13 solvents...
The correlation between the radical–radical coupling rate constant \( k \) and the solvent polarity \( \pi^* \) and viscosity \( \eta \) are shown in Fig. 11. For the non-cyclic diradical S-DR2, a good relationship between \( \log k \) and solvent polarity (Fig. 11a) was observed, although the data point obtained in glycerine triacetate was deviated from the linear correlation due to its high viscosity. For S-DR4d, the good correlation was not observed for either solvent polarity or viscosity alone (Fig. 11c and d). Thus, both the viscosity and polarity of the solvent should be considered in the solvent effect on the reactivity of singlet diradicals.

The contributions of solvent polarity and viscosity on the diradical lifetimes were analysed by regression analysis using eqn (1) with all data points shown in Table 3, which contains the polarity term \( \pi^* \), the viscosity term \( \eta \) and a constant \( C \) (Table 4). In the case of S-DR2, the polarity of the solvent was the dominant factor in determining the lifetime where coefficient \( A \) is much larger than coefficient \( B \). In contrast to S-DR2, coefficients \( A \) and \( B \) were of the same magnitude for S-DR4d, suggesting that the solvent polarity and viscosity both have a significant influence on the lifetime of S-DR4d. A good linear correlation between the experimental lifetime values and the predicted lifetime determined using eqn (1) was observed, despite the fact that the data points corresponding to benzene and toluene in S-DR4d and chloroform in S-DR2 deviated slightly from the fitting line (Fig. 12).

**Summary and outlook**

Approximately a decade has passed since the concept of the “stretch effect” emerged. Our research group has reported two studies on S-DR4a/b and S-DR4d based on experimental results

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**Table 3** Lifetimes \( \tau_{293} \) of S-DR2 and S-DR4d at 293 K in different solvents with varying polarity (\( \pi^* \)) and viscosity (\( \eta \)) properties

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>( \pi^*/\text{kcal mol}^{-1} )</th>
<th>( \eta/\text{cP} )</th>
<th>( \tau_{293}/\text{ms} ) of S-DR2</th>
<th>( \tau_{293}/\text{ms} ) of S-DR4d</th>
<th>( \tau_{293}/\text{ns} )</th>
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<tr>
<td>1</td>
<td>( n )-Hexane</td>
<td>-0.11 (1)</td>
<td>0.31 (2)</td>
<td>90.1 (1)</td>
<td>N.D.</td>
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<tr>
<td>2</td>
<td>Carbon tetrachloride</td>
<td>0.21 (2)</td>
<td>0.97 (10)</td>
<td>187.1 (5)</td>
<td>17.2 (1)</td>
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<tr>
<td>3</td>
<td>Diethyl ether</td>
<td>0.24 (3)</td>
<td>0.24 (1)</td>
<td>136.3 (2)</td>
<td>46.8 (5)</td>
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<tr>
<td>4</td>
<td>Ethyl acetate</td>
<td>0.45 (4)</td>
<td>0.46 (5)</td>
<td>182.6 (4)</td>
<td>73.1 (8)</td>
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<tr>
<td>5</td>
<td>Toluene</td>
<td>0.49 (5)</td>
<td>0.59 (7)</td>
<td>170.4 (3)</td>
<td>116.5 (10)</td>
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<td>1,4-Dioxane</td>
<td>0.49 (5)</td>
<td>1.18 (11)</td>
<td>250.6 (8)</td>
<td>61.4 (6)</td>
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<td>Benzene</td>
<td>0.55 (7)</td>
<td>0.65 (8)</td>
<td>210.0 (6)</td>
<td>155.9 (11)</td>
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<tr>
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<td>Acetone</td>
<td>0.62 (8)</td>
<td>0.32 (3)</td>
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<td>27.9 (3)</td>
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<td>Glycerin triacetate</td>
<td>0.63 (9)</td>
<td>23.00 (13)</td>
<td>517.3 (13)</td>
<td>400.2 (12)</td>
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<td>10</td>
<td>Chloroform</td>
<td>0.69 (10)</td>
<td>0.58 (6)</td>
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<td>Dichloromethane</td>
<td>0.73 (11)</td>
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<td>12</td>
<td>1,2-Dichloroethane</td>
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<td>0.79 (9)</td>
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<td>2.24 (12)</td>
<td>393.5 (11)</td>
<td>95.1 (9)</td>
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**Fig. 11** Correlations between the radical–radical coupling rate constant \( \log k \) and the solvent polarity \( \pi^* \) and viscosity \( \eta \) for (a and b) S-DR2 and (c and d) S-DR4d.
of the kinetic stabilisation of localised singlet diradicals using the stretch effect. S-DR4a and S-DR4d showed an approximate lifetime of 14 μs, whereas the lifetime of S-DR4d, which was constructed with a smaller macrocyclic ring, was found to be 1000 times longer (i.e., 156 μs at 293 K in benzene) compared to the non-macrocyclic S-DR2. Further, the π-bonded compound trans-CP4 was found to be thermally labile under aerobic conditions due to the molecular strain derived from the macrocyclic skeleton, which resulted in rapid decomposition via an endoperoxide intermediate. However, the non-macrocyclic trans-CP2 was stable under air even at 353 K. As predicted by theoretical calculations, isomerisation from cis-CP4 to trans-CP4 was observed at >199 K using in situ 1H NMR analyses.

According to the time-resolved laser flash photolysis measurements, the lifetime of non-macrocyclic S-DR2 was mainly determined by the solvent polarity. However, in the case of S-DR4d, the solvent polarity and viscosity both played a crucial role in controlling the reactivity of S-DR4d in the solution phase. Currently, our research group is conducting further molecular designs and syntheses of singlet diradicals with π-single bonding for more detailed studies. The concept of kinetic stabilisation based on the “stretch effect” and the “solvent dynamic effect” will also be further applied to the kinetic stabilisation of other reactive species in future work.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
This work was supported by JSPS KAKENHI Grant Number 21H01921 (MA).

Fig. 12 Correlation diagram between the experimental and theoretically calculated lifetime for (a) S-DR2 and (b) S-DR4d.

Table 4 Regression analyses for the lifetimes and solvent parameters of S-DR2 and S-DR4d

<table>
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<tr>
<th>Coefficient</th>
<th>A</th>
<th>B</th>
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<tr>
<td>S-DR2</td>
<td>278.43</td>
<td>11.06</td>
<td>88.69</td>
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<td>S-DR4d</td>
<td>15985.07</td>
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<td>45794.25</td>
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Notes and references