Received: 27 June 2016 | Revised: 6 August 2016 | Accepted: 9 August 2016

DOI 10.1002/poc.3636

WILEY Journal of Physical Organic Chemistry

SPECIAL ISSUE ARTICLE

Adiabatic process of higher electronically excited states: luminescence from an excited state biradical generated by irradiation of benzophenone-substituted cyclopropanes†

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Adiabatic photochemical reactions of cyclopropanes possessing a benzophenone moiety (*trans*- and *cis*-**5**), which generate a luminescent excited biradical $^{1}\mathbf{6}^{\bullet\bullet}{*}$, were studied. Various photochemical and spectroscopic techniques were used for this purpose. Excitation (350 nm, n,π* band) of **5** at 77 K affords the lowest excited state $^{1}\mathbf{5}{*}$ that undergoes intersystem crossing to form $^{3}\mathbf{5}{*}$, which deactivates through phosphorescence. In contrast, 295-nm excitation (π,π* band) of **5** affords the higher electronically excited state $^{1}\mathbf{5}{**}$, which undergoes adiabatic C–C bond cleavage reaction to form the excited biradical $^{1}\mathbf{6}^{\bullet\bullet}{*}$ that luminesces at 630 nm. The results suggest that **5** follows 2 photoreaction modes depending on the excitation wavelength, a finding that disobeys Kasha's rule.

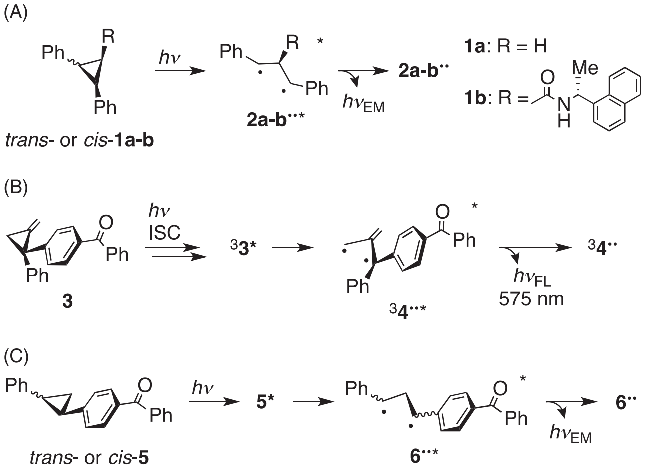
KEYWORDS

anti-Kasha's rule, biradical, C–C bond cleavage reaction, higher excited state, multiplicity

1 | INTRODUCTION

Photochemical homolytic bond cleavage reactions[1–3] that generate ground state radical pairs[4] are termed nonadiabatic processes. On the other hand, similar bond cleavage reactions that produce electronically excited states of radical pairs or biradicals are referred to as adiabatic processes.[3–5] Observations of luminescence associated with adiabatic photochemical reactions have been described previously. Examples of this phenomenon include fluorescence associated with excited state intramolecular proton transfer of azolylphenols[6–11] and chemiluminescence of 1,2-dioxetane derivatives.[12,13]

Photoreactions of 1,2-diphenylcyclopropanes (**1**), reported by Becker and Ramamurthy, also display "unusual" luminescence behavior associated with excited state biradical generation by photoinduced C–C bond cleavage (Scheme 1A).[14,15] Although many mechanistic studies of this photoreaction have been performed,[16–18] the detailed mechanism still remains unclear. In a recent study, we uncovered an adiabatic photoreaction of the methylenecyclopropane derivative **3** possessing a benzophenone



SCHEME 1 "The excited state C–C bond cleavage-luminescence" phenomena of (A) **1a-b**, (B) **3**, and (C) **5**

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†This article is published in Journal of Physical Organic Chemistry as a special issue on the Symposium on Reactive Intermediates and Unusual Molecules held at Pacifichem 2015.

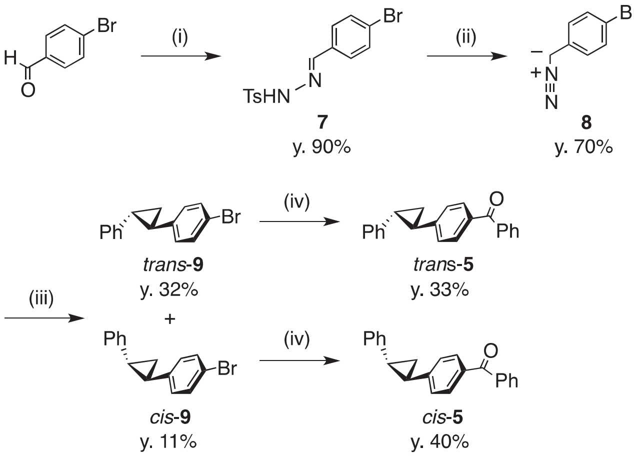
(BP) moiety (Scheme 1B) and demonstrated that emission in this system is a result of triplet-triplet fluorescence (575 nm) of the excited (noted by *) biradical ^{3}**4**$^{\bullet\bullet}$*.[19–23] We refer to this phenomenon as "excited state C–C bond cleavage-luminescence."[24,25] Analyses of transient absorption and emission results, obtained using double laser flash photolysis (LFP), showed that ^{3}**4**$^{\bullet\bullet}$* is formed adiabatically from ^{3}**3***, which itself is generated by rapid intersystem crossing (ISC) in ^{1}**3*** owing to the presence of the BP moiety. This observation suggests that introduction of 1 BP moiety into the methylenecyclopropane system is sufficient to enable ISC to be competitive with other undesirable reactions of ^{1}**3***.[26–28]

In the current investigation, we used the enhanced ISC effect of a BP moiety on a diarylcyclopropane system[29–31] to control the nature of electronic excited states and luminescence properties of biradicals generated by homolytic C–C bond cleavage. For example, n,π*-excitation ($\lambda_{\mathrm{EX}} = 355$ nm) of the BP moiety in *trans*- and *cis*-1-(4-benzoylphenyl)-2-phenylcyclopropane (**5**, Scheme 1C) should lead to production of biradical-derived luminescence, because it is expected that ^{3}**5***, formed by rapid ISC, will undergo adiabatic bond cleavage reaction to give excited biradical ^{3}**6**$^{\bullet\bullet}$*. However, the results show that ^{3}**5*** does not produce ^{3}**6**$^{\bullet\bullet}$* but rather it generates the ground state triplet biradical ^{3}**6**$^{\bullet\bullet}$. In contrast, luminescence occurs from upon π,π*-excitation (λ_{EX} = 295 nm) of **5**. In this case, the higher excited state (denoted by **) ^{1}**5**** is generated that, contrary to Kasha's rule, undergoes adiabatic C–C bond cleavage to form the excited biradical **6**$^{\bullet\bullet}$*. The results of a photochemical and spectroscopic investigation that led to the observation of adiabatic formation of **6**$^{\bullet\bullet}$* from ^{1}*trans*-**5**** are described below.

2 | RESULTS AND DISCUSSION

2.1 | Synthesis of *trans*- and *cis*-5 bearing BP moieties

The *trans*- and *cis*- isomers of the BP moiety containing a diarylcyclopropane **5** were synthesized starting with 4-bromobenzaldehyde using the procedure shown in Scheme 2. Condensation of 4-bromobenzaldehyde and tosylhydrazine in methanol gave 4-bromobenzaldehyde tosylhydrazone (**7**),[32] which upon treatment with $NaOCH_2CH_2OH$ generated 4-bromophenyldiazomethane (**8**). Addition of the carbene, formed by photodeazetation reaction of **7**, to styrene yielded a mixture of *trans*- and *cis*-1-(4-bromophenyl)-2-phenylcyclopropane (*trans*- and *cis*-**9**),[33,34] which were separated by using preparative gel permeation chromatography (GPC). Independent lithiation reactions of *trans*- and *cis*-**9** followed by addition of *N*,*N*-dimethylbenzamide produced *trans*- and *cis*-**5**.



SCHEME 2 Routes used for synthesis of *trans*- and *cis*-**5**. Reagents and conditions: (i) H_2NNHTs/methanol, rt; (ii) $NaOCH_2CH_2OH$/ethylene glycol/^{n}hexane, reflux; (iii) *hν*/BP/styrene, rt; and (iv) ^{n}BuLi/$PhCON(CH_3)_2$/THF

2.2 | Ultraviolet-Visible absorption spectra

The ultraviolet-visible absorption spectra of methylcyclohexane solutions of *trans*- and *cis*-**5** (MCH, Figure 1, red and blue) contain intense π,π* and weak n,π* bands at 280 and 340 nm, respectively. The π,π* bands of *trans*- and *cis*-**5** occur at longer wavelengths than that of BP (Figure 1, black) as a result of electronic coupling between the aryl ketone and phenylcyclopropane moieties.

2.3 | Matrix isolation experiments

In a manner similar to BP, *trans*- and *cis*-**5** do not exhibit photoluminescence in MCH at room temperature. Excitation of BP in a degassed MCH matrix at 77 K with either 350 (n,π*, Figure 2A, black) or 295 nm (π,π*, Figure 2B, black) light gives rise to a typical phosphorescence signal at 419 nm. Excitation of *trans*-**5** in a degassed MCH matrix at 77 K by using 350-nm light (n,π*) results in the formation of a relatively broad phosphorescence band (Figure 2A, blue), which is associated with emission from ^{3}BP*. In contrast, excitation of this substance at 295 nm (π,π* band) results in formation of a broad emission band at 630 nm, which is assignable to fluorescence of the singlet excited biradical ^{1}**6**$^{\bullet\bullet}$* (Figure 2B, blue), together with phosphorescence from ^{3}*trans*-**5***. The excitation spectrum of *trans*-**5** obtained monitoring emission at 419 nm (λ_{DET}) contains 2

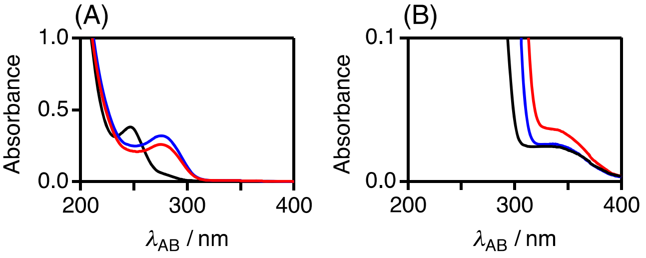


FIGURE 1 Ultraviolet-visible absorption spectra of (black) BP and (red) *trans*- and (blue) *cis*-**5** (A, 0.01mM; B, 0.1mM) in MCH at room temperature

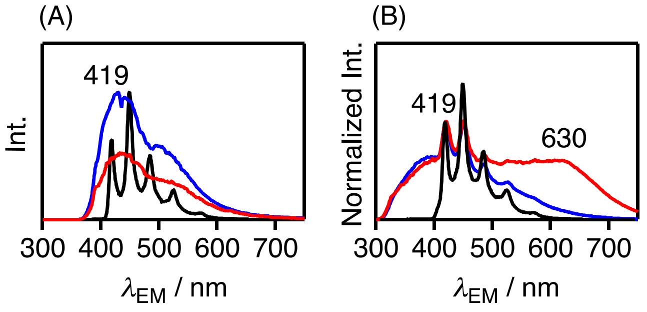


FIGURE 2 Emission spectra obtained by excitation at (A) λ_{EX} = 350 nm and (B) λ_{EX} = 295 nm of (black) BP and (red) *trans*- and (blue) *cis*-**5** (1mM) in the degassed MCH matrices at 77 K

bands at 266 and 340 nm (Figure 3, black). In contrast, the excitation spectrum of this substance obtained monitoring emission at 630 nm contains a broad band centered at 279 nm (Figure 3, red). In the case of *cis*-**5** (Figure 2B, red), intense phosphorescence from ^{3}*cis*-**5*** (419 nm) and relatively weak fluorescence from $^1\mathbf{6}^{\bullet\bullet}$* (630 nm) are also observed. The only difference between the behaviors of *trans*- and *cis*-**5** is the efficiencies of their primary photochemical processes. The combined results indicate that *trans*-**5** undergoes 2 photoreactions that occur via respective lower and higher energy ^{1}*trans*-**5*** and ^{1}*trans*-**5****. In addition, the results suggest that photochemical reaction of *trans*-**5** to form the excited biradical $^1\mathbf{6}^{\bullet\bullet}$* takes place upon excitation exclusively at 295 nm.

2.4 | *Cis*-*Trans* isomerization

Photoirradiation (350 nm) of *trans*- and *cis*-**5** (10mM) in degassed $CDCl_3$ at room temperature efficiently promotes *cis*-*trans* isomerization (Figure 4, Scheme 3).[35–42] This process probably proceeds via biradical $\mathbf{6}^{\bullet\bullet}$ (see below).

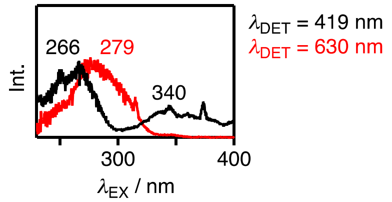


FIGURE 3 Excitation spectra of *trans*-**5** (1mM, λ_{DET} = 419 [black] and 630 nm [red]) in the degassed MCH matrix at 77 K

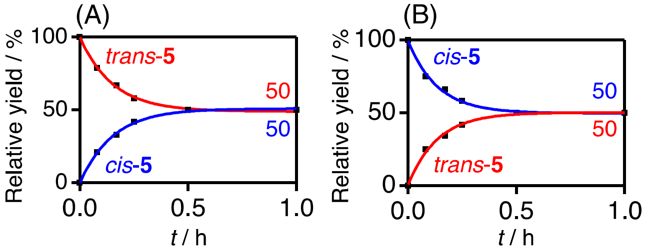


FIGURE 4 Relative yields (determined by using proton nuclear magnetic resonance spectroscopy) as a function of time in the photoisomerization reactions of (A) *trans*- and (B) *cis*-**5** (10mM) in $CDCl_3$

The photostationary state ratio of the stereoisomers is described by Equation 1,

$$\frac{[trans\text{-}\mathbf{5}]}{[cis\text{-}\mathbf{5}]} = \alpha \times \frac{\varepsilon_{cis\text{-}5} \times \Phi_{\mathrm{RO}cis\text{-}5^*}}{\varepsilon_{trans\text{-}5} \times \Phi_{\mathrm{RO}trans\text{-}5^*}} \qquad (1)$$

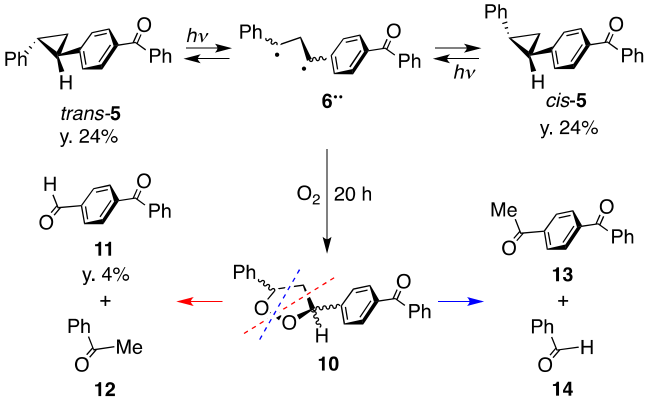
where α, ε, and Φ_{RO} are the ratio of branching *trans*-**5**/*cis*-**5** in the ring-closing reaction of $\mathbf{6}^{\bullet\bullet}$, molar absorption coefficients of the isomers of **5**, and quantum yields for the ring-opening reaction of **5*** to form $\mathbf{6}^{\bullet\bullet}$, respectively. Note that no significant difference exists between $\varepsilon_{trans\text{-}5}$ and $\varepsilon_{cis\text{-}5}$ (Figure 1B). The fact that [*trans*-**5**]/[*cis*-**5**] at the photostationary state is almost unity (Figure 4) indicates that α is ca 1, if Φ_{RO} for *trans*-**5*** ($\Phi_{\mathrm{RO}trans\text{-}5^*}$) and *cis*-**5*** ($\Phi_{\mathrm{RO}cis\text{-}5^*}$) is the same.

Photoirradiation of a CH_2Cl_2 solution of *trans*-**5** under an air atmosphere for 20 hours produces keto-aldehyde **11** in a 4% yield and trace amounts of the carbonyl compounds **12** to **14**, together with recovered *cis*- and *trans*-**5** both in 24% yields (Scheme 3). The products of this photoreaction originate from endoperoxide **10**[43] that is the primary photoproduct formed by trapping of $\mathbf{6}^{\bullet\bullet}$ with molecular oxygen ($^3O_2$). In accord with this proposal is the observation that transient absorption of $\mathbf{6}^{\bullet\bullet}$ observed in the LFP experiment decays faster in aerated relative to degassed CCl_4 (see below).

2.5 | Transient absorption spectroscopy

To gain additional insight into the intermediates that participate in the photoisomerization reactions of *trans*- and *cis*-**5**, LFP (355 nm) studies were performed. LFP (355-nm excitation) of *trans*- and *cis*-**5** at room temperature in degassed benzene or CH_2Cl_2 does not give rise to formation of absorption bands even after 50 ns even though the photoisomerization reaction occurs under similar conditions. It is likely that the reason for this is that C–C bond formation in the intermediate biradical $\mathbf{6}^{\bullet\bullet}$ occurs rapidly in these solvents.

In contrast, LFP of *trans*- or *cis*-**5** in degassed CCl_4 at room temperature leads to production of a transient



SCHEME 3 Products of photooxygenation reactions of *trans*- and *cis*-**5** in aerated CH_2Cl_2 solutions (isolated yields following 20-hour irradiation periods)

absorption band at 380 nm (Figure 5, decay time <90 μs), which is assigned to $\mathbf{6}^{\bullet\bullet}$. The characteristics of this band correspond to the electronic transitions of $^1\mathbf{6}^{\bullet\bullet}$ and/or $^3\mathbf{6}^{\bullet\bullet}$ (Figure 6) that are calculated by using time-dependent density functional theory.[44] Decay of the 380-nm transient absorption band, which takes place in a second-order manner with 2 rate constants of $k_{\mathrm{DECAY}} = 1.1 \times 10^4$ and 1.6×10^3 s^{-1}, is accelerated in the presence of air, possibly because of trapping of $\mathbf{6}^{\bullet\bullet}$ by $^3O_2$. The fact that no absorption band is observed in the 530-nm region, which is expected for absorption by the ^{3}BP* moiety,[45] suggests that rapid C–C bond cleavage of $^3\mathbf{5}^*$ occurs to form $^3\mathbf{6}^{\bullet\bullet}$ at room temperature. The most likely reason for the observation made using a CCl_4 solution is kinetic and/or thermodynamic stabilization of the triplet state $^3\mathbf{6}^{\bullet\bullet}$, which cannot afford the singlet product **5** directly.[46]

2.6 | Analysis of time-resolved emission

LFP (355 nm) of *trans*- and *cis*-**5** in degassed CCl_4 at room temperature gives rise to nearly identical weak fluorescence bands at 666 nm arising in both cases from $^1\mathbf{6}^{\bullet\bullet}*$ (Figure 7 A and C). Interestingly, this emission is not observed immediately following (red) but rather 10 ns (orange) after the laser pulse. The existence of this delay time strongly suggests that $\mathbf{6}^{\bullet\bullet}*$ is generated via a 2-photon process. The emission band corresponding to $\mathbf{6}^{\bullet\bullet}*$ arising from *trans*- or *cis*-**5** decays with a single exponential function with a lifetime of ca 260 ns (Figure 7B and D). This finding indicates that luminescence from $\mathbf{6}^{\bullet\bullet}*$ is fluorescence rather than phosphorescence.

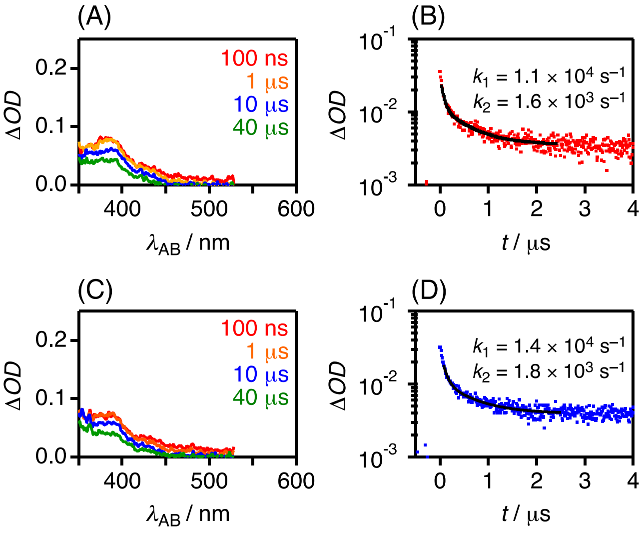


FIGURE 5 Transient absorption spectra obtained upon laser flash photolysis (355 nm) of (A) *trans*- and (C) *cis*-**5** (2mM) in degassed CCl_4 at room temperature and their time-dependent changes at 380 nm of (B) *trans*- and (D) *cis*-**5**

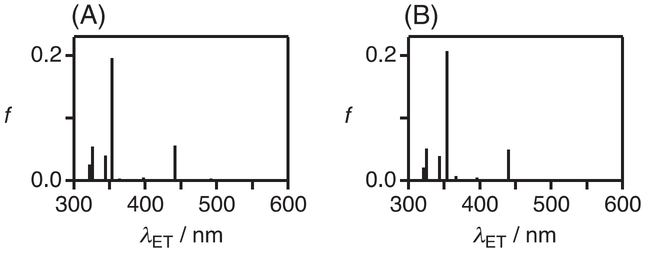


FIGURE 6 Electronic transitions of (A) $^1\mathbf{6}^{\bullet\bullet}$ and (B) $^3\mathbf{6}^{\bullet\bullet}$ calculated at the time-dependent–UB3LYP/cc-pVDZ level of theory

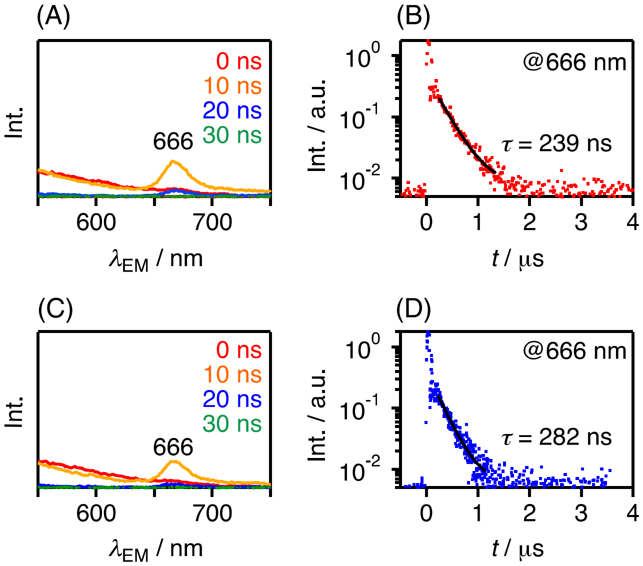


FIGURE 7 Time-resolved emission spectra and the corresponding time-profiles observed upon laser flash photolysis (355 nm) of (A and B) *trans*- and (C and D) *cis*-**5** (2mM) in degassed CCl_4 at room temperature

Insight into the proposal that formation of $^1\mathbf{6}^{\bullet\bullet}*$ involves a stepwise 2-photon absorption process was gained by determining the relationship between the intensity of the excitation laser pulse (I_L/mJ pulse^{-1}) and that of emission (I_E, Figure 8A). If $^1\mathbf{6}^{\bullet\bullet}*$ is generated via a 2-photon process, I_E should be proportional to ${I_L}^2$. However, the experimental results demonstrate that I_E is dependent on both I_L and ${I_L}^2$ (Figure 8B, solid) in the following relationship:

$$I_E = 0.00213 I_L + 0.00066 {I_L}^2$$

This finding indicates that a 1-photon process directly generating $^1\mathbf{6}^{\bullet\bullet}*$ occurs concurrently with a 2-photon

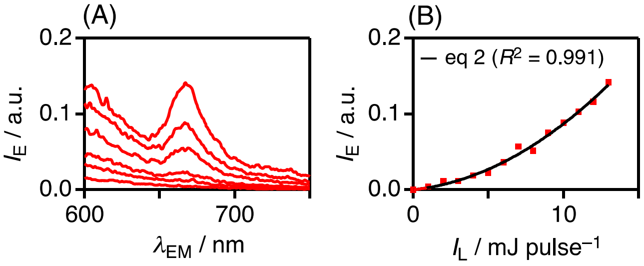


FIGURE 8 A, Emission spectra obtained upon laser flash photolysis (355 nm) of *trans*-**5** (2mM) in degassed CCl_4 at room temperature when I_L is 1, 3, 5, 8, 10, and 13 mJ pulse^{-1} (from the bottom to the top). B, Relationship of I_E against the I_L

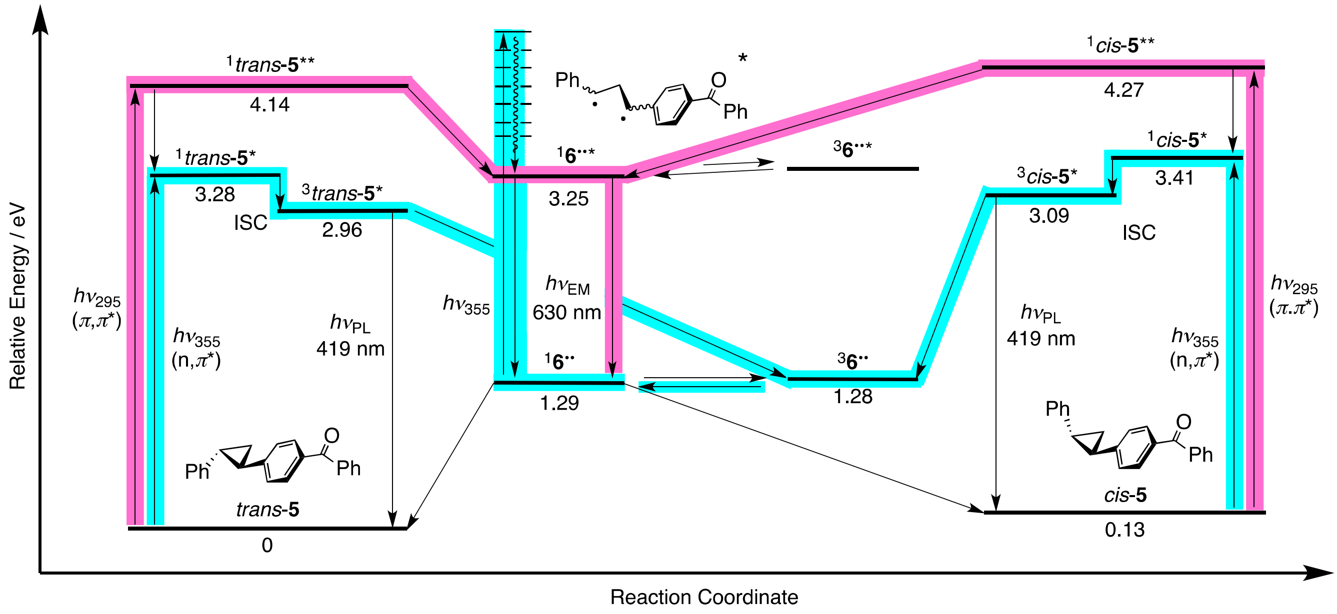


FIGURE 9 Energy diagrams for photoreactions of *trans*- and *cis*-**5**. Energy levels are determined by using wavelengths of luminescence and the results of density functional theory calculations [(U)B3LYP/cc-pVDZ]. Pink and light blue correspond to the formation of ^{1}**6**$^{\bullet\bullet}$* via adiabatic and stepwise 2-photon pathways, respectively. ISC, intersystem crossing

process. When I_L is 10 mJ pulse^{-1}, the ratio of the relative contribution of the 1- and 2-photon processes is calculated to be 24/76. Note that the I_E value at 666 nm used in this calculation includes not only fluorescence of ^{1}**6**$^{\bullet\bullet}$* but also the broad phosphorescence (Figure 8A) of ^{3}**5***, which is also generated via a 1-photon process. Thus, the actual contribution of the 2-photon process in the 666-nm band should be greater than 76%.

2.7 | Analysis of energy diagram

To analyze the energy changes occurring in photoreactions of *trans*- and *cis*-**5**, an energy diagram (Figure 9) was constructed using luminescence wavelengths and the energies obtained by using density functional theory [(U)B3LYP/cc-pVDZ] calculations. In this diagram, all energies are given relative to that of *trans*-**5**. The respective energies of ^{1}*trans*-**5*** and ^{3}*trans*-**5***, which are formed by 355-nm excitation and ISC, respectively, are determined to be 3.28 and 2.96 eV, according to the literature.[47] Because the energies of ^{1}**6**$^{\bullet\bullet}$ and ^{3}**6**$^{\bullet\bullet}$ are computed to be 1.29 and 1.28 eV, respectively, ring-opening reactions of ^{3}*trans*-**5*** to form ^{3}**6**$^{\bullet\bullet}$ occur in a highly exergonic manner. Note that the energy gap between ^{1}**6**$^{\bullet\bullet}$ and ^{3}**6**$^{\bullet\bullet}$ is negligibly small and, as a result, ^{1}**6**$^{\bullet\bullet}$ and ^{3}**6**$^{\bullet\bullet}$ should be in rapid thermal equilibrium.

Based on its fluorescence wavelength, biradical (^{1}**6**$^{\bullet\bullet}$*) should have an energy of at least 3.25 eV. Thus, adiabatic ring-opening reaction of ^{3}*trans*-**5*** (2.96 eV) to form ^{3}**6**$^{\bullet\bullet}$* (and then ^{1}**6**$^{\bullet\bullet}$*) is energetically unfavorable. Therefore, to explain its efficient formation, ^{1}**6**$^{\bullet\bullet}$* could be formed adiabatically from a higher excited state, ie, ^{1}*trans*-**5**** (Figure 9, pink). Of course, this proposal is contrary to the Kasha's rule, which states that internal conversion from the higher excited states to the lowest ones with the same multiplicity should be faster than any other processes involving light emissions.[48,49] Consequently, owing to conservation of multiplicity, the luminescent biradical most likely is the excited singlet ^{1}**6**$^{\bullet\bullet}$* rather than its triplet counterpart.

The energy of ^{1}*trans*-**5**** is 4.14 eV, owing to its absorption wavelength of 295 nm, and is sufficiently high for adiabatic and exergonic formation of **6**$^{\bullet\bullet}$* (>3.25 eV). Analyses of the excitation spectrum corresponding to the 630-nm emission band (Figure 3, blue) also support the conclusion that anti-Kasha behavior is taking place in that ^{1}*trans*-**5**** is converted directly to ^{1}**6**$^{\bullet\bullet}$*. Although luminescence associated with ^{1}**6**$^{\bullet\bullet}$* occurs following 355-nm LFP (Figure 8A), formation of this excited singlet biradical from an energetic viewpoint likely involves a stepwise 2-photon process (Figure 9, light blue). Note that the mechanism for the luminescence phenomenon of *cis*-**5** is similar to that of *trans*-**5**, except for the fact that *cis*-**5** has a higher energy than *trans*-**5** by 0.13 eV, and formation of ^{1}**6**$^{\bullet\bullet}$* from *cis*-**5** is less efficient than that from *trans*-**5**, possibly as a consequence of stereoelectronic factors (eg, differences in their ability to form an intramolecular exciplex).[50]

3 | CONCLUSIONS

In the investigation described above, we elucidated the mechanism for adiabatic photochemical reactions of *trans*- and *cis*-**5** by using photochemical (product analysis) and photophysical (spectroscopic) techniques. The results suggest that the excited biradical ^{1}**6**$^{\bullet\bullet}$* is not generated in an adiabatic reaction following n,π*-excitation that forms the lowest singlet excited state ^{1}**5***. Rather, ^{1}**6**$^{\bullet\bullet}$* is produced by C–C bond cleavage in the upper singlet excited state ^{1}**5**** formed by π,π^*-excitation. n,π^*-Excitation (350 nm) of **5** affords ^{3}**5*** through ISC of ^{1}**5*** but it does not produce **6**$^{\bullet\bullet}$* owing to the existence of a reasonably high energy gap.

Thus, the system probed in this effort has provided an important example of a process that breaks Kasha's rule.[1,2] In contrast, 355-nm (n,π^*) excitation of **5** does generate **6**$^{\bullet\bullet}$*, likely through a stepwise 2-photon pathway. The results of this effort demonstrate that exceptional stabilization of biradicals, such as by incorporating them in a trimethylenemethane moiety, is required to be able to promote adiabatic hemolytic C–C bond cleavage reactions from excited triplet states. It is significant that investigations of adiabatic photoreactions, like those performed in this study, contribute important information needed for the development of a new field of photochemistry, which focuses on photophysical and photochemical properties of higher electronically excited states.

4 | EXPERIMENTAL SECTION

4.1 | Preparation of substrates

4.1.1 | 4-Bromobenzaldehyde tosylhydrazone (7)

A mixture of H_2NNHTs (1.0 g, 5.5 mmol) and 4-bromobenzaldehyde (0.93 g, 5.0 mmol) in methanol was stirred at room temperature for 2 hours. After removal of the solvents, recrystallization of the resulting solid from methanol afforded **7** (1.49 g, 23 mmol, 85%) as colorless needles. **7**: mp 171°C to 174°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 2.42 (s, 3H), 7.33 (AA′XX′, $J = 8.4$ Hz, 2H), 7.45 (AA′BB′, $J = 8.7$ Hz, 2H), 7.50 (AA′BB′, $J = 8.7$ Hz, 2H), 7.69 (s, 1H), 7.79 (s, 1H), 7.87 (AA′XX′, $J = 8.4$ Hz, 2H).

4.1.2 | 4-Bromophenyldiazomethane (8)

Metallic sodium (0.210 g, 7.20 mmol) was slowly added to 10 mL of dry ethylene glycol to prepare a $NaOCH_2CH_2OH$ solution. The substrate **7** (1.27 g, 3.60 mmol) was slowly added to the solution and vigorously stirred. Ten milliliters of ^{n}hexane was added to the resultant solution, and the mixture was warmed with vigorous stirring for 5 minutes at 70°C to 80°C. The organic layer was removed by pipette and another 10 mL of ^{n}hexane was added with continued stirring. The procedure was repeated a total of 5 times. The combined organic extracts were washed with aqueous NaOH and brine. After filtration, the solvent was removed to afford **8** (0.553 g, 2.81 mmol, 78%) as red solid. Compound **8**[51] slowly decomposes in organic solution with evolution of N_2 at ambient temperature even in the dark. **8**: ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 4.90 (s, 1H), 6.78 (AA′XX′, $J = 4.5$ Hz, 2H), 7.38 (AA′XX′, $J = 4.5$ Hz, 2H); IR (ATR) $\nu = 814.8$, 1006.7, 1068.4, 1182.2, 1372.1, 1487.8, and 2044.2 cm^{-1}.

4.1.3 | *Trans*- and *cis*-1-(4-bromophenyl)-2-phenylcyclopropane (*trans*- and *cis*-9)

Under Ar atmosphere, **8** (0.79 g, 4.0 mmol) and BP (4.0 g, 22.0 mL) in 20 mL of styrene were photoirradiated with Rayonet Lamp (50 W, $\lambda_{\text{EX}} = 350$ nm) for 12 hours. The color of the solution turned yellow. After removal of the excess amount of styrene under reduced pressure, purification using column chromatography (silica gel, toluene) and preparative GPC afforded *trans*- (0.88 g, 3.21 mmol, 32%) and *cis*-**9** (0.42 g, 1.52 mmol, 11%)[48] as colorless oil. *trans*-**9**: ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 1.38 to 1.50 (m, 2H), 2.08 to 2.15 (m, 2H), 7.25 to 7.35 (m, 4H), 7.40 to 7.43 (m, 5H). *cis*-**9**: ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 1.25 to 1.40 (m, 2H), 2.35 to 2.55 (m, 2H), 6.77 (d, $J = 2.7$ Hz, 2H), 6.90 (d, $J = 2.7$ Hz, 2H), 7.02 to 7.40 (m, 5H).

4.1.4 | *Cis*-1-(4-benzoylphenyl)-2-phenylcyclopropane (*cis*-5)

Under Ar atmosphere at −78°C, ^{n}BuLi (2 M in ^{n}hexane, 1.14 mL, 2.3 mmol) was added dropwise to a 5.0 mL of THF solution containing *cis*-**9** (322 mg, 1.18 mmol). After stirring for 15 minutes, $PhCON(CH_3)_2$ (343 mg, 2.3 mmol) in 5 mL of THF was added dropwise to the mixture. After stirring for 3 hours, the mixture was allowed to warm to room temperature and quenched with aqueous NH_4Cl. The organic layer was extracted with ether (30 mL × 3) and washed with brine. After removal of the solvents, the residual mixture was purified using column chromatography (silica gel, toluene) and preparative GPC. Recrystallization of the resulting solid from methanol afforded *cis*-**5** (139 mg, 0.47 mmol, 40%) as colorless powder. *cis*-**5**: mp 42°C to 43°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 1.44 to 1.60 (m, 2H), 2.49 to 2.66 (m, 2H), 6.98 to 7.20 (m, 7H), 7.40 to 7.46 (m, 2H), 7.52 to 7.57 (m, 1H), 7.67 to 7.70 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta_{\pi\pi\mu}$ 12.2, 24.4, 25.7, 126.2, 128.1 (2C), 128.4 (2C), 128.7, 129.5 (2C), 129.9 (2C) 130.1 (2C), 132.3 (2C), 134.9, 137.7, 138.2, 144.6, 196.7; IR (KBr) 702, 1280, 1603, and 1647 cm^{-1}; Anal. Calcd for $C_{22}H_{18}O$: C 88.56 H 6.08 O 5.36; Found: C 88.60 H 6.14.

4.1.5 | *Trans*-1-(4-benzoylphenyl)-2-phenylcyclopropane (*trans*-5)

Under Ar atmosphere at −70°C, ^{n}BuLi (1.6 M in ^{n}hexane, 0.94 mL, 1.5 mmol) was added dropwise to a 5.0 mL of THF solution containing *trans*-**9** (273 mg, 0.84 mmol). After stirring for 15 minutes, $PhCON(CH_3)_2$ (224 mg, 1.5 mmol) in 5 mL of THF was added dropwise to the mixture. After stirring for 3 hours, the mixture was allowed to warm to room temperature and quenched with aqueous NH_4Cl. The organic layer was extracted with ether (30 mL × 3) and washed with brine. After removal of the solvents, the residual mixture was purified using column chromatography (silica gel, toluene) and preparative GPC. Recrystallization of the resulting solid from ^{n}hexane afforded *trans*-**5** (83 mg, 0.28 mmol, 33%) as colorless powder. *trans*-**5**[52]: mp 58°C to 59°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ_{ppm} 1.51 to 1.61 (m, 2H), 2.20 to 2.30 (m, 2H), 7.15 to 7.34 (m, 7H), 7.46 to 7.51 (m, 2H), 7.56 to 7.61 (m, 1H), 7.75 to 7.81 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) $\delta_{\pi\pi\mu}$ 19.2, 28.3, 29.3, 125.6 (2C), 126.0 (2C), 128.5 (2C), 128.7 (2C), 130.2 (2C), 131.0 (2C), 132.4 (2C), 135.2, 138.2, 142.0, 148.2, 196.3; IR (KBr) 687.1, 752.1, 1283.4, 1444.4, 1605.5, and 1643.1 cm^{-1}; Anal. Calcd for $C_{22}H_{18}O$: C 88.56 H 6.08 O 5.36; Found: C 88.63 H 6.05.

4.1.6 | Laser flash photolysis

LFP was performed using a Spectra Physics, Quanta-Ray GC-100 (355 nm, fwhm = 8 ns) Nd:YAG laser. Sample solutions were degassed with 5 freeze (77 K)-pump (0.1 mmHg)-thaw (room temperature) cycles. Suitable cutoff filters were used for the measurements.

4.1.7 | Quantum chemical calculations

Geometry optimizations were performed with the cc-pVDZ basis set, using the (U)B3LYP method. No imaginary frequencies were found. Electronic transitions were computed using the time-dependent–(U)B3LYP method with the cc-pVDZ basis set. All calculations were performed on the Gaussian 09 program.[41]

ACKNOWLEDGMENTS

Y.M. gratefully acknowledges Sasakawa Scientific Research (23-307) and Program to Disseminate Tenure Tracking System, MEXT, Japan. Y.M. and H.I. acknowledge the financial supports of Grant-in-Aid for Innovative area “Stimuli-responsive Chemical Species” (no. JP24109009) from JSPS. H.I. gratefully acknowledges financial supports in the form of a Grant-in-Aid for Innovative Area “π-space” (nos. JP21108520 and JP23108718), the Scientific Research (B) (nos. JP20044027 and JP23350023), and the Challenging Exploratory Research (nos. JP21655016 and JP24655037) from JSPS. E.O. acknowledges financial supports in the form of a Grant-in-Aid for Young Scientist (B) (no. JP24750044) and the Challenging Exploratory Research (no. JP26620034) from JSPS.

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How to cite this article: Matsui Y., Oishi T., Ohta E., and Ikeda H. (2016), Adiabatic process of higher electronically excited states: luminescence from an excited state biradical generated by irradiation of benzophenone-substituted cyclopropanes, *J. Phys. Org. Chem.*, doi: 10.1002/poc.3636