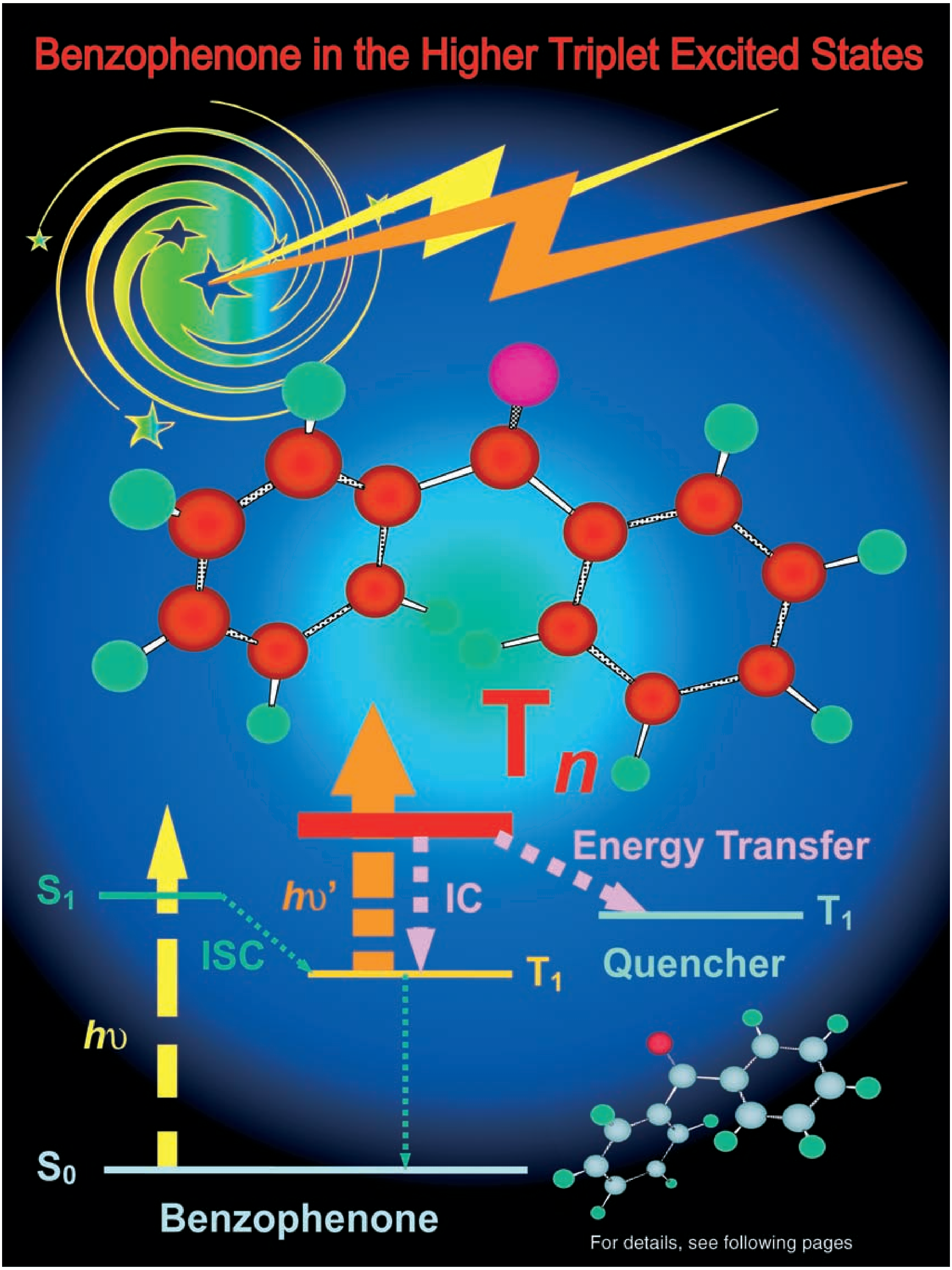
Benzophenone in the Higher Triplet Excited States
T_n
Energy Transfer
S_1
$h\nu'$
IC
T_1
ISC
T_1
Quencher
$h\nu$
S_0
Benzophenone
For details, see following pages

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Higher Triplet Excited States of Benzophenones and Bimolecular Triplet Energy Transfer Measured by Using Nanosecond–Picosecond Two-Color/Two-Laser Flash Photolysis

Xichen Cai, Masanori Sakamoto, Mamoru Fujitsuka, and Tetsuro Majima*[a]

Abstract: The lifetimes of benzophenone in the higher triplet excited state (BP(T_n)) and several BP derivatives in the T_n states were measured directly to be $\tau_{Tn}=37\pm7$ ps and 20–33 ps, respectively, by using the nanosecond–picosecond (ns–ps) two-color/two-laser flash photolysis method. Based on the direct measurements of τ_{Tn} of BP(T_n), the triplet energy transfer (TET) from BP(T_n) to quenchers (Q), such as carbon tetrachloride (CCl_4), benzene (Bz), and *p*-dichlorbenzene (DCB), was investigated. The fast TET from BP(T_n) to Q can be attributed to the lifetime-dependent quenching process, according to the Ware theoretical model of the bimolecular energy transfer reaction. The contribution of the lifetime-dependent term on k_{TET} was 27, 60, and 86% for CCl_4, Bz, and DCB as the Q of BP(T_n), respectively, indicating that the TET from BP(T_n) to Q is influenced not only by τ_{Tn}, but also by the size of Q.

Keywords: benzophenone · excited states · flash photolysis · laser chemistry · photochemistry

Introduction

Benzophenone (BP), one of the most important compounds in photochemistry, has been intensively studied for a long time.[1–5] BP in the lowest triplet excited state (T_1) (T_1-state energy, $E_{T1}=289\,\mathrm{kJ\,mol^{-1}}$), generated through intersystem crossing (ISC) from the singlet excited state (S_1) in a 100% yield upon photoirradiation, is widely used as the reference and triplet sensitizer to produce other organic molecules in the T_1 state with lower E_{T1} than BP(T_1).[5–8] Because BP(T_1) is so important, the study of BP in the higher triplet excited state (T_n, $n\geq2$) is also very attractive.[9–14] Obi and his coworkers described the hydrogen abstraction reaction of BP(T_n) from solvent molecules.[10] Later, they found that dissociation of BP(T_n) depends on the excitation wavelength. Rapid dissociation of BP(T_n) occurred upon irradiation of BP(T_1) with the 308 nm laser, but not with the 532 nm laser.[12,15] McGimpsey and Scaiano reported triplet energy transfer (TET) from BP(T_n) to benzene (Bz) used as solvent.[11] Recently, we reported the TET from BP(T_n) to various quenchers (Q) to give Q(T_1), and the sequential TET from Q(T_1) to BP.[13,16] It was found that in the case of *p*-dichlorobenzene (DCB) as Q, the sequential TET from DCB(T_1) to BP occurred with a yield of 100%; however, the yield for Bz as Q was not 100%, because of the competitive reactions from Bz(T_1).[11,13,16] No sequential TET process was observed for carbon tetrachloride (CCl_4) as Q, because of the rapid C–Cl bond cleavage of $CCl_4(T_1)$ to give $CCl_3^{\bullet}$ and $Cl^{\bullet}$. The lifetimes of BP(T_n) (τ_{Tn}) and several BP derivatives in the T_n states have been estimated from the dependence of the quenching efficiency on the concentration of Q ([Q]).[13] However, without the direct measurements of τ_{Tn}, the reaction mechanism from BP(T_n) to Q cannot be fully clarified. Here, we report the direct measurements of the τ_{Tn} value and bimolecular TET rate constant (k_{TET}) from BP(T_n) to Q by using the nanosecond–picosecond (ns–ps) two-color/two-laser flash photolysis method.

Results and Discussion

Direct measurement of τ_{Tn} of BP(T_n) by using ns–ps two-color/two-laser flash photolysis: The transient absorption

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Supporting Information for this article is available on the WWW under http://www.chemeurj.org/ or from the author: Direct measurement of τ_{Tn} of several BP derivatives in the T_n states by using ns–ps two-color/two-laser flash photolysis, and spectral changes of BP(T_1) during ns–ps two-color/two-laser flash photolysis of BP in CCl_4 and Bz.

spectrum of BP(T_1) with an absorption peak at 525 nm was observed during the 355 nm laser (laser pulse duration, 5 ns) flash photolysis of BP (7.0×10^{-3} M) in an Ar-saturated acetonitrile (AN) solution at room temperature (Figure 1). The bleaching of the BP(T_1) absorption at 525 nm and complete recovery were observed upon the second 532 nm laser (laser pulse duration, 30 ps) irradiation at 100 ns after the first 355 nm laser irradiation (Figures 1 and 2). Because BP(S_0) has no absorption at 532 nm, only BP(T_1) is excited with the second 532 nm laser irradiation. The bleaching of BP(T_1) indicates that BP(T_1) is excited to give BP(T_n). The complete recovery indicates that BP(T_n) decays to reproduce BP(T_1). The $\tau_{\mathrm{T}n}$ value was estimated to be 37 ± 7 ps, by applying the single exponential function to the recovery of transient absorption of BP(T_1) (Figure 2 inset). The recovery of BP(T_1) can be attributed to the internal conversion (IC). According to the energy gap law, $\tau_{\mathrm{T}n}$ can be expressed as $\tau_{\mathrm{T}n}^{-1}=k_{\mathrm{IC}}\approx10^{13}\exp(-\alpha\Delta E)$, in which ΔE(eV) is the energy gap between the T_1 and T_n states, and α is a constant less than 5 eV^{-1}.[8] The T_n state energy ($E_{\mathrm{T}n}$) of BP was calculated to be 403 kJ mol^{-1}, by assuming that $\alpha=5$ eV^{-1}. Because the 532 nm photon energy (225 kJ mol^{-1}) is larger than the energy gap between the T_1 and T_n states ($\Delta E_{\mathrm{T}n-\mathrm{T}1}=$ 114 kJ mol^{-1}), the 532 nm laser irradiation of BP(T_1) generates BP(T_m, $m\geq n$), from which the IC process generates BP(T_n), followed by BP(T_1) (Scheme 1).

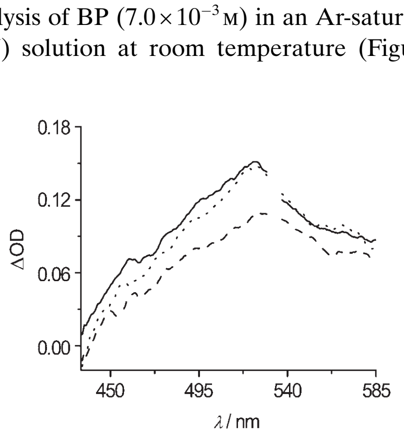


Figure 1. Transient absorption spectra observed at 50 ps before (solid line), 40 ps after (broken line), and 180 ps after (dotted line) the 532 nm 30 ps laser flash, during the ns–ps two-color/two-laser flash photolysis of BP (7.0×10^{-3} M) in Ar-saturated AN at RT by using the pump/probe system. The time delay of the second 532 nm 30 ps laser after the first 355 nm ns laser was 100 ns.

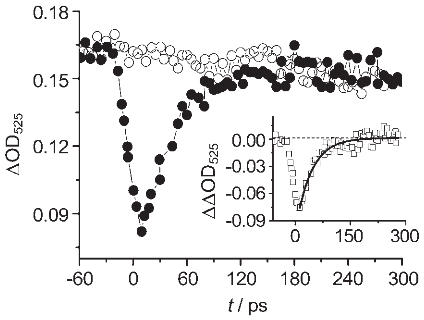
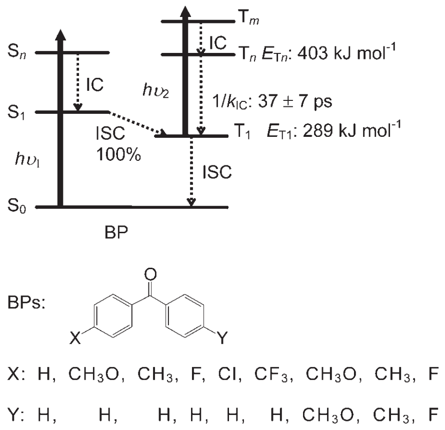


Figure 2. Time profiles of the transient absorption at 525 nm, assigned to BP(T_1), during the irradiation of one laser (open circles) and two lasers (closed circles). The delay time of the second 532 nm 30 ps laser after the first 355 nm ns laser was 100 ns. The inset (open squares) shows the time profile obtained by subtraction of the open circles from the closed circles. The solid line is a fitted curve, assuming the single exponential function.



Scheme 1. Schematic energy diagram of BP: $h\nu_1$, the first 355 nm ns laser. $h\nu_2$, the second 532 nm 30 ps laser; dotted lines indicate radiationless processes; IC, internal conversion; ISC, intersystem crossing; BPs, BP derivatives.

Usually, the k_{IC} values from the S_n state to the S_1 state, or from the T_n state to the T_1 state, are expected to be in the range of 10^{11}–10^{13} s^{-1}.[8] However, the electronic deactivation from BP(T_n) to BP(T_1) occurs slowly at $k_{\mathrm{IC}}=\tau_{\mathrm{T}n}^{-1}\sim3\times10^{10}$ s^{-1}. The small k_{IC} may be attributed to a “strongly avoided” crossing between two potential surfaces of BP(T_n) and BP(T_1). Large $\Delta E_{\mathrm{T}n-\mathrm{T}1}$ values (~110 kJ mol^{-1}) lead to the slow transition from BP(T_n) to BP(T_1).[8] The slow electronic deactivation of anthracene and its derivatives in the T_2 state to those in the T_1 state has been reported, because of the large $\Delta E_{\mathrm{T}2-\mathrm{T}1}$ (~130 kJ mol^{-1}) values.[17–19] Recently, a lifetime of chrysene(T_2) of 45 ± 7 ps was measured directly by using the ns–ps two-color/two-laser flash photolysis method.[20] The electronic deactivation from chrysene(T_2) to chrysene(T_1) occurs at $k_{\mathrm{IC}}=\tau_{\mathrm{T}n}^{-1}\sim2\times10^{10}$ s^{-1}. Therefore, the slow electronic deactivation from the T_n state to the T_1 state is not unique to BP. The slow internal conversion from the T_n state to the T_1 state could be observed for various compounds with a large $\Delta E_{\mathrm{T}n-\mathrm{T}1}$ value.

Similarly, the $\tau_{\mathrm{T}n}$ values of several BP derivatives in the T_n states (BPs(T_n)) were measured directly (Figure S1, Supporting Information), and the $E_{\mathrm{T}n}$ values were also calculated, as summarized in Table 1.

It was revealed that the introduction of a substituent to BP tends to decrease the $\tau_{\mathrm{T}n}$ value. This tendency was predicted from results of our previous work based on the bimolecular quenching of BPs(T_n).[13]

Table 1. The lifetimes ($\tau_{\mathrm{T}n}$) of BP and several substituted benzophenones (BPs, p-X-C_6H_4C(=O)C_6H_4-Y-p') in the T_n states (BP(T_n) and (BPs(T_n), respectively), the energies of the T_1 and T_n states (E_{T1} and $E_{\mathrm{T}n}$, respectively), and the energy gap between BPs(T_n) and BPs(T_1) ($\Delta E_{\mathrm{T}n-\mathrm{T1}}$).[a]

X	H	CH_3O	CH_3	F	Cl	CF_3	CH_3O	CH_3	F
Y	H	H	H	H	H	H	CH_3O	CH_3	F
$\tau_{\mathrm{T}n}$ [ps]	37±7	28±9	31±7	32±7	31±5	20±5	33±9	32±5	31±4
E_{T1} [kJ mol^{-1}]	289	290	290	292	288	285	292	290	294
$E_{\mathrm{T}n}$ [kJ mol^{-1}]	403	399	401	403	399	387	404	401	405
$\Delta E_{\mathrm{T}n-\mathrm{T1}}$ [kJ mol^{-1}]	114	109	111	111	111	102	112	111	111

[a] E_{T1}, triplet excited-state energy of the T_1 state, from reference [7]; $E_{\mathrm{T}n}$, triplet excited-state energy of the T_n state, calculated by using the energy gap law based on the $\tau_{\mathrm{T}n}$ value with $\alpha = 5$ eV^{-1}.

TET from BP(T_n) to Q: Previously, the TET from BP(T_n) to Q, such as DCB, Bz, and CCl_4, was investigated by using ns–ns two-color/two-laser flash photolysis.[13,16] The complete recovery of BP(T_1), due to the TET from Q(T_1) to BP, was observed in the case of DCB, but incomplete recovery and no recovery were observed in the cases of Bz and CCl_4, respectively. To clarify the TET process from BP(T_n) to Q, the ns–ps two-color/two-laser flash photolysis of BP in CCl_4 and Bz was performed. A fast-response streak camera detection system was employed to reveal the photoinduced processes. The transient absorption spectral changes of BP(T_1) during the ns–ps two-color/two-laser flash photolysis of BP in CCl_4 and Bz are shown in Figure S2 of the Supporting Information. The time profiles of the transient absorption of BP(T_1) in Ar-saturated CCl_4 during the ns laser flash photolysis and the ns–ps two-color/two-laser flash photolysis are shown in Figure 3.

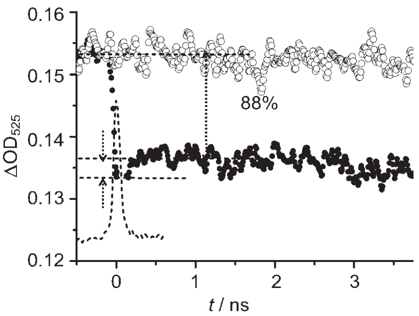
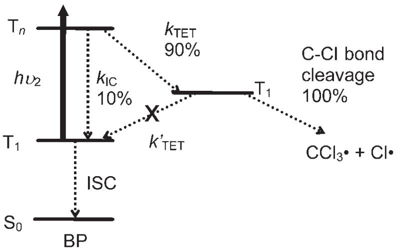


Figure 3. Kinetic traces of ΔOD_{525} during the 355 nm ns laser irradiation (open circles) and the ns–ps two-color/two-laser irradiation (closed circles) of BP (7.0×10^{-3} M) in Ar-saturated CCl_4 at RT. The time profile of a 532 nm 30 ps laser flash is shown as the broken line. The broken arrow lines show the ratio of unrecovered component of BP(T_1).



Scheme 2. Schematic energy diagram of BP(T_n) generation and decay processes. $h\nu_2$, the second 532 nm 30 ps laser; dotted lines indicate radiationless and reaction processes; IC, internal conversion; ISC, intersystem crossing.

The bleaching of BP(T_1) was observed upon the second 532 nm laser irradiation. After the second laser flash, only 12% of the bleaching was recovered promptly, and 88% was not recovered (Figure 3). The prompt recovery similar to $\tau_{\mathrm{T}n}$ indicates that a part of BP(T_n) decays to BP(T_1) by means of IC. The unrecovered component of BP(T_1) indicates that the TET from BP(T_n) to CCl_4 (k_{TET}) resulted in the rapid decomposition of CCl_4(T_1) through cleavage of the C–Cl bond to give $CCl_3^{\bullet}$ and $Cl^{\bullet}$ ([Eq. (1)–(3)] and Scheme 2):

$$\mathrm{BP(T}_n) \xrightarrow{k_{\mathrm{IC}}} \mathrm{BP(T_1)} \tag{1}$$

$$\mathrm{BP(T}_n) + \mathrm{CCl_4} \xrightarrow{k_{\mathrm{TET}}} \mathrm{BP} + \mathrm{CCl_4(T_1)} \tag{2}$$

$$\mathrm{CCl_4(T_1)} \rightarrow {}^{\bullet}\mathrm{Cl} + {}^{\bullet}\mathrm{CCl_3} \tag{3}$$

Similarly, no recovered component of BP(T_1) was observed at various [CCl_4] (0.1–2.0 M) in AN.[13,16] These results indicate that the k_{TET}[CCl_4] value is sufficiently large for the competitive occurrence with k_{IC} from BP(T_n) to BP(T_1). The generation of $CCl_3^{\bullet}$ and $Cl^{\bullet}$ according to Equation (3) was confirmed by the observation of the Bz/Cl complex with the absorption peak at 495 nm in the reaction system including Bz.[16]

Kinetic traces of BP(T_1) at 525 nm in Ar-saturated Bz during the ns laser flash photolysis and the ns–ps two-color/two-laser flash photolysis are shown in Figure 4.

The bleaching of BP(T_1) was also observed upon the second 532 nm 30 ps laser irradiation. After the second laser flash, 41% of the bleaching was not recovered. In contrast to the kinetic traces observed in CCl_4, the slow recovery indicates the TET from Bz(T_1) to BP. This slow recovery was well fitted by assuming pseudo-first-order kinetics. The bimolecular rate constant (k'_{TET}) was calculated to be 1.2×10^{10} M^{-1}s^{-1}, indicating that the sequential TET from Bz(T_1) to BP occurred at the diffusion-controlled rate constant (k_{diff}) in Bz ($k_{\mathrm{diff}} = 1.1\times10^{10}$ M^{-1}s^{-1}, 25 °C).[7] The lack of recovered component of BP(T_1) indicates that the yield of the

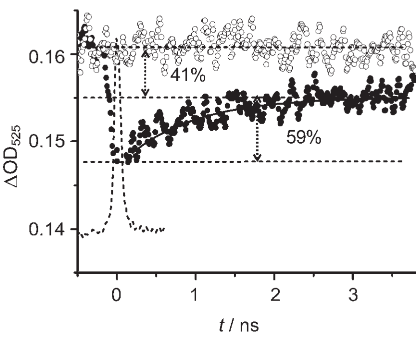


Figure 4. Kinetic traces of ΔOD_{525} during the 355 nm ns laser irradiation (open circles) and the ns–ps two-color/two-laser irradiation (closed circles) of BP (7.0×10^{-3} M) in Ar-saturated Bz at RT. The solid line is a fitted curve, assuming the pseudo-first-order exponential function. The time profile of a 532 nm 30 ps laser flash is shown as a broken line. The broken arrow lines show the ratio of recovered component and unrecovered component of $BP(T_1)$, respectively.

TET from $Bz(T_1)$ to BP is not 100 % because of other reaction pathways from $Bz(T_1)$. The possible pathways are summarized in Equations (4)–(8) and Scheme 3:

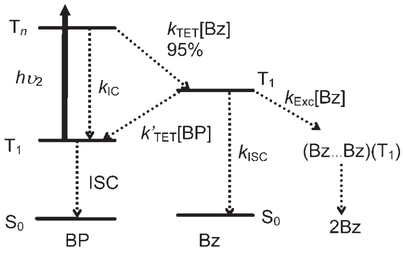
$$BP(T_n)\xrightarrow{k_{IC}}BP(T_1) \tag{4}$$

$$BP(T_n)+Bz\xrightarrow{k_{TET}}BP+Bz(T_1) \tag{5}$$

$$Bz(T_1)+BP\xrightarrow{k'_{TET}}Bz+BP(T_1) \tag{6}$$

$$Bz(T_1)+Bz \rightarrow (Bz\cdots Bz)(T_1) \tag{7}$$

$$(Bz\cdots Bz)(T_1) \rightarrow 2\,Bz \tag{8}$$



Scheme 3. Schematic energy diagram of $BP(T_n)$ generation and decay processes. $h\nu_2$, the second 532 nm 30 ps laser; dotted lines indicate radiationless and reaction processes; IC, internal conversion; ISC, intersystem crossing.

As possible competitive processes of the TET from $Bz(T_1)$ to BP, ISC from $Bz(T_1)$ to $Bz(S_0)$, and other reactions, such as the formation of the Bz triplet excimer $[(Bz\cdots Bz)(T_1)]$ are expected.[21–25] The phosphorescence spectrum of the halogen-substituted Bz triplet excimer, which is expected to have a "T" conformation, has been reported to show a peak at around 500 nm.[21–24] On the other hand, the phosphorescence from [3*n*]cyclophanes ($n=2,4,5$), in which two Bz rings are stacked in a face-to-face manner, has been observed in the region of 470–515 nm.[26] Therefore, the energy of $(Bz\cdots Bz)(T_1)$ is expected to be 232–255 kJ mol^{-1}, which is lower than that of $BP(T_1)$. Thus, the formation of $(Bz\cdots Bz)(T_1)$ is a possible deactivation pathway for $Bz(T_1)$. The TET from $Bz(T_1)$ to BP only partly occurred, as indicated by incomplete recovery. The rate constant of the formation of $(Bz\cdots Bz)(T_1)$ (k_{Exc}) can be calculated from $(k_{TET}[Bz]/(k_{IC}+k_{TET}[Bz]))\times((k_{ISC}+k_{Exc}[Bz])/(k_{ISC}+k'_{TET}[BP]+k_{Exc}[Bz]))=0.41$, in which k_{TET} is the TET rate constant from $BP(T_n)$ to Bz (see below). The k_{Exc} was estimated to be 3.5×10^{7} M^{-1}s^{-1}, based on the reported lifetime of $Bz(T_1)$, 470 ± 50 ns.[27]

The k_{TET} value of $BP(T_n)$ to Q depends on τ_{T_n} and Q: The TET from $BP(T_n)$ to Q occurred competitively with IC from $BP(T_n)$ to $BP(T_1)$. Based on the τ_{T_n} value, the k_{TET} value of $BP(T_n)$ to Q can be calculated from the plot of $(\Delta\Delta OD_{525})^{-1}$ vs $[Q]^{-1}$ [Eq. (9)],[28,29]

$$(\Delta\Delta OD_{525})^{-1} = \beta+\beta(k_{TET}\tau_{T_n}[Q])^{-1} \tag{9}$$

in which β is a constant that depends on the experimental conditions. From the plots of $(\Delta\Delta OD_{525})^{-1}$ vs $[Q]^{-1}$, a linear line with an intercept of β and a slope of $\beta(k_{TET}\tau_{T_n})^{-1}$ was obtained. The plots of $(\Delta\Delta OD_{525})^{-1}$ vs $[DCB]^{-1}$, $[Bz]^{-1}$, and $[CCl_4]^{-1}$ are shown in Figure 5.

The k_{TET} value of $BP(T_n)$ to DCB was calculated to be 1.4×10^{11} M^{-1}s^{-1}. Similarly, the k_{TET} values of $BP(T_n)$ to Bz

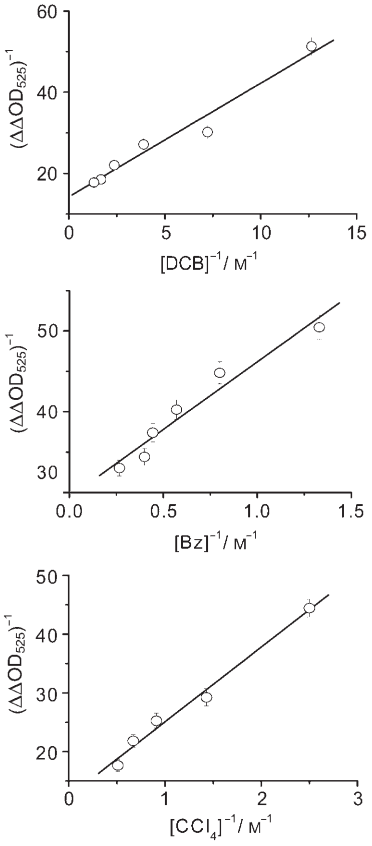


Figure 5. Plots of $(\Delta\Delta OD_{525})^{-1}$ vs $[DCB]^{-1}$, $[Bz]^{-1}$, and $[CCl_4]^{-1}$.

and CCl_4 were calculated to be $4.7\times10^{10}\,\text{M}^{-1}\text{s}^{-1}$ and $2.6\times10^{10}\,\text{M}^{-1}\text{s}^{-1}$, respectively. The ratio of the decay of BP(T_n) through the TET and IC in CCl_4 or Bz can be calculated from the relationship $k_{\text{TET}}[\text{Q}]/(k_{\text{IC}}+k_{\text{TET}}[\text{Q}])$, and was found to be 0.90, indicating that 90% of BP(T_n) decayed through the TET in CCl_4. This result agreed with the observation that 88% of BP(T_1) was not recovered, as seen in Figure 3. Similarly, about 95% of BP(T_n) was quenched by the TET in Bz, although the recovered component, due to IC from BP(T_n) to BP(T_1), was not clearly observed in Figure 4 because of the minor contribution.

The fast TET from BP(T_n) to Q can be attributed to the lifetime-dependent quenching process, according to the Ware theoretical model of the bimolecular energy transfer reaction [Eq. (10)],[19,30]

$$k_{\text{TE}T} = k_{\text{diff}}+k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5} \tag{10}$$

in which $k_{\text{diff}}=4\pi N\sigma D$, N is the Avogadro number, σ is the reaction distance between two molecules, and D is the sum of the diffusion coefficients for BP(T_n) ($D_{\text{BP(T}n)}$) and Q (D_{Q}). The $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ term was calculated to be 0.7×10^{10}, 2.8×10^{10}, and $1.2\times10^{11}\,\text{M}^{-1}\text{s}^{-1}$ for CCl_4, Bz, and DCB, respectively, based on $k_{\text{diff}}=1.9\times10^{10}\,\text{M}^{-1}\text{s}^{-1}$ in AN at 25 °C.[7] Therefore, the contribution of the lifetime-dependent term on k_{TET} was 27, 60, and 86% for CCl_4, Bz, and DCB as Q of BP(T_n), respectively. The various contribution of the lifetime-dependent term indicates that the TET from BP(T_n) to Q is influenced not only by $\tau_{\text{T}n}$, but also by σ and D. Because an electron-exchange mechanism operates in the TET from BP(T_n) to Q,[8] the collision between BP(T_n) and Q occurs in the $\tau_{\text{T}n}$ timescale. Therefore, σ can be assumed to be equal to the sum of the radii of BP(T_n) and Q (r_{Q}). The radius of BP(T_n) is constant during the quenching of BP(T_n) by Q. The change in σ is due to the change in r_{Q}. On the other hand, the D_{Q} value can be expressed by Equation (11),[7]

$$D_{\text{Q}} = k_{\text{B}}T/6\pi\eta r_{\text{Q}} \tag{11}$$

in which k_{B} is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of AN. D_{Q} is proportional to the reciprocal of r_{Q}. Therefore, one of the important factors in $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ is r_{Q}. The r_{Q} values were estimated from the bond lengths calculated at the PM3 level to be 1.75, 2.49, and 3.01 Å for CCl_4, Bz, and DCB, respectively. Therefore, one of the factors governing the rate should be the molecular size, which suggests that various $\tau_{\text{T}n}$ values may be obtained by using different Q of BP(T_n) in the calculation of the $\tau_{\text{T}n}$ by using the quenching method.

Previously, the $\tau_{\text{T}n}$ values of BPs(T_n) were evaluated indirectly from the dependence of the quenching efficiency on [DCB] during the ns–ns two-color/two-laser flash photolysis, and were found to be 110–450 ps.[13,16] These calculated $\tau_{\text{T}n}$ values of BPs(T_n) are almost ten times greater than the $\tau_{\text{T}n}$ values measured directly in the present study. In Equation (10), the effect of the $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ term on the k_{TET} value can be ignored if the $\tau_{\text{T}n}$ value is sufficiently large, for example, if $\tau_{\text{T}n}\geq10$ ns. In the case of $\tau_{\text{T}n}<1$ ns, the $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ term has a considerable effect on the k_{TET} value. Therefore, during the calculation of $\tau_{\text{T}n}$ of BPs(T_n) from the quenching method, the $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ term in Equation (10) must be considered according to the Ware theoretical model. Consequently, evaluation of $\tau_{\text{T}n}$ values based on the TET quenching process of BPs(T_n) by Q is not appropriate, and direct measurement of the $\tau_{\text{T}n}$ value is necessary.

Importantly, the $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ term is also a function of the σ and D values, which relate to the size of Q. In a previous paper, we assumed the σ value to be 6 Å,[13,16] based on the reported values for the energy transfer.[19,30] One of the factors that induces a large error in $\tau_{\text{T}n}$ is the large σ value, because the TET is governed by an exchange mechanism in which collision between the donor and acceptor is essential. The $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ value increases as the size of Q increases. This result suggests that a relatively small Q, such as CCl_4, for the TET quenching of BP(T_n), gives a small $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ value ($0.7\times10^{10}\,\text{M}^{-1}\text{s}^{-1}$), and that a relatively large Q, such as DCB, gives a large $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ value ($1.2\times10^{11}\,\text{M}^{-1}\text{s}^{-1}$).

Conclusion

The $\tau_{\text{T}n}$ values of BP(T_n) and several BPs(T_n) were measured directly to be 37 ± 7 ps and 20–33 ps, respectively, by using the ns–ps two-color/two-laser flash photolysis method. The introduction of substituents to BP tends to decrease the $\tau_{\text{T}n}$ values. Based on the direct measurements of $\tau_{\text{T}n}$ of BP(T_n), the TET from BP(T_n) to Q, such as CCl_4, Bz, and DCB, was clarified. The $k_{\text{TET}}[\text{Q}]$ value was sufficiently large for the competitive occurrence with k_{IC} from BP(T_n) to BP(T_1). According to the Ware theoretical model of the bimolecular energy transfer reaction, the lifetime-dependent quenching process, the $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ term, has a considerable effect on the TET processes. The present study shows that the $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ term is not only a function of $\tau_{\text{T}n}$, but also a function of the σ and D values, which relate to the size of the Q. A relatively small Q, such as CCl_4, for the TET quenching of BP(T_n), gives a small $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ value ($0.7\times10^{10}\,\text{M}^{-1}\text{s}^{-1}$), and a relatively large Q, such as DCB, gives a large $k_{\text{diff}}\sigma/(\pi D\tau_{\text{T}n})^{0.5}$ value ($1.2\times10^{11}\,\text{M}^{-1}\text{s}^{-1}$). Therefore, the evaluation of $\tau_{\text{T}n}$ values based on the TET quenching process of BPs(T_n) by Q is not appropriate, and direct measurement of the $\tau_{\text{T}n}$ value is required.

Experimental Section

Materials: Benzophenone and 4-methylbenzophenone were purchased from Nacalai Tesque. *p*-Methoxybenzophenone, *p*-fluorobenzophenone, *p*-chlorobenzophenone, *p,p'*-difluorobenzophenone, *p,p'*-dimethylbenzophenone, and *p,p'*-dimethoxybenzophenone were purchased from Tokyo Kasei Kogyo. *p*-(Trifluoromethyl)benzophenone was purchased from Aldrich. All compounds were recrystallized two or three times from ethanol before use. Acetonitrile (AN), carbon tetrachloride (CCl_4), benzene

(Bz), all spectral grade, were purchased from Nacalai Tesque, and were used directly. Sample solutions were freshly prepared and deoxygenated by bubbling with argon (Ar) gas before irradiation. A rectangular Suprasil flow cell (1 cm×0.5 cm×2 cm) was used to ensure that each laser shot was irradiated on the fresh sample. All experiments were carried out at room temperature.

Two-color/two-laser flash photolysis: The first laser flash at 355 nm was obtained by using a ns Nd:YAG laser (Continuum, Surelite II-10; 5 ns fwhm, 10 Hz). The second laser flash at 532 nm was obtained by using a ps Nd:YAG laser (Continuum, RGA69–10; 30 ps fwhm, 10 Hz) seeded by a picosecond diode laser (1064 nm, 5 ps, 100 MHz, time-bandwidth, GE-100). Two laser flashes were synchronized by using a pulse generator with a delay time of 10 ns–10 ms, and overlapped through the sample. Transient absorption spectra and time profiles in the picosecond region were measured by using the pump and probe method, and the fast-response streak camera (Hamamatsu Photonics, C7700) equipped with a CCD camera (Hamamatsu Photonics, C4742–98) detection system, respectively. In the case of the pump and probe measurements, the probe pulse generated by focusing the fundamental light of the ps Nd:YAG laser on a D_2O:H_2O cell was detected by using a MOS linear image sensor (Hamamatsu Photonics, M2493–40) equipped with a polychromator (Hamamatsu Photonics, C5094) after passing through the sample. The systems were controlled by using a personal computer and GP-IB interface.

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