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Steady-State, One-, and Two-Color Laser Flash Photolysis Studies of α-Bond Cleavage of *S*-Acyl-4-phenylthiophenols in Solution

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Photochemical properties of α-cleavage of the C−S bond in excited states of *p*-biphenyl thioacetate and *p*-biphenyl thiobenzoate (Me-SBP and Ph-SBP) in solution are investigated using steady-state and laser flash photolyses in comparison with those of *S*-phenyl thiobenzoate, where the photo-Fries rearrangement was reported to be absent. Although Me-SBP and Ph-SBP decompose upon 254 nm photolysis in acetonitrile irrespective of the amount of the dissolved oxygen, no definite photoproducts due to the photo-Fries rearrangement were found. Laser flash photolysis (266 nm) of these molecules reveals the occurrence of the C−S bond cleavage in the excited state based on the observation of the formation of the biphenylylthiyl radical (BTR) in the transient absorption. Quantum yields (Φ_{rad}) of the BTR formation were determined to be 0.20 and 0.15 for Me-SBP and Ph-SBP, respectively. Triplet sensitization of Ph-SBP using xanthone (XT) as a sensitizer shows that the lowest triplet (T_1) state of Ph-SBP is dissociative for the C−S bond with an efficiency of ≥0.56. In contrast, triplet sensitization of Me-SBP using acetone as a sensitizer demonstrates the efficient formation of triplet Me-SBP, and the molar absorption coefficient of the triplet−triplet absorption was determined. No photochemical reactions are found in the T_1 state of Me-SBP. Upon 355 nm laser flash photolysis of the T_1 state of Me-SBP, the formation of BTR is confirmed in the transient absorption. This observation indicates the C−S bond cleavage in a highly excited triplet (T_n) state of Me-SBP. The quantum yield (Φ_{dec}) of the α-cleavage in the T_n state of Me-SBP was determined to be 0.69. Photochemical features of Me-SBP and Ph-SBP are discussed from the viewpoint of the spin-multiplicity of the bond dissociative states.

1. Introduction

Photoinduced bond cleavage of carbonyl compounds is a well-known process in photochemistry and photobiology. Norrish type I and II reactions and carbon−heteroatom bond cleavage occurring at the α- and *β*-positions of aromatic carbonyl compounds have been widely investigated by means of product analysis and time-resolved transient measurements.[1,2] In particular, homolytic α-cleavage of C−C, −O, −S, −P, and −N bonds in carbonyl compounds leading to the formation of radicals has been used to initiate photopolymerizable formulations that can be activated by UV irradiation.[3] Photo-Fries rearrangements are one of typical consecutive reactions after α-cleavage of carbon−heteroatom bonds in the lowest excited singlet (S_1) state of acyl aromatic compounds in solution.[4] It is reported that the occurrence of photo-Fries rearrangements efficiently proceeds after C−O and C−N bond dissociation in the S_1 state of phenyl acetate[5−7] and acetanilide, respectively.[8,9] With these molecules, efficient quenching of the S_1 state by bond dissociation processes prevents intersystem crossing to the triplet state. Therefore, the photochemical properties in the triplet states are not uncovered.

Photo-Fries rearrangements of molecules having C−S bond have been also studied by photoproduct analysis. Grunwell reported the photolysis of *S*-(*p*-tolyl) thioacetate in cyclohexane using 254 nm light.[10] No photo-Fries photoproducts were observed, whereas the correspondiung disulfide (77%) and sulfide (7%) were major products. Loveridge et al. studied photoproducts of *S*-methyl thioacetate (Me-SPh) in various solvents.[11] They obtained the two photo-Fries products with each yield of 4% upon 254 nm photolysis of Me-SPh in benzene, although no photoproducts were obtained in methyl carbitol and ethanol. In contrast to Me-SPh, one photo-Fries product, 4-benzoyl thiophenol was obtained upon photolysis of *S*-phenyl thiobenzoate (Ph-SPh) in ethanol.[12] Another photo-Fries product was not found. It seems that photochemical processes of carbonyl compounds with α-C−S bond are not simple reactions. Tomioka et al. reported photodecomposition of Ph-SPh in benzene because of α-cleavage of the C−S bond by photoproduct analysis and laser flash photolysis.[13,14] The photoproducts of Ph-SPh in benzene were reported to be benzaldehyde, diphenylsulfide, and biphenyl, whereas no photoproducts originating from the photo-Fries rearrangements were found. On the basis of the absence of photoproducts by the photo-Fries rearrangement and quenching experiments using 1-methylnaphthalene as a triplet quencher at the high concentration, they concluded that the dissociative state for the C−S bond is the triplet. Contribution of the excited singlet states of Ph-SPh to α-cleavage was not mentioned.

Triplet sensitization technique using triplet energy transfer has been widely used to investigate photochemical properties in the triplet state of molecules having small triplet yields. Acetone, acetophenone, or benzophenone whose triplet energies are ca. 76, 74, or 69 kcal mol^{-1}, respectively, have been often

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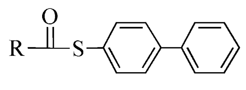
TABLE 1: Photophysical and Photochemical Parameters for R-SBP Obtained in the Present Work

R	E_T[a] kcal mol^{-1}	Φ_{rad}[b]	ε_{380}^{T-T}[c] dm^3 mol^{-1} cm^{-1}	$k_q/10^9$[d] dm^3 mol^{-1} s^{-1}	α_{rad}[e]	Φ_{dec}[f]	BDE(C−S)[g] kcal mol^{-1}
Me		0.20	15 700	2.0	~0	0.69	52.1
Ph	62.2	0.15		11.0	≥0.56		53.9

[a] Determined from the 0−0 origin of the phosphorescence spectrum obtained in MP at 77 K. Phosphorescence from Me-SBP was absent in MP at 77K. [b] Quantum yield of appearance of BTR upon 266 nm laser photolysis of R-SBP in ACN. Errors ±0.01. [c] Molar absorption coefficients of the triplet absorption at 380 nm. Errors ±500 dm^3 mol^{-1} cm^{-1}. [d] Quenching rate constant of triplet sensitizers by [R-SBP]. Errors ±5%. The used sensitizers were acetone for Me-SBP and xanthone for Ph-SBP. [e] Efficiencies of the radical formation in the T_1 states of R-SBP. [f] Quantum yields of decomposition of the T_n state of R-SBP. Errors ±0.03. [g] BDE values for the C−S bond were determined by eq 3.

used as triplet sensitizers.[1] With *S*-phenyl thiobenzoate (Ph-SPh), because the phosphorescence is not detectable in a rigid matrix at 77 K (Supporting Information), the triplet energy cannot be determined from the phosphorescence feature. Considering the similarity of the molecular structure of Ph-SPh with that of phenyl benzoate (Ph-OPh), the triplet energy may be close to that (ca. 78 kcal mol^{-1})[15] of Ph-OPh, which will not allow triplet energy transfer from any known triplet sensitizers to Ph-SPh in solution. However, when a phenyl group is attached to the phenylthiyl moiety of Ph-SPh to make one of the biphenyl derivatives whose triplet energies are known to be ca. 65 kcal mol^{-1},[16,17] some triplet sensitizers can be used for the formation of the corresponding triplet state. After successful triplet sensitization of the biphenylylthiyl compounds, two-color two-laser photolysis techniques could be applicable to the triplet states for investigating photochemical features in highly excited triplet (T_n; with n, 2 and over) state. The method of multistep excitation has been widely used to investigate photophysical and photochemical processes in highly excited states.[18−27] We have been studying bond cleavage reactions in T_n states of biphenyl derivatives by means of two-color two-laser photolysis techniques.[15,28−31] We found no photoproducts due to the successive photo-Fries rearrangements after the α-bond cleavage of C-O bond in the T_n states of acyl biphenyl derivatives.[15] It is of interest to reveal the relationship between the spin-multiplicity of the dissociative states and the formation of photoproducts via the consecutive photo-Fries rearrangement. Therefore, it is crucial to examine photochemical processes of acyl biphenylylthiyl derivatives not only in the excited singlet state but also in the triplet states (T_1 and T_n) using triplet sensitization techniques.

In the present study, we have investigated photochemical reactions of triplet *S*-acyl-4-phenylthiophenols (R-SBP) using steady-state photolysis and single and double laser flash photolysis techniques. (Photophysical and photochemical parameters are shown in Table 1.) R-SBPs are shown to undergo α-cleavage upon direct excitation. Triplet sensitization of R-SBP demonstrates the different photochemical behavior in the triplet states, and consecutive excitation of the triplet state reveals α-cleavage in a highly excited triplet state. The photochemical features of R-SBP are discussed from the viewpoint of the spin-multiplicities of α-cleavage of C−S bond.



R = Me; thioacetic acid *S*-biphenyl-4-yl ester (Me-SBP)
R = Ph; thiobenzoic acid *S*-biphenyl-4-yl ester (Ph-SBP)

2. Experimental Section

S-Acyl-4-phenylthiophenols (R-SBP, *p*-biphenyl thioacetate (R = Me), and *p*-biphenyl thiobenzoate (R = Ph)) were synthesized by a reaction of *p*-phenylthiophenol with acetyl chloride and benzoyl chloride, respectively, in methylene chloride in the presence of triethylamine. These compounds were purified by repeated recrystallizations from hexane. Acetonitrile (ACN) and ethanol were distilled for purification, whereas diethyl ether (Kanto, spectroscopic grade) and isopentane (IP, Merck, spectroscopic grade) were used as supplied. ACN was used as solvent at 295 K, whereas ethanol and a mixture of diethyl ether, IP, and ethanol (EPA, 5:5:3 v/v/v) were used as matrices at 77 K. Absorption and emission spectra were recorded on a U-best 50 spectrophotometer (JASCO) and a Hitachi F-4010 fluorescence spectrophotometer, respectively.

A XeCl excimer laser (308 nm, Lambda Physik, Lextra 50) and the third (355 nm) and the fourth (266 nm) harmonics of a Nd^{3+}/YAG laser (JK Lasers HY-500; pulse width 8 ns) were used as excitation light source. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere.[32] The incidence direction of the second 355 nm laser beam was kept parallel to that of the first 308 nm laser light. The transient data obtained by laser flash photolysis were analyzed by using the least-squares best-fitting method. The transient absorption spectra were taken with a USP-554 system from Unisoku, which can provide a transient absorption spectrum with one laser pulse.

All samples for transient absorption measurements were prepared in darkness and degassed in a quartz cell with a path length of 1 cm using several freeze−pump−thaw cycles on a high vacuum line. The concentration of R-SBP for 266 nm laser photolysis was adjusted to maintain the optical density at 266 nm being ca. 0.8 in ACN. Usual measurements were carried out at 295 K. The number of the repetition of laser pulsing was kept at less than four pulses to avoid excess exposure. Several transient data obtained in the same concentration systems were averaged, and the experimental errors in the values were kept within ±5% deviation.

3. Results and Discussion

3.1. Absorption and Emission Measurements. Figure 1 shows absorption spectra of R-SBP in ACN at 295 K and a phosphorescence spectrum of Ph-SBP in ethanol at 77 K.

Fluorescence from R-SBP in ACN at 295 K and phosphorescence from Me-SBP in ethanol at 77 K were not observed with our instrument. It was confirmed that the excitation spectrum for the phosphorescence of Ph-SBP agreed well with the absorption spectrum. The absence of fluorescence indicates that the electronic character of R-SBP is n,π^* in nature. The energy level of the lowest triplet (T_1) state of Ph-SBP was determined to be 62.2 kcal mol^{-1} from the 0−0 origins of the phosphorescence spectrum.

3.2. Steady-State Photolysis of R-SBP. Absorption spectral changes upon 254 nm photolysis of R-SBP were measured in ACN at 295 K. The spectral data are deposited in the Supporting

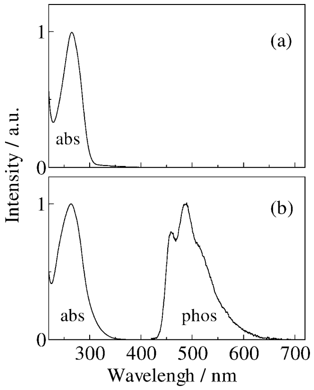


Figure 1. Absorption spectra in ACN at 295 K for (a) Me-SBP and (b) Ph-SBP and a phosphorescence spectrum in ethanol at 77 K for Ph-SBP (b). Phosphorescence from Me-SBP was absent in ethanol at 77 K.

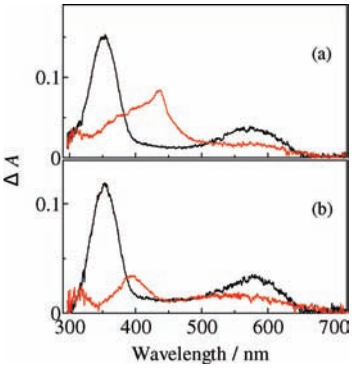
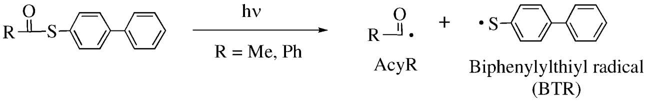


Figure 2. Transient absorption spectra obtained at 100 ns obtained upon 266 nm laser photolysis of (a) Me-SBP and (b) Ph-SBP in ACN at 295 K (solid) and in EPA glass at 77 K (red color).

Information along with optical and photoproduct data of the related sulfide compounds. From the fact that isosbestic points were seen during the 254 nm light irradiation of R-SBP in ACN, it was inferred that a definite photochemical reaction proceeds to form the corresponding products. However, we were unable to identify the final photoproducts from the corresponding absorption spectra. To investigate the initial photochemical reaction of R-SBP, we carried out nanosecond laser flash photolysis of R-SBP.

3.3. Photochemical Reactions upon 266 nm Laser Photolysis of R-SBP. Figure 2 shows transient absorption spectra at 100 ns upon 266 nm laser pulsing in R-SBP in ACN at 295 K and in EPA at 77 K.

Considering that the triplet−triplet ($T_n \leftarrow T_1$) absorption spectra of *p*-phenylthiophenol and *p*-biphenyl methyl sulfide, respectively, have absorption bands at 435 and 470 nm at 77 K (Supporting Information), the absorption spectrum can be ascribed to the $T_n \leftarrow T_1$ absorption of the corresponding R-SBP. It seems that the wavelength of the absorption maximum in the triplet absorption of biphenylylthiyl derivatives depends on the substituent groups on the sulfur atom. Conversely, the transient absorption spectrum having the maxima at 353 nm at 295 K can be ascribable to that of *p*-biphenylylthiyl radical (BTR) having the molar absorption coefficient of 27 000 ± 2000 dm^3 mol^{-1} cm^{-1} at 353 nm. (See the Supporting Information.) From these observations, it is shown that upon photolysis of R-SBP, C−S bond cleavage proceeds in the excited states to produce BTR. Because the corresponding acyl radicals, AcyR, have the absorption in the shorter wavelength than 320 nm,[33] we were not able to observe them in the transient absorption spectrum.



Quantum yields (Φ_{rad}) for the formation of BTR upon 266 nm photolysis of R-SBP were determined with eq 1

$$\Phi_{rad} = \Delta A_{BTR}(1-10^{-A\lambda})^{-1} I_0^{\lambda\text{-}1} \varepsilon_{353}^{BTR\text{-}1} \tag{1}$$

where ΔA_{BTR}, A_λ, I_0^λ, and ε_{353}^{BTR}, respectively, represent an absorbance change at 353 nm due to BTR, the absorbance of R-SBP at the excitation wavelength, λ, the photon flux of the incident λ (nanometer) laser pulse, and the molar absorption coefficient of BTR at 353 nm (27 000 dm^3 mol^{-1} cm^{-1}). The quantity of I_0^λ ($\lambda = 266$ nm) was determined to be 2.9 × 10^{-5} quanta dm^{-3} pulse^{-1} by using absorption of triplet benzophenone in ACN as a chemical actinometer with the use of eq 2

$$\Delta A_T^{BP} = \varepsilon_T^{BP}(1-10^{-A_\lambda^{BP}}) I_0^\lambda \Phi_{ISC}^{BP} \tag{2}$$

where ΔA_T^{BP}, ε_T^{BP}, A_λ^{BP}, and Φ_{ISC}^{BP} are, respectively, the initial absorbance at 520 nm for the formation of triplet benzophenone obtained immediately after laser pulsing, the molar absorption coefficient of triplet BP at 520 nm in ACN (6500 dm^3 mol^{-1} cm^{-1}),[34] the absorbance of BP at the excitation wavelength, λ, and the triplet yield of benzophenone (1.0).[16] According to eqs 1 and 2, the Φ_{dec} values were determined to be 0.20 ± 0.01 for Me-SBP and 0.15 ± 0.01 for Ph-SBP. These values were independent of the amount of the dissolved oxygen. It is worthy to compare these Φ_{dec} values with those of *S*-phenyl thioacetate (Me-SPh) and *S*-phenyl thiobenzoate (Ph-SPh) (0.35 ± 0.02 for both the compounds, see Supporting Information).

The bond dissociation energies (BDEs) of the C−S bond in R-SBP were obtained by eq 3 on the basis of the heats of formation ($\Delta_f H$) for R-SBP, the corresponding acyl radical (AcyR), and the biphenylylthiyl radical (BTR) computed by using a semiempirical PM3 program contained in MOPAC ′97.

$$\Delta_f H(\text{R-SBP}) = \Delta_f H(\text{AcyR}) + \Delta_f H(\text{BTR}) - \text{BDE(C−S)} \tag{3}$$

The estimated BDE values were 52.1 and 53.9 kcal mol^{-1} for Me- and Ph-SBP, respectively.

The $\Delta_f H$ values calculated for BTR, R-SBP, and AcyR are deposited in the Supporting Information.

3.4. Photochemical Reaction of Triplet Ph-SBP Using Xanthone Sensitization. To efficiently produce triplet states of Ph-SBP, we performed triplet sensitization by using xanthone (XT) as a triplet energy donor upon 355 nm laser photolysis. Because the triplet energy (74.0 kcal mol^{-1}) of XT is higher than that (62.2 kcal mol^{-1}) of Ph-SBP, triplet energy transfer efficiently proceeds from triplet XT to Ph-SBP. Triplet XT has the absorption maximum at 625 nm in ACN.[35] Figure 3 shows a time profile of the absorbance of triplet XT at 625 nm obtained upon 355 nm laser pulsing in a XT(3.1 × 10^{-3} mol dm^{-3})/Ph-SBP(1.0 × 10^{-3} mol dm^{-3}) system.

The intensity of the absorbance increases with a first-order rate (k_{obsd}) of 1.2 × 10^7 s^{-1}. A transient absorption spectrum obtained at 500 ns after laser pulsing in the XT/Ph-SBP system was due to BTR. (See the inset in Figure 3.) The observation of BTR after the depletion of triplet XT indicates the occurrence

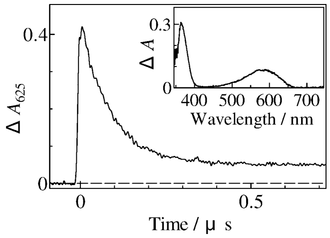


Figure 3. Temporal absorbance at 625 nm obtained upon 355 nm laser pulsing in an XT(3.1×10^{-3} mol dm^{-3}/Ph-SBP(1.0×10^{-3} mol dm^{-3}) system in ACN. Inset: a transient absorption spectrum obtained at 500 ns after the 355 nm laser photolysis.

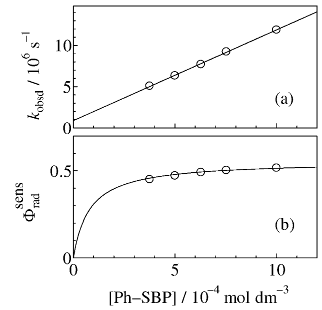


Figure 4. Decay rates (k_{obsd}) of (a) triplet XT by Ph-SBP and (b) quantum yields (Φ_{rad}^{sens}Z) of the radical formation plotted as a function of [Ph-SBP] obtained upon 355 nm laser pulsing in an XT(3.1×10^{-3} mol dm^{-3})/Ph-SBP(1.0×10^{-3} mol dm^{-3}) system in ACN. The solid curve in part b was drawn according to eq 5.

of the C−S bond cleavage of Ph-SBP via the lowest triplet (T_1) state. Upon triplet sensitization, only the formation of BTR was seen in transient absorption spectra.

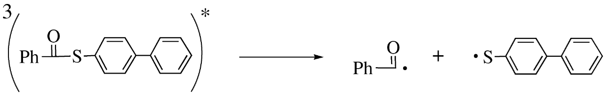


Figure 4a shows rates (k_{obsd}) of the decay of triplet XT plotted as a function of the concentration, [Ph-SBP], of Ph-SBP.

Because the plots give a corresponding straight line, the k_{obsd} can be formulated by eq 4

$$k_{obsd} = k_0 + k_q[\text{Ph-SBP}] \tag{4}$$

where k_0 and k_q, respectively, represent the decay rate of triplet XT in the absence of Ph-SBP and the rate constant for quenching of triplet XT by Ph-SBP. From the intercept and the slope of the line, the values of k_0 and k_q were determined to be 8.8×10^5 s^{-1} and 1.1×10^{10} dm^3 mol^{-1} s^{-1}.

Quantum yields (Φ_{rad}^{sens}) for the BTR formation upon XT sensitization of Ph-SBP were determined with eq 1. Here A_λ and I_0^λ, respectively, were the absorbance of XT at the excitation wavelength, λ (= 355 nm), and the photon flux at 355 nm (3.4×10^{-5} quanta dm^{-3} pulse^{-1}) determined by using eq 2. Figure 4b shows the quantum yields (Φ_{rad}^{sens}) thus obtained for the formation of BTR upon XT sensitization of Ph-SBP plotted as a function of [Ph-SBP]. The value of Φ_{rad}^{sens} increases with increasing [Ph-SBP], but the increase is not linear with [Ph-SBP]. The Φ_{rad}^{sens} values can be formulated by eq 5

$$\Phi_{rad}^{sens} = k_q[\text{Ph-SBP}]\alpha_{TET}^{XT}\alpha_{rad}(k_0 + k_q[\text{Ph-SBP}])^{-1} \tag{5}$$

where α_{TET}^{XT} and α_{rad} are efficiencies of triplet energy transfer from triplet XT to Ph-SBP and the C−S bond cleavage in the triplet state of Ph-SBP, respectively. By using eq 5 and the determined values of k_0 and k_q, the product value of α_{TET}^{XT}, α_{rad}, was determined to be 0.56 ± 0.03. Because the α_{TET}^{XT} is not more than unity, the α_{rad} is estimated to be ≥ 0.56. It is of our interest to compare this efficiency with that (0.35, this value was not influenced by the amount of the dissolved oxygen; Supporting Information) of *S*-phenyl benzoate (Ph-SPh), where the C−S bond is reported to dissociate in the triplet state.[13,14]

In the present study, it is revealed that the T_1 state of Ph-SBP is dissociative for the C−S bond from the observation of the BTR formation. According to the spin-conservation rule, a triplet radical pair, $^3(\text{BzoyR} + \text{BTR})_{cage}$, of the benzoyl radical, BzoyR, and BTR would be formed in the solvent cage immediately after the C−S bond cleavage in the T_1 state. However, because of the spin-multiplicity of triplet-manifold, the occurrence of geminate recombination or radical reactions would be difficult in the solvent cage, resulting in the radicals readily escaping from the solvent cage to be free radicals. Therefore, the determined efficiency, α_{rad}, can be regarded to be equivalent to that, α_{dis}, of the bond cleavage in the triplet state of Ph-SBP. Conversely, we have determined the quantum yield, Φ_{rad} (= 0.15), for the radical formation upon direct excitation of Ph-SBP. The potential dissociative excited states for the radical formation are plausibly the S_1 and the T_1 states. That is, intersystem crossing from the S_1 to the T_1 state might compete with the dissociation process in the S_1 state. When we note the net quantum yield, $\Phi_{rad}(S_1)$, for the radical formation from the S_1 state, the determined yield, Φ_{rad}, is represented by using the efficiency, α_{rad}, for the C−S bond cleavage in the T_1 state and a quantum yield, Φ_{isc}, of intersystem crossing of Ph-SBP as follows

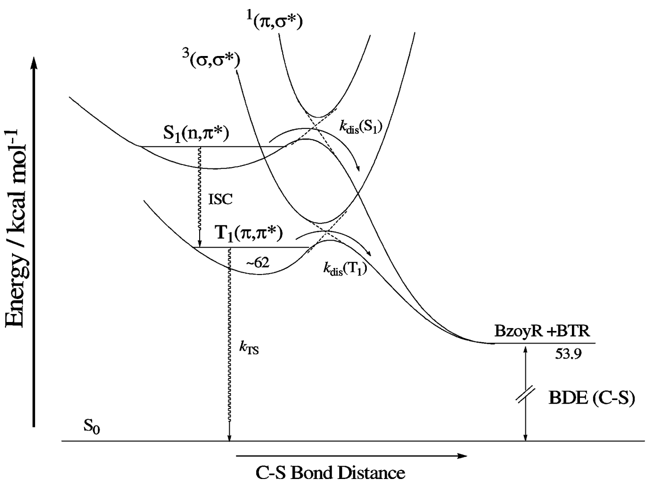
$$\Phi_{rad} = \Phi_{rad}(S_1) + \Phi_{isc}\alpha_{rad} \tag{6}$$

Because the α_{rad} value is estimated to be ≥ 0.56, the Φ_{isc} is evaluated to be ≤ 0.27 (= 0.15/0.56). When the α-cleavage occurs in the S_1 state of Ph-SBP, a singlet radical pair, $^1(\text{BzoyR} + \text{BTR})_{cage}$, would be formed in the solvent cage. Some of the singlet radical pairs may undergo geminate recombination to form the parent molecule, and the other will escape from the solvent cage to be free radicals. Therefore, the quantum yield, Φ_{dis}, of the actual bond dissociation in the S_1 state of the R-SBP must be larger than the $\Phi_{rad}(S_1)$ value. Because the $\Phi_{rad}(S_1)$ value (0.15) of Ph-SBP was not affected by the amount of the dissolved oxygen, the dissociative excited state of Ph-SBP is probably the S_1 state. In the present work, however, we are unable to assign clearly the spin-multiplicity of the dissociative excited state upon direct excitation of Ph-SBP.

A schematic energy diagram in the excited triplet states of Ph-SBP along with the α-cleavage pathway is depicted in Scheme 1.

It is originally suggested that the bond dissociation in the excited states proceeds by avoided crossings between the reactive excited state and dissociative potential surfaces of the same overall symmetry.[36] The electronic configuration of the dissociative state, which strongly interacts with the $S_1(n,\pi^*)$ state, is $^1(\pi,\sigma^*)$ of the C−S bond of Ph-SBP, whereas the T_1 of a π,π^* type does with the interactive potential surface of $^3(\sigma,\sigma^*)$. In both cases, it is considered that the α-bond dissociation proceeds without activation energies from the S_1 and T_1 states along the corresponding dissociative surface with the rates of dissociation, $k_{dis}(S_1)$ and $k_{dis}(T_1)$, respectively. The rate of $k_{dis}(T_1)$

SCHEME 1: Schematic Energy Diagram of Excited States of Ph-SBP Including the C−S Bond Dissociative Potential



is related to the use of the dissociation efficiency, α_{rad}, in the T_1 state and a rate, k_{TS}, of intersystem crossing from the T_1 to the S_0 state as follows

$$\alpha_{rad} = k_{dis}(T_1)(k_{dis}(T_1) + k_{TS})^{-1} \qquad (7)$$

Therefore, the residual efficiency, $1 - \alpha_{rad}$, is due to the intersystem crossing. In general, triplet π,π^* molecules that have no photochemical reactions deactivate in the microsecond time domain in solution at room temperature, and thus the magnitude of k_{TS} would be as large as 10^5 s^{-1}. According to eq 7, the magnitude of $k_{dis}(T_1)$ for Ph-SBP can be estimated to be equivalent to ~10^5 s^{-1} or >10^5 s^{-1}.

3.5. Photochemical Profiles in the Triplet States of Me-SBP. We performed triplet sensitization of Me-SBP by using acetone (Ac) as a triplet energy donor upon 308 nm laser photolysis because triplet Me-SBP showed different photochemical features than those of triplet Ph-SBP. Figure 5 shows transient absorption spectra obtained upon 308 nm laser pulsing in an Ac(0.6 mol dm^{-3})/Me-SBP(1.2 × 10^{-3} mol dm^{-3}) system in the absence and presence of the second 355 nm laser pulsing.

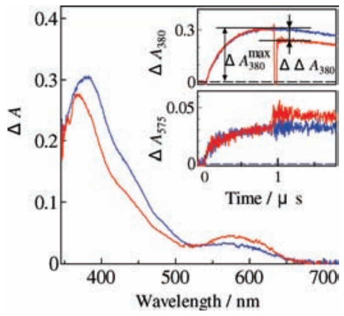


Figure 5. Transient absorption spectra obtained at 1.1 μs upon 308 nm laser pulsing an Ac (0.6 mol dm^{-3})/Me-SBP (1.2 × 10^{-3} mol dm^{-3}) system in ACN in the absence (blue) and the presence (red) of the second 355 nm laser pulsing at 950 ns. A dimple at 355 nm in the transient absorption spectrum in red is due to scattering of the second 355 nm laser pulse. Insets: time profiles at 380 nm (upper) and at 575 nm (lower) in the absence (blue) and the presence (red) of the second 355 nm laser pulsing. The spike at 950 ns is due to scattering of the second 355 nm laser pulse.

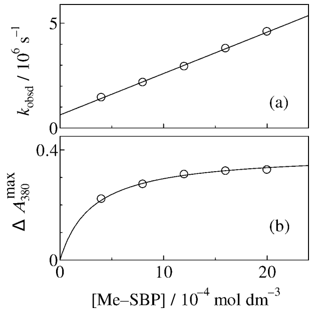


Figure 6. Formation rates (k_{obsd}) of (a) triplet-sensitized Me-SBP and (b) the maximum absorbance changes, ΔA_{380}^{max}, at 380 nm plotted as a function of [Me-SBP] obtained upon 308 nm laser photolysis in the Ac (0.6 mol dm^{-3})/Me-SBP system in ACN. The solid curve in part b was drawn according to eq 9.

The intensity of the absorbance at 380 and 575 nm increases with a first-order rate, k_{obsd}, of 2.9 × 10^6 s^{-1}. (See insets in Figure 5.) In the absence of the second laser pulsing, a transient absorption spectrum obtained at 1.1 μs after 308 nm laser pulsing in the Ac/Me-SBP system is due to triplet Me-SBP. The growth of the absorption of triplet Me-SBP, therefore, is caused by the triplet energy transfer from triplet acetone to Me-SBP. Upon triplet sensitization, only the formation of triplet Me-SBP was seen in transient absorption spectra. After the absorption of triplet Me-SBP had decayed, no residual absorption was observed in the wavelength region, 320−720 nm. These observations indicate that the C−S bond of Me-SBP does not cleave in the T_1 states.

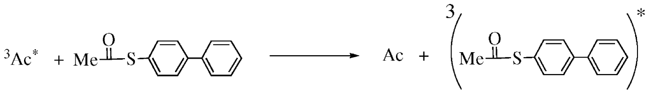


Figure 6a shows rates (k_{obsd}) of the formation of triplet Me-SBP, which should be equivalent to the decay of triplet Ac, plotted as a function of the concentration ([Me-SBP]) of Me-SBP.

Because the plots give a corresponding straight line, k_{obsd} can be formulated by eq 8

$$k_{obsd} = k_0 + k_q[\text{Me-SBP}] \qquad (8)$$

where k_0 and k_q, respectively, represent the decay rate of triplet Ac in the absence of Me-SBP and the rate constant for quenching of triplet Ac by Me-SBP. From the intercept and the slope of the line, the values of k_0 and k_q were determined to be 6.3 × 10^5 s^{-1} and 2.0 × 10^9 dm^3 mol^{-1} s^{-1}. From the efficient triplet energy transfer from triplet Ac to Me-SBP, it is inferred that the triplet energy of Me-SBP is smaller than that (74.0 kcal mol^{-1})[16] of Ac.

Figure 6b shows the maximum absorbance, ΔA_{380}^{max}, of triplet Me-SBP (upper inset in Figure 5) produced by triplet sensitization plotted as a function of [Me-SBP]. The value of ΔA_{380}^{max} increases with increasing [Me-SBP], but the increase is not linear with [Me-SBP]. The quantity of ΔA_{380}^{max} of triplet Me-SBP produced by triplet sensitization can be formulated by eq 9

$$\Delta A_{380}^{max} = k_q[\text{Me-SBP}]\alpha_{TET}^{Ac}\varepsilon_{380}^{T-T}\Phi_{ISC}^{Ac}(1-10^{-A_{308}^{Ac}})I_0^{\lambda}(k_0 + k_q[\text{Me-SBP}])^{-1} \qquad (9)$$

where α_{TET}^{Ac}, ε_{380}^{T-T}, Φ_{ISC}^{Ac}, A_{308}^{Ac}, and I_0^{λ} are, respectively, an efficiency of triplet energy transfer from triplet Ac to Me-SBP,

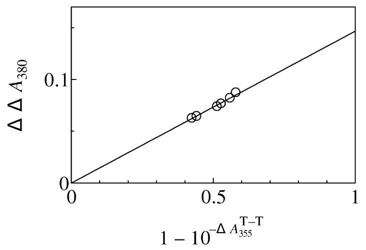
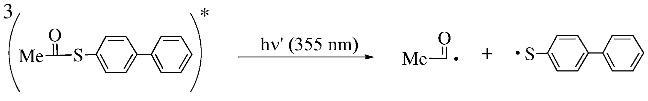


Figure 7. Change, $\Delta\Delta A_{380}$, in the absorbance change at 380 nm upon stepwise two-color laser flash photolysis of the Ac/Me-SBP system in ACN plotted as a function of the term $1-10^{-\Delta A_{355}^{T-T}}$.

the molar absorption coefficients of triplet Me-SBP at 380 nm, the triplet yield of acetone (1.0),[16] the absorbance of Ac at 308 nm, and the number of photon flux of the incident 308 nm laser pulse. We determined the quantity of I_0^{λ} (λ =308 nm) to be 3.1 × 10^{-5} quanta dm^{-3} pulse^{-1} by using eq 2. By using eq 9 and the determined values of k_0 and k_q and assuming the efficiency of α_{TET}^{Ac} to be 0.73,[37] we determined the ε_{380}^{T-T} values of triplet Me-SBP to be 15 700 ± 500 dm^3 mol^{-1} cm^{-1}.

Because triplet Me-SBP shows the absorption at 355 nm, it is possible to excite the triplet to the higher triplet states by using the second 355 nm laser pulsing. A transient absorption spectrum obtained upon 355 nm laser pulsing in triplet Me-SBP is shown in Figure 5. The intensity of the absorption of the triplet at 380 nm was found to decrease without showing the recovery to the initial intensity before the second laser pulsing. (See upper inset in Figure 5.) In contrast, an increase in the intensity of absorbance at 575 nm can be recognized in the transient absorption in Figure 5 and in the time profile of the absorbance at 575 nm (lower inset in Figure 5), indicating the formation of BTR. These changes in absorbance upon photolysis of triplet Me-SBP show that the T_1 state of Me-SBP undergoes the C−S bond dissociation in a highly excited triplet (T_n; with n over 2) state of Me-SBP.

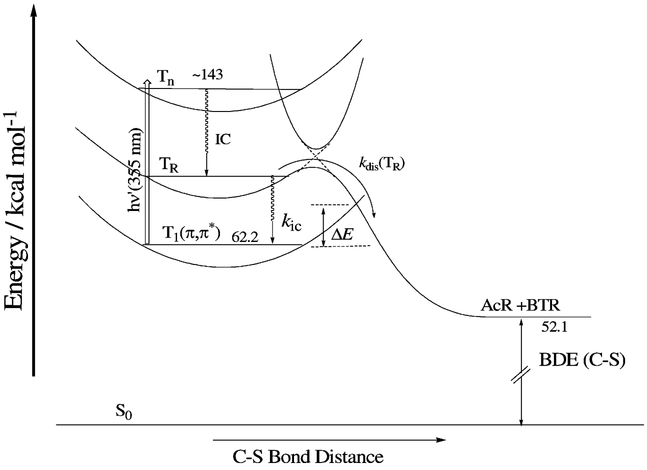


Quantum yields (Φ_{dec}) of the decomposition in the T_n state of Me-SBP upon the second 355 nm laser pulsing were determined on the basis of measurements of the change in absorbance change, $\Delta\Delta A_{380}$, at 380 nm due to the decomposition of triplet Me-SBP and the formation of BTR upon the second 355 nm laser photolysis. When the dissociation process is single-photonic, $\Delta\Delta A_{380}$ can be expressed by eq 10 as a function of the absorbance, ΔA_{355}^{T-T}, of triplet Me-SBP at 355 nm generated upon Ac sensitization

$$\Phi_{dec} = \Delta\Delta A_{380} I_0^{\lambda -1} (1-10^{-\Delta A_{355}^{T-T}})^{-1} \Delta\varepsilon_{380}^{\ -1} \qquad (10)$$

Here I_0^{λ} and $\Delta\varepsilon_{380}$, respectively, represent the intensity of the incident second 355 nm laser pulse. The quantity of I_0^{λ} (λ = 355 nm) was determined to be 4.7 × 10^{-5} quanta dm^{-3} pulse^{-1} by using eq 2 and the difference (4500 dm^3 mol^{-1} cm^{-1}) in the molar absorption coefficients at 380 nm between triplet Me-SBP (15700 dm^3 mol^{-1} cm^{-1}) and BTR (11200 dm^3 mol^{-1} cm^{-1}). Figure 7 shows the $\Delta\Delta A_{380}$ values plotted as a function of the term, $1-10^{-\Delta A_{355}^{T-T}}$, which corresponds to absorptivity of the incident 355 nm laser pulse.

SCHEME 2: Schematic Energy Diagram of Triplet States of Me-SBP Including the Dissociative Potential Pathway



Because the plots show straight lines, the C−S bond cleavage in the T_n state is shown to be a single photonic process. The Φ_{dec} value was determined to be 0.69 ± 0.03 by using eq 10.

A schematic energy diagram for the excited triplet states of Me-SBP including the dissociation potential of the C−S bond is depicted in Scheme 2.

Upon the second 355 nm laser photolysis of the T_1 state of Me-SBP, the T_n state, whose state energy is located at 143 kcal mol^{-1}, is produced. The molecule in the T_n state will be deactivated through internal conversion to a dissociative state, T_R. Although the electronic character of the T_R state cannot be revealed in the present work, α-cleavage of the C−S bond proceeds in the T_R state to produce the acetyl radical (AcR) and BTR without activation energies, according to the avoided crossing rule, via the correlated dissociative potential of $^3(\pi,\sigma^*)$ or $^3(\sigma,\sigma^*)$ with a rate $k_{dis}(T_R)$ and the yield (Φ_{dec}) of 0.69. The residual yield (1 − Φ_{dec} = 0.31) is due to internal conversion from the T_R to the T_1 state with a rate, k_{ic}. In contrast, the absence of fragmentation in the T_1 state can be interpreted by considering a large energy barrier, ΔE, for the interaction between the $T_1(\pi,\pi^*)$ state and a dissociative $^3(\sigma,\sigma^*)$ potential. It is noteworthy that the reactivity of α-cleavage in the $T_1(\pi,\pi^*)$ state of Me-SBP is quite different from that of Ph-SBP. The triplet energy (ca. 62 kcal mol^{-1}) and the shape of the triplet absorption spectrum of Me-SBP are similar to those of biphenylylthiyl compounds (Supporting Information), indicating that the triplet energy of R-SBP may be localized on the biphenylylthiyl moieties. Furthermore, the BDE(C−S) values of R-SBP are close to each other. Therefore, the difference in the reactivity toward the α-cleavage in the triplet states of R-SBP should be originated from that in interaction between the triplet states and the corresponding dissociative potentials that depend on the variety of the acyl groups. It is of interest to compare the reactivity for α-cleavage of excited R-SBP with those of α-acetyl and α-benzoyl-4-phenylphenols, R-OBP (R = Me and Ph), which have similar molecular structures and BDE values (ca. 52 kcal mol^{-1}) to those of R-SBP.[15] It is found that triplet R-OBP is inert to α-cleavage of the C−O bond in solution, whereas the S_1 and T_n states are unambiguously dissociative for the α-cleavage. As with the photo-Fries rearrangement processes, no photoproducts from R-OBP were obtained,[15] whereas phenyl acetate is shown to provide the photoproducts due to the α-cleavage in the S_1 state.[6,7] On the basis of these results, it is inferred that no photo-Fries rearrangements proceed between acyl radicals and *p*-phenyl-substituted phenoxy or phenylthiyl radical irrespective of the spin-multiplicity of the dissociative states.

4. Conclusions

We have investigated photochemical behaviors of R-SBP in the S_1, T_1, and T_n ($n \geq 2$) states using steady-state photolysis and laser photolysis techniques. On the basis of the results from stationary photolysis of R-SBP, the photo-Fries rearrangements are absent, although photodecomposition of R-SBP was confirmed. The transient absorption measurements using laser flash photolysis of R-SBP showed that the pronounced photochemical reaction is α-cleavage of the C−S bond, resulting in BTR formation with yields of 0.20 for Me-SBP and 0.15 for Ph-SBP. Triplet sensitization of R-SBP revealed the different photoreactivities of the corresponding T_1 states. Triplet sensitization of Me-SBP using acetone as a sensitizer demonstrated that efficient triplet energy transfer proceeds to produce triplet Me-SBP where no photochemical reactions were found in the triplet state. These observations indicated that only the S_1 state of Me-SBP is involved in the C−S bond cleavage upon direct photolysis of Me-SBP. Furthermore, upon 355 nm laser flash photolysis of triplet Me-SBP, the formation of BTR was confirmed in the transient absorption, indicating the C−S bond cleavages in a highly excited triplet state, T_n ($n \geq 2$) of Me-SBP. The quantum yield of the α-cleavage in the T_n state of Me-SBP was determined to be 0.69. Conversely, triplet sensitization of Ph-SBP using XT as a sensitizer showed that the lowest triplet (T_1) state of Ph-SBP is dissociative for the C−S bond with an efficiency of ≥ 0.56. With the α-cleavability in the S_1 state of Ph-SBP, it was difficult to show clearly, although the radical yield (0.15) upon photolysis of Ph-SBP was not influenced by the amount of the dissolved oxygen. The yield of the intersystem crossing from the S_1 to the T_1 state of Ph-BSP was estimated to be ≤ 0.27. In the present work on the photochemical processes of R-SBP, the absence of photo-Fries rearrangements is concluded irrespective of the spin-multiplicity of the excited states. From the viewpoint of yields of the radical formation, α-cleavage of the C−S bond in the T_n state of Me-SBP may be more feasible than that in the lowest excited states of R-SPh and R-SBP (R = Me and Ph) when acyl and/or S-centered radicals are required for the use as photoinitiating systems for radical photopolymerization reactions. The reaction mechanisms for α-cleavage in the excited states of R-SBP are shown in Schemes 1 and 2.

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Supporting Information Available: Absorption spectrum changes upon steady-state photolysis of R-SBP and photophysical and photochemical features of *p*-phenylthiophenol, *p*-biphenyl methyl sulfide, *S*-methyl thioacetate, and *S*-phenyl thiobenzoate. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) Turro, N. J. *Modern Molecular Photochemistry*; The Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978.

(2) Fleming, S. A.; Pincock, J. A. Chapter 5. In *Organic Molecular Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 1999; Vol. 3, p 211.

(3) Schnabel, W. Chapter 5. In *Laser in Polymer Science and Technology: Applications*; Fouassier, J.-P., Rabek, J. F., Eds.; CRC Press: Boca Raton, FL, 1990; Vol. 2, p 95.

(4) Miranda, M. A.; Galindo, F. Chapter 2. In *Organic Molecular Photochemistry*; Ramamurthy, V., Schanze, K. S., Eds.; Marcel Dekker: New York, 2003; Vol. 9, p 43.

(5) Shizuka, H.; Morita, T.; Mori, Y.; Tanaka, I. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 1831.

(6) Arai, T.; Tobita, S.; Shizuka, H. *Chem. Phys. Lett.* **1994**, *223*, 521.

(7) Arai, T.; Tobita, S.; Shizuka, H. *J. Am. Chem. Soc.* **1995**, *117*, 3968.

(8) Shizuka, H.; Tanaka, I. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2343.

(9) Shizuka, H. *Bull. Chem. Soc. Jpn.* **1969**, *42*, 52.

(10) Grunwell, J. R. *J. Chem. Soc., Chem. Commun.* **1969**, 1437.

(11) Loveridge, E. L.; Beck, B. R.; Bradshaw, J. S. *J. Org. Chem.* **1971**, *36*, 221.

(12) Raveendran Pillai, R.; Eapen, K. C. *Curr. Sci.* **1977**, *46*, 75.

(13) Tomioka, H.; Takimoto, Y.; Kawabata, M.; Harada, M.; Fouassier, J.-P.; Ruhlmann, D. *J. Photochem. Photobiol., A* **1990**, *53*, 359.

(14) Morlet-Savary, F.; Fouassier, J. P.; Tomioka, H. *Polymer* **1992**, *33*, 4202.

(15) Yamaji, M. *Photochem. Photobiol. Sci.* **2008**, *7*, 711.

(16) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*, 2nd ed., rev. and expanded; Marcel Dekker: New York, 1993.

(17) Yamaji, M.; Kobayashi, J.; Tobita, S. *Photochem. Photobiol. Sci.* **2005**, *4*, 294.

(18) Yamamoto, S.; Kikuchi, K.; Kokubun, H. *Chem. Lett.* **1977**, 1173.

(19) Martin, M.; Bréhéret, E.; Tfibel, F.; Lacourbas, B. *J. Phys. Chem.* **1980**, *84*, 70.

(20) McGimpsey, W. G.; Scaiano, J. C. *Chem. Phys. Lett.* **1987**, *138*, 13.

(21) Kajii, Y.; Suzuki, T.; Takatori, Y.; Shibuya, K.; Obi, K. *Bull. Chem. Soc. Jpn.* **1992**, *65*, 1349.

(22) Gannon, T.; McGimpsey, W. C. *J. Org. Chem.* **1993**, *58*, 5639.

(23) Wang, Z.; McGimpsey, W. C. *J. Phys. Chem.* **1993**, *97*, 9668.

(24) Smith, G. A.; McGimpsey, W. C. *J. Phys. Chem.* **1994**, *98*, 2923.

(25) Miranda, M. A.; Pérez-Prieto, J.; Font-Sanchis, E.; Scaiano, J. C. *Acc. Chem. Res.* **2001**, *34*, 717.

(26) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Ouchi, A.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *J. Am. Chem. Soc.* **2004**, *126*, 7432.

(27) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Ouchi, A.; Sugimoto, A.; Kawai, K.; Endo, M.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2005**, *109*, 3797.

(28) Yamaji, M.; Kojima, A.; Tobita, S. *J. Phys. Chem. A* **2007**, *111*, 770.

(29) Yamaji, M.; Mikoshiba, T.; Masuda, S. *Chem. Phys. Lett.* **2007**, *438*, 229.

(30) Yamaji, M.; Nishio, M. *J. Photochem. Photobiol., A* **2008**, *193*, 288.

(31) Yamaji, M.; Cai, X.; Sakamoto, M.; Fujitsuka, M.; Majima, T. *J. Phys. Chem. A* **2008**, *112*, 11306.

(32) Yamaji, M.; Aihara, Y.; Itoh, T.; Tobita, S.; Shizuka, H. *J. Phys. Chem.* **1994**, *98*, 7014.

(33) Melnilov, M. Y.; Smirnov, V. A. *Handbook of Photochemistry of Organic Radicals: Absorption and Emission Properties. Mechanisms and Aging*; Begell House: New York, 1996.

(34) Bensasson, R. V.; Gramain, J.-C. *J. Chem. Soc., Faraday Trans. 1* **1980**, *76*, 1801.

(35) Yamaji, M.; Inomata, S.; Nakajima, S.; Akiyama, K.; Tobita, S.; Marciniak, B. *J. Phys. Chem. A* **2005**, *109*, 3843.

(36) Dauben, W. G.; Salem, L.; Turro, N. J. *Acc. Chem. Res.* **1975**, *8*, 41.

(37) Yamaji, M. Unpublished data determined in an Ac/BP system for triplet energy transfer. The data will be published elsewhere soon.

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