Effects of Localized Triplet Exciton on Reactivity of Photoinduced ω-Bond Dissociation in Naphthyl Phenyl Ketones Having π,π^* Lowest Triplet (T_1) States Studied by Laser Flash Photolysis

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Photochemical properties of photoinduced ω-bond dissociation in naphthyl phenyl ketones having a phenylthiyl moiety as a leaving group, *p*-(α-naphthoyl)benzyl phenyl sulfide (NBPS) and 4-benzoyl-1-naphthylmethyl phenyl sulfide (BNMPS), in solution were investigated by laser flash photolysis techniques. Both ketones were shown to undergo photoinduced ω-bond cleavage of the C−S bond to release the phenyl thiyl radical (PTR) at room temperature. Irrespective of excitation wavelengths of NBPS, a quantum yield (Φ_{rad}) of the PTR formation was obtained to be 0.1, whereas that for BNMPS was found to depend on the excitation wavelength, i.e., absorption bands from the ground state (S_0) to the excited singlet states, S_3, S_2, and S_1 of BNMPS; $\Phi_{rad}(S_3) = 0.77$ and $\Phi_{rad}(S_2) = \Phi_{rad}(S_1) = 1.0$. By using triplet sensitization of *p*-phenylbenzophenone (PBP), efficiencies (α_{rad}) of the radical formation in the lowest triplet state ($T_1(\pi,\pi^*)$) of NBPS and BNMPS were determined to be 0 and 1.0, respectively. The agreement between $\Phi_{rad}(S_1)$ and α_{rad} values for BNMPS indicates that the C−S bond dissociation occurs in the T_1 state via the S_1 state via a fast intersystem crossing from the S_1 to the T_1 state. The wavelength dependence of the radical yields upon direct excitation of BNMPS was interpreted in terms of the C−S bond cleavage in the S_3 state competing with internal conversion from the S_3 to the S_2 state. The smaller value of $\Phi_{rad}(S_3)$ than those of $\Phi_{rad}(S_1)$ and $\Phi_{rad}(S_2)$ was proposed to originate from the geminate recombination of singlet radical pairs produced by the bond dissociation via the S_3 state. Photoinduced ω-cleavage of NBPS was concluded to take place only in the $S_1(n,\pi^*)$ state. Difference in reactivity of ω-cleavage between the triplet states of NBPS and BNMPS was interpreted in terms of localized triplet exciton in the naphthoyl moieties.

Introduction

Photoinduced bond cleavage of aromatic carbonyl compounds, namely, Norrish Type I and II reactions where bond fission occurs at the α and β positions of the carbonyl, respectively, has been widely studied by means of product analysis and time-resolved transient measuremens.[1−29] As with photoinduced dissociation of carbon-heteroatom bonds in aromatic carbonyls, it is known that acetanilide[4a,b] and phenyl acetate,[4c] respectively, undergo C−N and C−O bond dissociation at the α position of the carbonyl group. Much attention has been paid to β-bond dissociation of such as C−O or C−S in excited acetophenone derivatives from the viewpoint of the mechanism of the competitive deactivation processes and spin multiplicities of the dissociative excited states.[15−29] In contrast, bond cleavage at positions other than α- and β-bonds in aromatic carbonyls having a benzophenone skeleton has been paid less attention.[30−35] Since benzophenone is one of the most fundamental compounds in photochemical and photobiological investigations, its photophysical processes are well understood through pico- and nanosecond time-resolved measurements.[36] The lowest excited triplet state (T_1) of benzophenone is produced within 10 ps in solution due to a fast intersystem crossing upon photoexcitation, and the reactive state of the photochemical bimolecular reactions is the T_1 state. Recently, we have been interested in unimolecular photoreactions of benzophenone derivatives, that is, photoinduced bond cleavage at the ω-position.[37−40] ω-Bond cleavage of benzophenone derivatives having C−S, C−Cl and C−Br bonds was characterized to take place mainly in the $T_1(n,\pi^*)$ state.[37−39] With a benzophenone derivative having the C−Br bond, the $S_1(n,\pi^*)$ state was also shown to be reactive for ω-cleavage as well as the $T_1(n,\pi^*)$ state.[37] Novel wavelength dependence of radical yields found upon photolysis of benzoylbenzyl phenyl sulfide was interpreted by considering the ω-bond cleavage in the $S_2(\pi,\pi^*)$ state competing with an internal conversion from the S_2 to the S_1 state.[39] For the occurrence of bond dissociation in excited states, the enthalpy of the cleaving bond must be smaller than the excited energy of the reactive excited state. The estimated bond enthalpies for the C−Cl, C−S, or C−Br bond breaking in the benzophenone derivatives were indeed smaller than the corresponding triplet energies,[37−39] and C−O bond cleavage in *p*-hydroxymethylbenzophenone whose enthalpy for the C−O bonding is larger than the triplet energy was absent.[37] Vice versa, it was shown by using a *p*-phenylbenzophenone derivative that ω-cleavage does not always occur even in aromatic carbonyls

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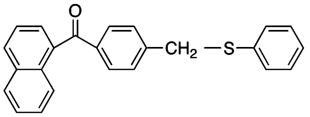
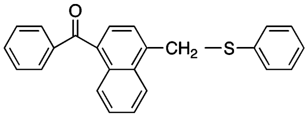
having a smaller bond enthalpy than the excited-state energy.[40] It seems that the spin multiplicity and electronic character of the excited states reactive for ω-cleavage may be closely related to the bond breaking enthalpy and the nature of dissociative energy potentials.

On going from benzophenone to naphthyl phenyl ketone (NPK), the electronic character of the T_1 state changes from n,π* to π,π*, and the triplet energy level decreases.[41] In the present work, two NPK derivatives, naphthoylbenzyl phenyl sulfide (NBPS) and benzoylnaphthylmethyl phenyl sulfide (BNMPS) having C−S bond at the ω position, are used to investigate their reactivity of photoinduced ω-bond cleavage from the viewpoints of electronic structures of reactive states and the relationship between the reactive state energy and the bond dissociation energy. Although the electronic structure and character of their triplet states seem to be the same, there was a significant difference in ω-cleavage in their triplet states in solution as found by means of laser photolysis techniques.



NBPS



BNMPS

Experimental Section

p-(α-Naphthoyl)toluene (NT) and 4-benzoyl-1-methylnaphthalene (BMN) were synthesized by usual Friedel−Crafts acylations of toluene with α-naphthoyl chloride and of α-methylnaphthalene with benzoyl chloride, respectively. NT and BMN were brominated by NBS in CCl_4 at room temperature in the presence of dibenzoylperoxide to provide p-(α-naphthoyl)-α-bromotoluene (NBT) and 4-benzoyl-1-bromomethylnaphthalene (BBMN), respectively. p-(α-Naphthoyl)benzyl phenyl sulfide (NBPS) and 4-benzoyl-1-naphthylmethy phenyl sulfide (BNMPS) were synthesized by the reaction of NBT and BBMN with thiophenol in the presence of K_2CO_3 in acetone, respectively. NBPS and BNMPS were passed through a silica gel column with a mixture of hexane and ethyl acetate (10:1 v/v) and recrystallized from hexane for purification. Acetonitrile (ACN), methanol, and ethanol were distilled for purification. Diethyl ether (spectroscopy grade, Kanto) and isopentane (spectroscopy grade, Fluka) were used as supplied. ACN was used as the solvent at 295 K, and a mixture of diethyl ether-isopentane-ethanol (EPA, 5:5:2 v/v/v) or a mixture of methanol and ethanol (1:1 v/v) was used as matrixes at 77 K. Absorption and emission spectra were recorded on a U-best 50 spectrophotometer (JASCO) and a Hitachi F-4010 fluorescence spectrophotometer, respectively. All of the samples for transient absorption measurements were prepared in the dark and degassed in a quartz cell with a 1 cm path length by several freeze−pump−thaw cycles on a high vacuum line. The concentrations of NBPS or BNMPS for direct laser photolysis were adjusted to achieve the optical density at the excitation wavelength (266, 308, or 355 nm) being less than 1.0 in ACN. Transient absorption measurements were carried out at 295 K unless noted. A XeCl excimer laser (308 nm, Lambda Physik, Lextra 50) and third (355 nm) and fourth harmonics (266 nm) of a Nd^{3+}:YAG laser (JK Lasers HY-500; pulse width 8 ns) were used as light sources for flash photolysis. Less than five repeated pulses were used to avoid excess exposure. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere.[42] The transient data obtained by laser flash photolysis was analyzed by using the least-squares best-fitting method. The transient absorption spectra were taken with a USP-554 system from Unisoku with which can provide a transient absorption spectrum with one laser pulse.

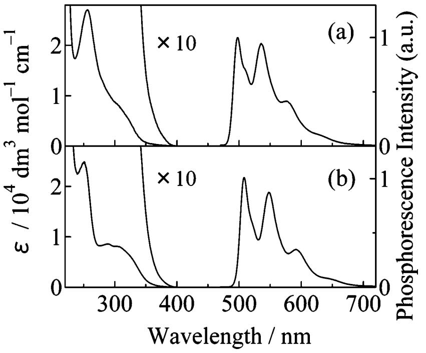


Figure 1. Absorption spectra in ACN at 295 K and phosphorescence spectra in a mixture of methanol and ethanol (1:1 v/v) at 77 K of NBPS (a) and BNMPS (b).

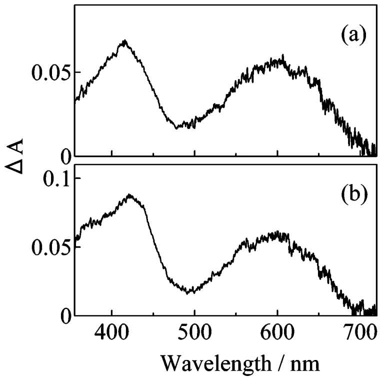


Figure 2. Transient absorption spectra obtained at 500 ns after 266 nm laser pulsing in EPA glass of NBPS (a) and BNMPS (b) at 77 K.

Results and Discussion

Figure 1 shows absorption and phosphorescence spectra of NBPS and BNMPS in ACN at 295 K and in a glass matrix of a mixture of methanol and ethanol (1:1 v/v) at 77 K, respectively.

As with both the absorption spectra, the absorption bands at 260 and 300 nm, having a molar absorption coefficient of the order of $10^3 - 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$ can be classified to be the $S_3(\pi, \pi^*)$ and $S_2(\pi, \pi^*)$ absorption bands due to ^1L_b and ^1L_a bands of the naphthalene moiety, respectively,[43] whereas that at 350 nm can be assigned to the $S_1(n, \pi^*)$ band. It was confirmed that the phosphorescence excitation spectra of NBPS and BNMPS agreed well with the corresponding absorption spectra. The energy levels of the lowest triplet (T_1) state of NBPS and BNMP were determined to be 57.5 and 56.3 kcal mol^{-1} from the phosphorescence origins, respectively. From the similarity in the features of the phosphorescence spectra of NBPS and BNMPS to that of 1-naphthyl phenyl ketone (NPK) whose triplet character is of π,π*,[41] the electronic character of the T_1 states of NBPS and BNMPS are of π,π* in nature.

Figure 2 shows transient absorption spectra observed at 500 ns after 266 nm laser pulsing in EPA glass of NBPS and BNMPS at 77 K.

The absorption spectrum having two bands at 430 and 600 nm is similar to each other and resembles that of triplet NPK.[41] The obtained absorption spectra are ascribed to the triplet states

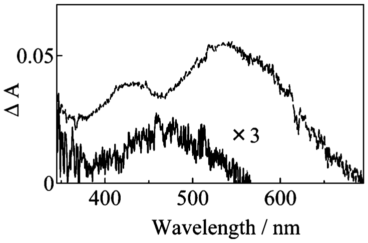
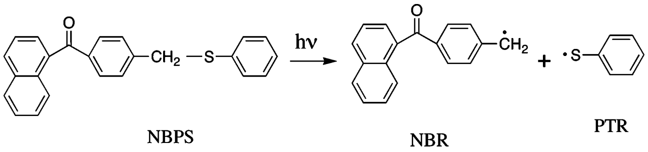


Figure 3. Transient absorption spectrum obtained at 500 ns upon 266 nm laser pulsing in a degassed ACN solution of NBPS at 295 K (dashed) and one at 4.8 μs in an aerated ACN solution of NBPS at 295 K (solid).

of NBPS and BNMPS. After depletion of the triplet absorption, residual absorbance was absent in the wavelength region studied, 350−720 nm. From this observation, any photochemical reactions of NBPS and BNMPS are absent in glass matrixes at 77 K.

Figure 3 shows transient absorption spectra obtained upon 266 nm laser pulsing in ACN solution of NBPS at 295 K.

The absorption spectrum obtained immediately after laser photolysis is due to triplet NBPS. Dissolved oxygen in the ACN solution quenched triplet NBPS, providing a residual absorption band at 450 nm after depletion of triplet NBPS in the transient absorption. The absorption spectrum thus obtained is similar to that of the phenylthiyl radical (PTR) having a molar absorption coefficient, $\epsilon = 2000$ dm^3 mol^{-1} cm^{-1} at 450 nm.[41] The formation of PTR indicates that NBPS undergo ω-cleavage of the C−S bond.The counter radical, *p*-naphthoylbenzyl radical (NBR) was not seen in the wavelength region studied, 350−700 nm. Upon 355 and 308 nm laser photolysis of NBPS in ACN, it was confirmed that a transient absorption spectrum of PTR appeared.



The quantum yield (Φ_{rad}) of the radical formation upon laser pulsing of NBPS was determined with the use of eq 1

$$\Phi_{rad} = \Delta A_{450}\epsilon_{450}{}^{-1}I_{abs}{}^{-1} \qquad (1)$$

where ΔA_{450}, ϵ_{450}, and I_{abs} are respectively the absorption change at 450 nm due to radical formation at 100 ns after laser pulsing, the molar absorption coefficient of PTR at 450 nm (2000 dm^3 mol^{-1} cm^{-1}),[41] and the number of the photon flux of an incident laser pulse at the excitation wavelength. The quantity of I_{abs} was determined by using the absorption of triplet benzophenone (BP) in ACN as an actinometer[44]

$$\Delta A_T^{BP} = \epsilon_T^{BP}\,\Phi_{ISC}^{BP} I_{abs} \qquad (2)$$

where ΔA_T^{BP}, ϵ_T^{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}),[45] and triplet yield of benzophenone (1.0).[46] By using eqs 1 and 2, the Φ_{rad} values were determined to be 0.11 ± 0.01, 0.10 ± 0.01, and 0.09 ± 0.02 upon 266, 308, and 355 nm laser photolyses, respectively. The wavelengths of 266 and 308 nm are located in the S_3 and S_2 absorption bands of NBPS while 355 nm light is absorbed by the S_1 band. The obtained results indicate that the Φ_{rad} values are independent of the excitation wavelength or the absorption bands of NBPS.

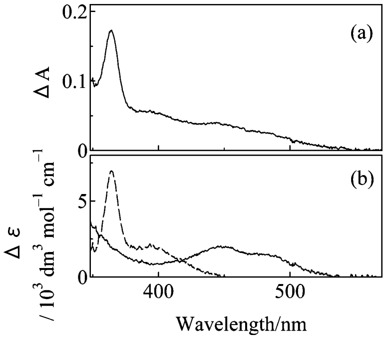
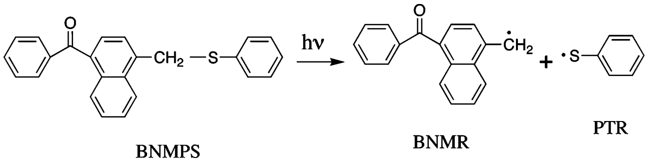


Figure 4. (a) Transient absorption spectrum obtained at 100 ns after 266 nm laser pulsing in an ACN solution of BNMPS at 295 K. (b) Reference absorption spectra of PTR (solid line) and BNMR (broken line) in ACN.

Figure 4a shows a transient absorption spectrum at 100 ns obtained upon 266 nm laser pulsing in ACN solution of BNMPS at 295 K.

The obtained absorption spectrum can be analyzed into those of PTR and the benzoylnaphthylmethyl radical (BNMR, $\epsilon = 6900$ dm^3 mol^{-1} cm^{-1} at 395 nm).[47] Formation of these radicals shows that BNMPS also undergoes ω-cleavage upon photoexcitation.



Upon photolysis of BNMPS with 308 or 355 nm laser pulse, similar absorption spectra to that in Figure 4a were obtained. A quantum yield (Φ_{rad}) of the radical formation upon laser pulsing of BNMPS was determined also with the use of eqs 1 and 2 since BNMR has a negligible ϵ value at 450 nm compared with that of PTR. Interestingly, the Φ_{rad} values obtained for BNMPS were 0.77 ± 0.03, 1.0 ± 0.04, and 1.0 ± 0.04 respectively upon 266, 308, and 355 nm laser photolyses. Therefore, it is apparent that the Φ_{rad} value depends on the excitation wavelength or absorption bands of BNMPS.

To investigate photochemical profiles in the triplet states of NBPS and BNMPS, triplet sensitization by the use of *p*-phenylbenzophenone (PBP) was carried out by transient absorption measurements. Efficient triplet energy transfer from triplet PBP ($E_T = 61.1$ kcal mol^{-1})[48] to NBPS and BNMPS ($E_T =$ 57.5 and 56.3 kcal mol^{-1}) should occur. 4-Benzoyl-1-methylnaphthalene (BMN, $E_T = 56.8$ kcal mol^{-1})[48] was used to compare efficiencies of triplet energy transfer with that of BNMPS. Figure 5 shows transient absorption spectra obtained upon 355 nm laser pulsing in PBP−NBPS (0.01 mol dm^{-3}), PBP−BMN, and PBP−BNMPS systems in ACN.

In the presence of NBPS, BMN, or BNMPS, the intensity of transient absorption due to triplet BPP at 455 nm decreases according to first kinetics with rates of 6.6 × 10^6, 4.7 × 10^6, and 3.0 × 10^6 s^{-1}, respectively (see insets in Figure 5). The residual absorption spectra in Figure 5, panels a and b, which were taken after depletion of triplet PBP, are due to those of triplet NBPS and BMN, respectively, whereas that for BNMPS in Figure 5c is due to the formation of BNMR and PTR (see

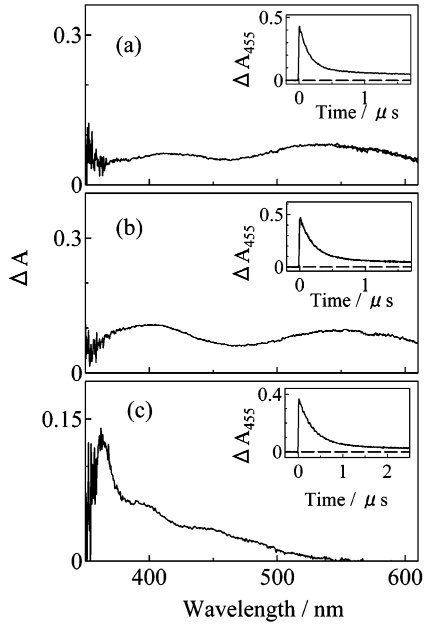


Figure 5. (a) Transient absorption spectrum obtained at 800 ns upon 355 nm laser photolysis of a PBP (7.0×10^{-3} mol dm^{-3})-NBPS (1.0×10^{-3} mol dm^{-3}) system in ACN. Inset; a temporal absorbance change at 455 nm for triplet PBP. (b) A transient absorption spectrum obtained at 1.0 μs upon 355 nm laser photolysis of a PBP (7.0×10^{-3} mol dm^{-3})-BMN (6.0×10^{-4} mol dm^{-3}) system in ACN. Inset; a temporal absorbance change at 455 nm for triplet PBP. (c) A transient absorption spectrum obtained at 1.8 μs upon 355 nm laser photolysis of a PBP (7.0×10^{-3} mol dm^{-3})-BNMPS (4.0×10^{-4} mol dm^{-3}) system in ACN. Inset; a temporal absorbance change at 455 nm for triplet PBP.

Figure 4a). From these observations, it is inferred that ω-cleavage proceeds in the triplet state of BNMPS whereas that is absent in triplet NBPS.

The rates (k_{obsd}) for the decay of triplet PBP obtained in the studied systems are plotted as a function of the concentration, [Q] of NBPS, BMN, or BNMPS as quenchers of triplet PBP in Figure 6a.

Since plots give straight lines, the k_{obsd} can be formulated by

$$k_{obsd} = k_0 + k_q[Q] \tag{3}$$

where k_0 and k_q respectively represent the decay rate of triplet PBP in the absence of Q and the rate constant for quenching of triplet PBP by Q. From the intercept and the slope of the line, the values of k_0 and k_q were determined to be 4.0×10^6 s^{-1} and 6.3×10^9 dm^3 mol^{-1} s^{-1} for NBPS, 7.1×10^9 dm^3 mol^{-1} s^{-1} for BMN and 6.3×10^9 dm^3 mol^{-1} s^{-1} for BNMPS, respectively.

Quantum yields (Φ_{TET} and Φ_{rad}^{sens}) for triplet energy transfer from triplet PBP to BMN, and the formation of the radicals (BNMR and PTR) upon triplet sensitization were respectively determined by eqs 4 and 5

$$\Phi_{TET} = \Delta A_{410}\epsilon_{410}^{\ \ -1}I_{abs}^{PBP-1} \tag{4}$$

$$\Phi_{rad}^{sens} = \Delta A_{450}\epsilon_{450}^{\ \ -1}I_{abs}^{PBP-1} \tag{5}$$

where ΔA_{410}, ΔA_{450}, ϵ_{410} and ϵ_{450}, and I_{abs}^{PBP} are, respectively, the maximum absorption changes due to the formation of triplet BMN at 410 nm and the formation of PTR at 450 nm, molar absorption coefficients of triplet BMN at 410 nm (3300 dm^3 mol^{-1} cm^{-1})[49] and PTR at 450 nm (2000 dm^3 mol^{-1} cm^{-1}), and the number of photon flux of an incident 355 nm laser pulse absorbed by PBP. The value of I_{abs}^{PBP} at 355 nm was determined by using triplet−triplet absorption of benzophenone as an actinometer (see eq 2). The obtained values of Φ_{TET} and Φ_{rad}^{sens} for the XT−BMN and −BNMPS systems are plotted as a function of [Q] in Figure 6b. The value of each yield increases nonlinearly with increasing [Q]. On the other hand, these quantum yields are related with the kinetic parameters, k_0 and k_q by

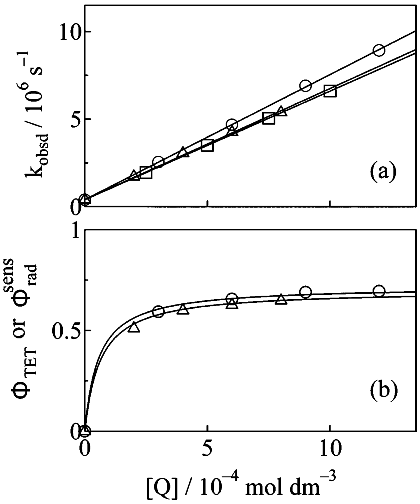


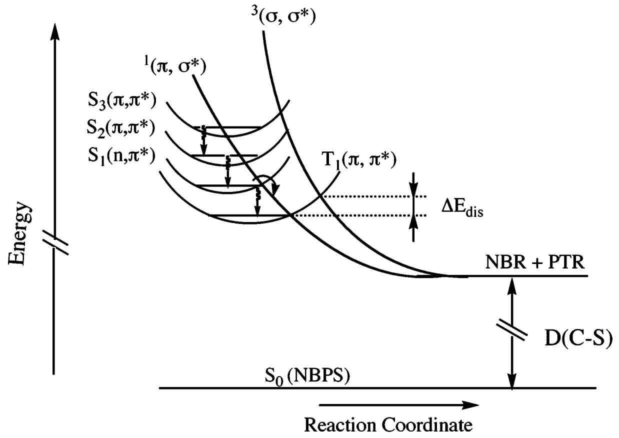
Figure 6. (a) Rate (k_{obsd}) for the decay of triplet PBP plotted as a function of [Q] upon 355 nm laser photolysis in PBP−BMN (7.0×10^{-3} mol dm^{-3}) (○), PBP−BNMPS (△), and PBP−NBPS (□) systems in ACN at 295 K. (b) The quantum yields for formation of triplet BMN (Φ_{TET}) plotted as a function of [Q] obtained upon 355 nm laser photolysis in PBP (7.0×10^{-3} mol dm^{-3})-BMN systems in ACN at 295 K (○) and for radical formation (Φ_{rad}^{sens}) plotted as a function of [Q] obtained upon 355 nm laser photolysis in PBP−BNMPS (7.0×10^{-3} mol dm^{-3}) systems in ACN at 295 K (△). The solid curves were calculated by eqs 6 and 7.

$$\Phi_{TET} = k_q[Q]\alpha_{TET}\,\Phi_{ISC}^{PBP}(k_0 + k_q[Q])^{-1} \qquad \text{Q for BMN} \tag{6}$$

$$\Phi_{rad}^{sens} = k_q[Q]\alpha_{rad}\alpha_{TET}\,\Phi_{ISC}^{PBP}\,(k_0 + k_q[Q])^{-1} \qquad \text{Q for BNMPS} \tag{7}$$

where α_{TET}, α_{rad}, and Φ_{ISC}^{PBP} are efficiencies for triplet energy transfer from triplet PBP to Q and the radical formation in the triplet state of BNMPS, and the triplet yield of PBP (1.0),[46] respectively. By best-fitting eqs 6 and 7 to the experimental values of Φ_{TET} and Φ_{rad}^{sens}, respectively, with the use of the k_0 and k_q values obtained above, a value of α_{TET} for BMN was obtained to be 0.72 ± 0.04 and a product value of α_{rad} and α_{TET} for BNMPS was 0.70 ± 0.04. Assuming that triplet energy transfer from triplet PBP proceeds to naphthylphenyl ketones (BMN and BNMPS) with the same efficiency, α_{TET}, the efficiency for BNMPS is evaluated to be 1.0 within experimental errors. On the other hand, triplet sensitization of NBPS by PBP revealed that ω-dissociation is absent in the triplet state of NBPS, i.e., $\alpha_{rad} = 0$ for NBPS. It is noteworthy that the reactivity for ω-cleavage of triplet BNMPS is quite different from that of triplet NBPS although the electronic character and structure of these triplets are quite similar (see Figure 2). We have determined the quantum yields for ω-dissociation upon direct excitation of NBPS being Φ_{rad} = ca. 0.1 independent of excitation wavelength. From the quantum yield ($\Phi_{rad} = 0.1$) and the efficiency ($\alpha_{rad} = 0$) for photoinduced fragmentation

SCHEME 1: Energy Diagram of Photoexcited NBPS Including the C−S Bond Cleavage Processes



of NBPS, it can be concluded that the reactive state for ω-cleavage of NBPS is only the S_1 state.

We have determined the quantum yields ($\Phi_{rad}(S_1)$ and $\Phi_{rad}(S_2)$) of radical formation upon 355 and 308 nm laser photolyses of BNMPS being unity in the present study. The agreement of the determined α_{rad} value (1.0) with that of Φ_{rad} (= 1.0) indicates that the cleavage of the C−S bond upon the S_2 or S_1 band excitation of BNMPS proceeds in the T_1 state produced by the efficient intersystem crossing from the S_1 state having a quantum yield (Φ_{ISC}) of unity. The $\Phi_{rad}(S_3)$ (= 0.77) value, which is unambiguously smaller than those of $\Phi_{rad}(S_1)$ and $\Phi_{rad}(S_2)$ (= 1.0), implies that there must be a competitive process with internal conversion from the S_3 to the S_2 state. A plausible process is the C−S bond dissociation in the $S_3(\pi,\pi^*)$. When homolytic cleavage proceeds in excited singlet states of NBPS, a singlet radical pairs in solvent cages, $^1(\mathrm{NBR} + \mathrm{PTR})_{cage}$ is initially formed according to the spin-conservation rule. The singlet pair readily undergoes geminate recombination forming the parent molecule. The half-lifetime of geminate recombination, e.g., for PTR, was reported to be ca. 10∼40 ps in solution.[50] Therefore, the geminate recombination between NBR and PTR would be an event during the laser pulse duration (∼8 ns) in the present system. The residual yield ($1 - \Phi_{rad}(S_3)$) of 0.23 would be responsible for ω-dissociation in the S_3 state followed by the geminate recombination.

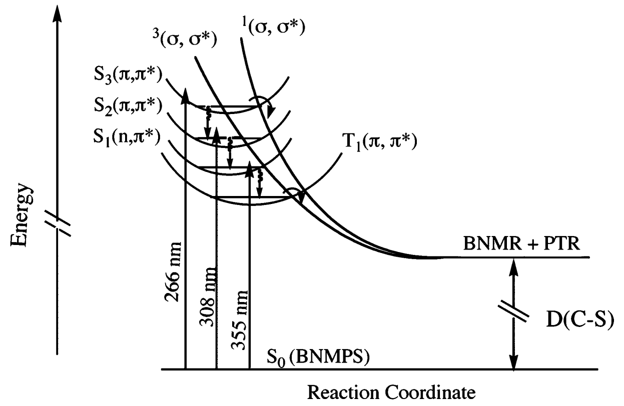
The enthalpies, D(C−S) of the C−S bond in BNPS and BNMPS, were obtained on the basis of the heat of formation ($\Delta_f H$) for BNPS, BNMPS, NBR, BNMR, and PTR computed by using a semiempirical PM3 program contained in *MOPAC '97*. The D(C−S) values are calculated to be 56.4 kcal mol^{-1} for NBPS and 55.0 kcal mol^{-1} for BNMPS by using eqs 9 and 10, respectively, using $\Delta_f H$ (NBPS) = 70.4 kcal mol^{-1}, $\Delta_f H$ (BNMPS) = 65.6 kcal mol^{-1}, $\Delta_f H$ (NBR) = 70.7 kcal mol^{-1}, $\Delta_f H$ (BNMR) = 64.5 kcal mol^{-1}, and $\Delta_f H$ (PTR) = 56.1 kcal mol^{-1}.

$$\Delta_f H(\mathrm{NBPS}) = \Delta_f H(\mathrm{NBR}) + \Delta_f H(\mathrm{PTR}) - D(\mathrm{C{-}S})_{\mathrm{NBPS}} \quad (9)$$

$$\Delta_f H(\mathrm{BNMPS}) = \Delta_f H(\mathrm{BNMR}) + \Delta_f H(\mathrm{PTR}) - D(\mathrm{C{-}S})_{\mathrm{BNMPS}} \quad (10)$$

Based on the obtained results, schematic energy diagrams of photoexcited NBPS and BNMPS are depicted in Schemes 1 and 2, respectively, including the C−S bond cleavage processes.

SCHEME 2: Energy Diagram of Photoexcited BNMPS Including the C−S Bond Cleavage Processes



The dissociation mechanism in the excited states of NBPS and BNMPS can be interpreted to be a thermally activated crossing of the reactive excited state with dissociative potential surfaces leading to free radicals.[51] The electronic configurations of the plausible potentials for the C−S bond rupture are of π,σ^* and σ,σ^*, and the energy level of the former would be located lower than that of the latter at a reaction coordinate. It was originally suggested that radical cleavages of excited states proceed by avoided crossings between states of the same overall symmetry.[52] In that case, excited states of π,π^* would correlate with a σ,σ^* state which leads to a pair of σ radicals, whereas those of n,π^* would interact with a π,σ^* state. With respect to NBPS in Scheme 1, the $S_1(n,\pi^*)$ interacts with a singlet π,σ^* potential, $^1(\pi,\sigma^*)$ of the C−S antibonding, leading to the formation of NBR and PTR with a quantum yield of 0.1 which is independent of the excited absorption bands of NBPS. Absence of fragmentation in the triplet state of NBPS can be interpreted by considering a large energy barrier (ΔE_{dis}) for crossing between the $T_1(\pi,\pi^*)$ state and a dissociative triplet σ,σ^* potential, $^3(\sigma,\sigma^*)$.[51] On the other hand, the crossing profile of triplet BNMPS for ω-cleavage is different from that of triplet NBPS as drawn in Scheme 2. The very efficient cleavage in the triplet state of BNMPS may be responsible for a strong interaction between the $T_1(\pi,\pi^*)$ state and the $^3(\sigma,\sigma^*)$ potential without any energy barriers. When the C−S bond dissociates in the triplet state of BNMPS, a triplet σ-radical pair of BNMR and PTR may be initially produced in a solvent cage according to the spin conservation rule. The triplet radical pair escapes from the solvent cage without geminate recombination which requires that the spin-multiplicity of the radical pair is changed from triplet to singlet via intersystem crossing. Since the rate of escaping from the solvent cage is considered to be much larger than that of intersystem crossing at 295 K, the bond cleavage in triplet BNMPS results in efficient formation of free radicals, BNMR and PTR. The electronic configuration of σ-radical in BNMR immediately after bond dissociation may convert to that of π-radical due to stabilization accrued from π-delocalization in BNMR.

The electronic structure and configuration of triplet NBPS and BNMPS were investigated by measurements of transient absorption (Figure 2) and zero-field splitting parameters (see the Supporting Information) at 77 K where ω-cleavage is absent, presumably, due to rigidity of the media. From the similarity in triplet absorption spectra between NBPS and BNMPS, it is inferred that triplet exciton in the triplets is not delocalized on the phenylthiyl moieties of NMPS and BNMPS. Furthermore, the obtained zero-field splitting parameters for NBPS and BNMPS were similar to each other and closed to those for triplet naphthalene. These similarities in triplet absorption spectra and zero-field splitting parameters indicate that triplet exciton on

TABLE 1: Triplet Energies, Quantum Yields and Efficiencies for Radical Formation, and Enthalpies of C−S Bond Obtained in the Present Work

compounds	E_T/ kcal mol^{-1}	Φ_{rad} (S_3)	Φ_{rad} (S_2)	Φ_{rad} (S_1)	α_{rad} (T_1)	D(C−S)/ kcal mol^{-1}
NBPS	57.5	0.11[a]	0.10[a]	0.09[b]	0	56.4
BNMPS	56.3	0.77[c]	1.0[d]	1.0[d]	1.0	55.0

[a] ±0.01. [b] ±0.02. [c] ±0.03. [d] ±0.04.

NBPS and BNMPS is not delocalized on the naphthyphenyl ketone moiety but localized on the naphthoyl moiety. Consequently, by considering the localized triplet exciton, the presence and the absence of energy barriers for ω-cleavage in the triplet states can be explained. With triplet NBPS, the localized triplet energy is unable to be distributed to an antibonding state, $^3(\sigma,\sigma^*)$, owing to the presence of the benzyl moiety between the naphthoyl and phenylthiyl moieties. On the other hand, with triplet BNMPS, since the naphthoyl moiety where the triplet energy is localized is directly connected with the phenylthiyl moiety, interactions between these moieties are strong enough for triplet energy flow to a $^3(\sigma,\sigma^*)$, resulting in efficient bond dissociation in fluid media. We previously reported that ω-bond dissociation in the triplet π,π^* state of *p*-phenylbenoylbenzyl phenyl sulfide is absent at room temperature.[40] The mechanism was interpreted by the presence of a large energy barrier from the triplet state to a dissociative potential. Effect of localized triplet exciton on ω-bond cleavage in triplet aromatic compounds may be generalized by research of ω-cleavage reactivity of triplet 4-(*p*-benzoyl)phenylbenzyl phenyl sulfide. This work is under investigation.

Conclusion

The reactivity and mechanism of ω-bond dissociation in NBPS and BNMPS were investigated by laser flash photolysis techniques. Both ketones were shown to undergo ω-bond cleavage at room temperature from the observation of the PTR formation. Irrespective of excitation wavelengths of NBPS, a quantum yield (Φ_{rad}) of the PTR formation was obtained to be 0.1 whereas that for BNMPS was found to depend on the absorption bands; $\Phi_{rad}(S_3) = 0.77$ and $\Phi_{rad}(S_2) = \Phi_{rad}(S_1) = 1.0$. Triplet sensitization of PBP revealed that the α_{rad} values for triplet NBPS and BNMPS were 0 and 1.0, respectively. The agreement between $\Phi_{rad}(S_1)$ and α_{rad} values for BNMPS indicates that the C−S bond dissociates in the T_1 state via the S_1 state via a fast intersystem crossing from the S_1 to the T_1 state. A decrease in $\Phi_{rad}(S_3)$ from the unitary values of $\Phi_{rad}(S_1)$ and $\Phi_{rad}(S_2)$ was due to the C−S bond cleavage in the S_3 state followed by the geminate recombination. On the other hand, the ω-cleavage channel of NBPS was found to be only the S_1 state. Due to a large energy barrier from triplet NBPS to a dissociative $^3(\sigma,\sigma^*)$ state, ω-cleavage is absent in the triplet state of NBPS. The presence and the absence of energy barriers for ω-cleavage in NBPS and BNMPS are interpreted in terms of localized triplet exciton in the naphthoyl moieties. Localized triplet exciton in naphthyl phenyl ketones having triplet π,π^* character was proposed through observation of ω-bond cleavability for the first time.

Supporting Information Available: Absorption spectra of NBPS, NT, TA, BNMPS, and BMN and zero-field splitting parameters of naphthalene, NBPS, and BNMPS. This material is available free of charge via the Internet at http://pubs.acs.org.

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(48) The E_T values were determined from the 0−0 origin of the phosphorescence spectrum in a mixture of methanol and ethanol at 77 K.

(49) The ϵ value of triplet BMN was determined by comparing with that of triplet benzophenone (6500 dm^3 mol^{-1} cm^{-1} at 520 nm).[45]

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