J. Phys. Chem. A **2005,** *109,* 3797−3802

Stepwise Photocleavage of C−O Bonds of Bis(substituted-methyl)naphthalenes with Stepwise Excitation by Two-Color Two-Laser and Three-Color Three-Laser Irradiations

Xichen Cai,† Masanori Sakamoto,† Michihiro Hara,† Sachiko Tojo,† Akihiko Ouchi,† Akira Sugimoto,‡ Kiyohiko Kawai,‡ Masayuki Endo,‡ Mamoru Fujitsuka,‡ and Tetsuro Majima*,‡

National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1, Higashi, Tsukuba, Ibaraki 305-8565, Japan, and The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

Received: January 13, 2005; In Final Form: March 17, 2005

Stepwise photocleavage of naphthylmethyl−oxygen (C−O) bonds of mono(substituted-methyl)naphthalenes [1- and 2-$ROCH_2Np$, R = 4-benzoylphenyl (BP), phenyl (Ph), and methyl (CH_3)] and bis(substituted-methyl)-naphthalenes [1,8-$(ROCH_2)_2Np$ and 1,4-$(ROCH_2)_2Np$, R = BP and Ph] was observed to give the naphthylmethyl radicals ($NpCH_2^\bullet$ or $ROCH_2NpCH_2^\bullet$) in almost 100% yield with two-step or three-step excitation by the two-color two-laser or three-color three-laser irradiation, respectively, at room temperature. The C−O bond cleavage quantum yields of 1-$PhOCH_2Np$, 2-$PhOCH_2Np$, 1,8-$(PhOCH_2)_2Np$, and 1,4-$(PhOCH_2)_2Np$ were higher than those of 1-$BPOCH_2Np$, 2-$BPOCH_2Np$, 1,8-$(BPOCH_2)_2Np$, and 1,4-$(BPOCH_2)_2Np$. No C−O bond cleavage occurred from 1,8-$(HOCH_2)_2Np$ and 2-CH_3OCH_2Np in the higher triplet excited state (T_n). The experimental results show that the C−O bond cleavage was determined not only by the position of the substituents on Np but also by the type of the substituents. The C−O bond cleavage of 1-$ROCH_2Np$ was more efficient than that of 2-$ROCH_2Np$. In the case of 1,8-$(ROCH_2)_2Np$ and 1,4-$(ROCH_2)_2Np$ (R = BP and Ph), the first C−O bond cleavage from the T_n states occurred to give $ROCH_2$-substituted naphthylmethyl radicals (1,8- and 1,4-$ROCH_2$-$NpCH_2^\bullet$) when the T_1 states, generated with the 308-nm first laser irradiation, were excited using the 430-nm second laser. The second C−O bond cleavage occurred when 1,8- and 1,4-$ROCH_2NpCH_2^\bullet$ in the ground state [1,8- and 1,4-$ROCH_2NpCH_2^\bullet(D_0)$] were excited to the excited states [1,8- and 1,4-$ROCH_2NpCH_2^\bullet(D_n)$] using the third 355-nm laser during the three-color three-laser flash photolysis at room temperature. It was revealed that acenaphthene was produced as the final product during the stepwise C−O bond cleavages of 1,8-$(BPOCH_2)_2Np$ and 1,8-$(PhOCH_2)_2Np$. This is a successful example of stepwise cleavage of two equivalent C−O bonds in a molecule using the three-color three-laser photolysis method.

Introduction

Photocleavage reactions are very important in photochemistry with respect to bond cleavage in the excited states and formation of radicals.[1,2] Free radicals generated from photocleavages are used practically as radical initiators for polymerization.[3,4] The photocleavage depends on the characteristic of the excited state generated by a one-photon excitation process. For example, a sigma bond cleavage at the benzylic carbon in $ArCH_2$−LG (LG, leaving group) in the singlet (S_1) and triplet (T_1) excited states depends on the bond dissociation energy.[5] The C−N sigma bond cleavage of benzylic ammonium salts occurs through the S_1 and T_1 states,[6] while that of 1-naphthylmethylammonium salts proceeds through the S_1 state but not the T_1 state.[7] These findings can be explained by the difference between the excitation and bond dissociation energies. If the excitation energy is lower than the bond dissociation energy, the bond cleavage does not occur. In addition to the excitation energy, the barrier between the excited state potential surface and bond dissociation surface is another important factor.[5] If a high barrier exists, the occurrence of the bond cleavage is difficult even when the excitation energy is higher than the bond dissociation energy.

Herein, we report that generation of the naphthylmethyl radical, produced through the naphthylmethyl−oxygen (C−O) bond cleavage, can be controlled by two- or three-laser irradiations through the higher triplet excited states (T_n). The occurrence of the C−O bond cleavage is regulated by both excitation energy and crossing between potential surfaces of the T_n state and C−O bond dissociation. In other words, the excitation energy dissipation or delocalization in the T_n state molecule is important for the bond dissociation.[3,8]

Naphthylmethyl radical ($NpCH_2^\bullet$) as a typical organic radical can be produced through photochemical bond cleavage reactions.[9−11] It is well-known that photolysis of halomethylnaphthalenes leads to the efficient formation of $NpCH_2^\bullet$ from both the S_1 and T_1 states through the methyl−halogen bond cleavage.[10,12] On the other hand, in the case of (4-benzoylphenoxylmethyl)naphthalene ($BPOCH_2Np$) or (4-phenoxylmethyl)-naphthalene ($PhOCH_2Np$), $NpCH_2^\bullet$ is produced only from the S_1 state, but not from the T_1 state, because of the higher C−O bond cleavage energy than the excitation energy of the T_1 state.[13,14] Recently, we have reported that the fast C−O bond cleavage occurred to give $NpCH_2^\bullet$ in 1- and 2-$BPOCH_2Np$ in the T_n states.[15] We have also found that the two C−O bond

---

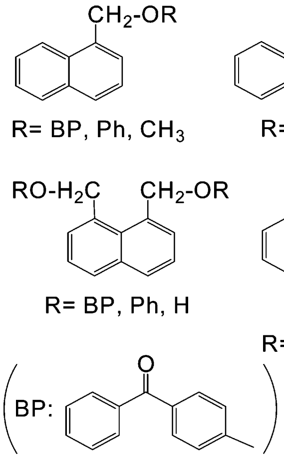
* Corresponding author. E-mail: majima@sanken.osaka-u.ac.jp. Phone: +81-6-6879-8495. Fax: +81-6-6879-8499.

† National Institute of Advanced Industrial Science and Technology (AIST).

‡ Osaka University.

10.1021/jp050232q CCC: $30.25

CHART 1



cleavages of 1,8-$(BPOCH_2)_2Np$ occurred in a stepwise manner to give acenaphthene as a final product through photocleavage from the T_n and excited state radical [1,8-$BPOCH_2NpCH_2^{\bullet}$-(D_n)].[16]

We have conducted two-color two-laser and three-color three-laser photolyses of various mono- and bis(substituted-methyl)-naphthalenes such as 1-(4-benzoylphenoxymethyl)naphthalene (1-$BPOCH_2Np$), 1-phenoxymethylnaphthalene (1-$PhOCH_2Np$), 1-methoxymethylnaphthalene (1-CH_3OCH_2Np), 2-(4-benzoylphenoxymethyl)naphthalene (2-$BPOCH_2Np$), 2-phenoxymethylnaphthalene (2-$PhOCH_2Np$), 2-methoxymethylnaphthalene (2-CH_3OCH_2Np), 1,8-bis(4-benzoylphenoxymethyl)naphthalene [1,8-$(BPOCH_2)_2Np$], 1,8-bis(phenoxymethyl)naphthalene [1,8-$(PhOCH_2)_2Np$], 1,8-bis(hydroxymethyl)naphthalene [1,8-$(HOCH_2)_2Np$], 1,4-bis(4-benzoylphenoxymethyl)naphthalene [1,4-$(BPOCH_2)_2Np$], and 1,4-bis(phenoxymethyl)naphthalene [1,4-$(PhOCH_2)_2Np$] (Chart 1).

The determined quantum yields of the C−O bond cleavages have indicated that the position and the type of the substituents have an influence on the C−O bond cleavage; namely, the C−O bond cleavage occurs more efficiently for 1-$ROCH_2Np$ than for 2-$ROCH_2Np$, and the properties of the T_n state are different from those of the T_1 state.

Experimental Section

Materials. 1-(4-Benzoylphenoxymethyl)naphthalene, 1-phenoxymethylnaphthalene, and 1-methoxymethylnaphthalene were synthesized from 1-(chloromethyl)naphthalene. 2-(4-Benzoylphenoxymethyl)naphthalene, 2-phenoxymethylnaphthalene, and 2-methoxymethylnaphthalene were synthesized from 2-(bromomethyl)naphthalene. 1,8-Bis(4-benzoylphenoxymethyl)naphthalene, 1,8-bis(phenoxymethyl)naphthalene, 1,4-bis(4-benzoylphenoxymethyl)naphthalene, and 1,4-bis(phenoxymethyl)naphthalene were synthesized from 1,8-bis(bromomethyl)naphthalene and 1,4-bis(bromomethyl)naphthalene.[13] 1,8-Bis(hydroxymethyl)-naphthalene was synthesized from 1,8-naphthalic anhydride.[13] Benzophenone, acetonitrile, and cyclohexane were purchased from Nacalai Tesque Inc. Benzophenone was purified from ethanol before use as the triplet sensitizer. Acetonitrile and cyclohexane (spectral grade) were used as received. All sample solutions were freshly prepared and deoxygenated by bubbling with argon (Ar) gas before irradiation. All experiments were carried out at room temperature.

Two-Color Two-Laser and Three-Color Three-Laser Flash Photolyses. The laser flash at 355 nm from a Nd:YAG laser (Continuum, Surelite II-10; 5-ns fwhm, 10 Hz) and the laser flash at 430 nm (7 mJ $pulse^{-1}$) from an OPO laser (Continuum, Surelite OPO) which was pumped by a Nd:YAG laser (355 nm, 150 mJ $pulse^{-1}$) were used for the two-color two-laser flash photolysis experiments. The laser flashes at 308 (Lambda Physik, COMPex, 5 mJ $pulse^{-1}$, 20 ns), 355, and 430 nm were used for the three-color three-laser flash photolysis experiments. Two or three laser flashes that were irradiated to the sample were synchronized by a pulse generator with a delay time of 10 ns−10 μs. The probe beam was obtained by passing the light from a 450-W Xe lamp (Osram XBO-450) through an iris with a diameter of 0.3 cm. The transient phenomena was monitored by the probe beam that was guided into the sample perpendicular to the laser beams at an area very close to the incident side of the laser beam. The transmitted probe beam was then focused on a monochromator (Nikon G250). The output of the monochromator was monitored using a photomultiplier tube (PMT; Hamamatsu Photonics R928). The signal from the PMT was recorded on a transient digitizer (TDS 580D four-channel digital phosphor oscilloscope, 1 GHz, Tektronix). A Hamamatsu Photonics multichannel analyzer (C5967) system was used for the measurement of the transient absorption spectra. The total system was controlled with a personal computer via GP-IB interface. To avoid any damage of the sample solution by the probe light, a suitable cutoff filter was used in front of the sample.

Results and Discussion

C−O Bond Cleavage of $ROCH_2Np$ in the T_n State during the Two-Color Two-Laser Flash Photolysis. The two-color two-laser (355- and 430-nm lasers) transient absorption measurements of 1-$ROCH_2Np$ and 2-$ROCH_2Np$ (R = BP, Ph, and CH_3) were carried out in Ar-saturated acetonitrile at room temperature. Because the hydrogen abstraction reaction of BP in the T_1 state from hydrogen-donor solvents such as hexane and cyclohexane occurs to give the BP ketyl radical during the laser flash photolysis, the two-color two-laser photolysis experiments of $ROCH_2Np$ were done in acetonitrile.

In the cases of 1-$ROCH_2Np$ and 2-$ROCH_2Np$ (R = Ph and CH_3), benzophenone (6.0×10^{-3} M) was used as the triplet sensitizer. The transient absorption of the naphthalene moiety in the T_1 state [$Np(T_1)$] was observed during the first 355-nm laser irradiation, which was generated by the intramolecular (by the BP substituent) or intermolecular (by the benzophenone triplet sensitization) energy transfer reactions.[15,17]

The transient absorption spectra of all $ROCH_2Np$ in the T_1 states [$ROCH_2Np(T_1)$] showed the characteristic absorption of $Np(T_1)$ with two peaks around 425 and 400 nm.[18,19] Therefore, BP, Ph, and CH_3 substituents have little effect on the electronic property of $Np(T_1)$, indicating that the excitation energy of the T_1 state is localized on the Np moiety. Because of the higher C−O bond dissociation energy (285 kJ mol^{-1}) than the excitation energy of $Np(T_1)$ (254 kJ mol^{-1}), no C−O bond cleavage occurred from $ROCH_2Np(T_1)$.[14,19]

The transient absorption spectra observed during the two-color two-laser flash photolysis of 1-$PhOCH_2Np$ and 2-$PhOCH_2Np$ are shown in parts a and b of Figure 1, respectively. The bleaching of the absorption of $ROCH_2Np(T_1)$ at 425 nm ($\Delta\Delta O.D._{425}$) and growth of the transient absorption in the region of 330−380 nm increased with an increase in the second 430-nm laser power. The plots of $\Delta\Delta O.D._{425}$ versus 430-nm laser power are shown in Figure 2a and b. The same results have been observed during the two-color two-laser flash photolysis of 1-$BPOCH_2Np$ and 2-$BPOCH_2Np$, as reported previously.[15] On the other hand, according to extinction coefficient (ϵ) values

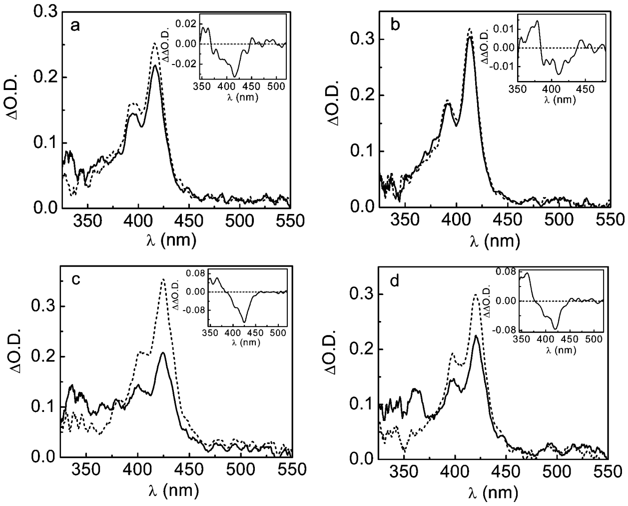


Figure 1. Transient absorption spectra observed during the two-color two-laser photolysis of 1-$PhOCH_2Np$ (a), 2-$PhOCH_2Np$ (b), 1,8-$(PhOCH_2)_2Np$ (c), and 1,4-$(PhOCH_2)_2Np$ (d) in Ar-saturated acetonitrile at room temperature. Benzophenone (6.0×10^{-3} M) was used as the triplet sensitizer. The transient absorption spectra were observed during the 355-nm laser irradiation (at 500 ns after the laser flash) (dotted line), successive irradiation with 355- and 430-nm lasers (at 100 ns after the second 430-nm laser flash; delay time between the two lasers, 400 ns) (solid line). The inset shows the transient absorption spectral changes (ΔΔO.D.) which were obtained by subtraction of the dotted line from the solid line for parts a—d.

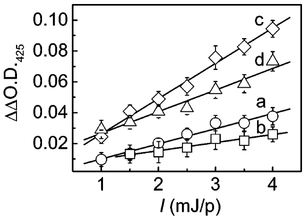


Figure 2. Plots of $\Delta\Delta O.D._{425}$ vs 430-nm laser power: 1-$PhOCH_2Np$ (circles, a); 2-$PhOCH_2Np$ (squares, b); 1,8-$(PhOCH_2)_2Np$ (diamonds, c); 1,4-$(PhOCH_2)_2Np$ (triangles, d).

of 1-$NpCH_2^\bullet$ at 365 nm ($\epsilon_{365} \approx 10\,000$ M^{-1} cm^{-1})[15] and 2-$NpCH_2^\bullet$ at 380 nm ($\epsilon_{380} = 5000 \pm 300$ M^{-1} cm^{-1}),[20] the concentration of $ROCH_2Np(T_1)$ disappeared ([1-$PhOCH_2Np(T_1)$] = ($\Delta\Delta O.D._{425} = 0.019$)/($\epsilon_{425} = 9135$ M^{-1} cm^{-1}) = 2.08×10^{-6} M; [2-$PhOCH_2Np(T_1)$] = ($\Delta\Delta O.D._{425} = 0.009$)/($\epsilon_{425} = 5769$ M^{-1} cm^{-1}) = 1.56×10^{-6} M, ϵ_{425} values are given in Table 1) was almost equal to those of 1- and 2-$NpCH_2^\bullet$ formed ([1-$NpCH_2^\bullet$] = ($\Delta\Delta O.D._{365} = 0.017$)/($\epsilon_{365}$ = 10,000 M^{-1} cm^{-1}) = 1.7×10^{-6} M; [2-$NpCH_2^\bullet$] = ($\Delta\Delta O.D._{380} = 0.009$)/($\epsilon_{380}$ = 5000 ± 300 M^{-1} cm^{-1}) = $1.8 \pm 0.1 \times 10^{-6}$ M) within the second laser duration, where $\Delta\Delta O.D._{425}$, $\Delta\Delta O.D._{365}$, and $\Delta\Delta O.D._{380}$ were the decrease and increase of the transient absorption at 425, 365, and 380 nm, assigned to $ROCH_2Np(T_1)$, 1-$NpCH_2^\bullet$, and 2-$NpCH_2^\bullet$ radicals, respectively. Therefore, the growth of the transient absorption in the region of 330—380 nm was assigned to the formation of $NpCH_2^\bullet$.[10,11,13,14] The C—O bond cleavage occurred from the T_n states during the second 430-nm laser excitation of the T_1 states.[15] The transient absorptions of $BPO^\bullet$ and $PhO^\bullet$ radicals around 395 nm overlapped with the T_1 state absorption at 400 nm.[14,21]

The transient absorption spectra observed for 1-CH_3OCH_2Np and the plots of $\Delta\Delta O.D._{425}$ versus 430-nm laser power are shown in Supporting Information Figure S1. No $\Delta\Delta O.D._{425}$ was observed in the cases of 2-CH_3OCH_2Np during the two-color two-laser flash photolysis experiments, as shown in Figure 3a.

TABLE 1: Φ Values of Cleavage of One of the C—O Bonds of $ROCH_2Np$ and $(ROCH_2)_2Np$

$ROCH_2Np$ and $(ROCH_2)_2Np$	ϵ_{425}[a] (M^{-1} cm^{-1})	Φ[b]
1,8-$(PhOCH_2)_2Np$	16827	0.25 ± 0.02
1,4-$(PhOCH_2)_2Np$	12980	0.15 ± 0.01
1-$PhOCH_2Np$	9135	0.11 ± 0.01
2-$PhOCH_2Np$	5769	0.06 ± 0.02
1,8-$(BPOCH_2)_2Np$	9140	0.09 ± 0.01
1,4-$(BPOCH_2)_2Np$	6350	0.07 ± 0.01
1-$BPOCH_2Np$	12250	0.04 ± 0.01
2-$BPOCH_2Np$	9052	0.02 ± 0.01
1-CH_3OCH_2Np	8173	0.05 ± 0.02
2-CH_3OCH_2Np	5300	0
1,8-$(HOCH_2)_2Np$	11058	0

[a] ϵ_{425} is the extinction coefficient for $ROCH_2Np$ and $(ROCH_2)_2Np$ in the T_1 states at 425 nm, with ϵ_{525} = 6250 M^{-1} cm^{-1} of benzophenone(T_1) as the reference.[19] [b] Φ is the quantum yield of the C—O bond cleavage which is calculated from the bleaching of the T_1 state ($\Delta\Delta O.D._{425}$) and the number of the second laser photons absorbed by the T_1 state using an actinometry of T—T absorption of zinc tetraphenylporphyrin at 470 nm in cyclohexane ($\epsilon_T\Phi_T$ = 50 000 M^{-1} cm^{-1} at 470 nm).[22]

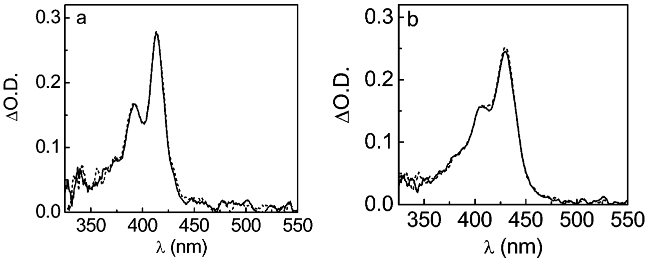


Figure 3. Transient absorption spectra observed during the two-color two-laser photolysis of 2-CH_3OCH_2Np (a) and 1,8-$(HOCH_2)_2Np$ (b) in Ar-saturated acetonitrile at room temperature. Benzophenone (6.0 × 10^{-3} M) was used as the triplet sensitizer. The transient spectra were observed during the 355-nm laser irradiation (at 500 ns after the laser flash) (dotted line), successive irradiation with 355- and 430-nm lasers (at 100 ns after the second 430-nm laser flash; delay time between the two lasers, 400 ns) (solid line). The dotted and solid lines overlapped completely.

From the slopes of the linear plots of $\Delta\Delta O.D._{425}$ versus the second 430-nm laser intensity, the quantum yield (Φ) of the C—O bond cleavage of monosubstituted naphthalenes was calculated, as shown in Table 1.

C—O Bond Cleavage of $(ROCH_2)_2Np$ in the T_n State during the Two-Color Two-Laser Flash Photolysis. Similarly, the two-color two-laser (355- and 430-nm laser) transient absorption measurements were carried out for 1,8-$(ROCH_2)_2Np$ (R = BP, Ph, and H) and 1,4-$(ROCH_2)_2Np$ (R = BP and Ph) in Ar-saturated acetonitrile at room temperature. The transient absorption of $Np(T_1)$ generated by the intramolecular (by the BP substituent) or intermolecular (by the benzophenone triplet sensitization) energy transfer reactions was observed during the first 355-nm laser irradiation.[15,17]

It was found that the transient absorption spectra of all $(ROCH_2)_2Np(T_1)$ showed the characteristic $Np(T_1)$ absorption with two peaks around 425 and 400 nm.[18,19] Therefore, BP, Ph, and H substituents have little effect on $Np(T_1)$ in $(ROCH_2)_2Np(T_1)$, indicating that the excitation energy of $(ROCH_2)_2Np(T_1)$ is localized on the Np moiety and that no C—O bond cleavage occurs from $(ROCH_2)_2Np(T_1)$.[14,16]

$\Delta\Delta O.D._{425}$ and growth of the new absorption bands in the region of 330—380 nm due to the absorption of the naphthylmethyl radicals ($ROCH_2NpCH_2^\bullet$)[10,11,13,14] were observed from 1,8- and 1,4-$(BPOCH_2)_2Np$ and $(PhOCH_2)_2Np$. The C—O bond cleavage also occurred from the T_n states during the second

430-nm laser excitation of the T_1 states generated from the first 355-nm laser excitation.[15]

Because the second 430-nm laser excitation energy is not enough for a concomitant cleavage of two C$-$O bonds, only one C$-$O bond cleavage occurred from the T_n states of 1,8-$(BPOCH_2)_2Np$, 1,4-$(BPOCH_2)_2Np$, 1,8-$(PhOCH_2)_2Np$, and 1,4-$(PhOCH_2)_2Np$.[16] It was confirmed by the results that the concentration of $(ROCH_2)_2Np(T_1)$ disappeared ([1,8-$(PhOCH_2)_2Np(T_1)$] = ($\Delta\Delta O.D._{425} = 0.13$)/($\epsilon_{425} = 16\,827$ M^{-1} cm^{-1}) = 7.73×10^{-6} M; [1,4-$(PhOCH_2)_2Np(T_1)$] = ($\Delta\Delta O.D._{425} = 0.075$)/($\epsilon_{425} = 12\,980$ M^{-1} cm^{-1}) = 5.78×10^{-6} M, ϵ_{425} values are given in Table 1) was almost equal to those of 1,8- and 1,4-$PhOCH_2NpCH_2^\bullet$ formed within the second laser duration ([1,8-$ROCH_2NpCH_2^\bullet$] = ($\Delta\Delta O.D._{365} = 0.072$)/($\epsilon_{365} = 10\,000$ M^{-1} cm^{-1}) = 7.2×10^{-6} M; [1,4-$ROCH_2NpCH_2^\bullet$] = ($\Delta\Delta O.D._{365} = 0.063$)/($\epsilon_{365} = 10\,000$ M^{-1} cm^{-1}) = 6.3×10^{-6} M, suggesting that the ϵ_{365} values of 1,8-$ROCH_2NpCH_2^\bullet$ and 1,4-$ROCH_2NpCH_2^\bullet$ are the same as that of 1-$NpCH_2^\bullet$ at 365 nm). The transient absorption spectra observed during the two-color two-laser flash photolysis of 1,8-$(PhOCH_2)_2Np$ and 1,4-$(PhOCH_2)_2Np$ are also shown in parts c and d of Figure 1, respectively. Plots of $\Delta\Delta O.D._{425}$ versus the 430-nm laser power are shown in Figure 2c and d. Similar transient absorption was observed during the two-laser flash photolysis of 1,8- and 1,4-$(BPOCH_2)_2Np$.[16]

No $\Delta\Delta O.D._{425}$ was observed in the cases of 1,8-$(HOCH_2)_2Np$ during the two-color two-laser flash photolysis experiments, as shown in Figure 3b.

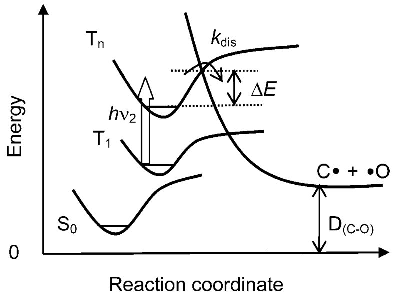
From the slope of the linear plots of $\Delta\Delta O.D._{425}$ versus the second 430-nm laser intensity, Φ of the C$-$O bond cleavage of bis-substituted naphthalenes was calculated, Table 1.

These results indicate that the C$-$O bond cleavage was affected by both the type and the position of the substituent on Np. In the case of $ROCH_2Np$, the Φ value for 1-substituted Np was larger than that for 2-substituted Np, which is similar to the former results.[15] The Φ value dependence on the type of the substituents indicates the importance of the delocalization of the excitation energy in the T_n states for the C$-$O bond cleavage. The delocalization of the π-electrons on the phenyl group and oxygen atom should occur in the cases of 1-$BPOCH_2Np$, 2-$BPOCH_2Np$, 1-$PhOCH_2Np$, and 2-$PhOCH_2Np$, so that similar delocalization of the excitation energy is expected in the T_n state. On the other hand, such delocalization of the π-electrons is not possible with a methyl substituent on the oxygen atom in the case of 1-CH_3OCH_2Np and 2-CH_3OCH_2Np.

Therefore, the Φ values of 1-$BPOCH_2Np$, 2-$BPOCH_2Np$, 1-$PhOCH_2Np$, and 2-$PhOCH_2Np$ were much larger than those of 1-CH_3OCH_2Np and 2-CH_3OCH_2Np. The occurrence of the C$-$O bond cleavage can be explained by the excitation energy of the T_n state and the crossing of the potential surfaces of the T_n state and C$-$O bond dissociation of the $ROCH_2Np$, which are regulated by the structure and position of the substituents on Np (Scheme 1).

Since a low energy barrier (ΔE) exists between the potential surfaces of the T_n states and the C$-$O bond dissociation, C$-$O bond cleavage of 1-$BPOCH_2Np$, 2-$BPOCH_2Np$, 1-$PhOCH_2Np$, and 2-$PhOCH_2Np$ occurred from the T_n states. On the other hand, no C$-$O bond cleavage occurred from 2-CH_3OCH_2Np in the T_n states. It is explained by the existence of a large ΔE value between the potential surfaces of the T_n states and the C$-$O bond dissociation, although the excitation energy of the T_n state is larger than the C$-$O bond dissociation energy. The larger Φ values for 1-$PhOCH_2Np$ and 2-$PhOCH_2Np$ than those for 1-$BPOCH_2Np$ and 2-$BPOCH_2Np$ can be explained by the presence of the benzoyl group on the phenyl substituent. The excitation energy of the T_n states is more efficiently delocalized in 1-$BPOCH_2Np$ and 2-$BPOCH_2Np$ due to the benzoyl group. Thus, the ΔE values of 1-$BPOCH_2Np$ and 2-$BPOCH_2Np$ may be slightly larger than those of 1-$PhOCH_2Np$ and 2-$PhOCH_2Np$. Therefore, the Φ values for 1-$PhOCH_2Np$ and 2-$PhOCH_2Np$ should be larger than those for 1-$BPOCH_2Np$ and 2-$BPOCH_2Np$.

SCHEME 1: Energy Diagram of $ROCH_2Np$ in the S_0, T_1, and T_n States during the Two-Color Two-Laser Flash Photolysis of $ROCH_2Np$ and $(ROCH_2)_2Np$[a]



[a] $h\nu_2$, the second 430-nm laser excitation; k_{dis}, rate constant of the C$-$O bond cleavage; ΔE, energy barrier between the potential surfaces; $D_{(C-O)}$, C$-$O bond dissociation energy; $C^\bullet$, $NpCH_2^\bullet$ or $ROCH_2NpCH_2^\bullet$; $^\bullet O$, $RO^\bullet$.

In the case of $(ROCH_2)_2Np$, only one C$-$O bond cleavage occurred from the T_n states during the two-color two-laser flash photolysis, because the 430-nm laser photon energy is not enough for the simultaneous two C$-$O bond cleavages.[16] The higher Φ values for 1,8-$(BPOCH_2)_2Np$, 1,4-$(BPOCH_2)_2Np$, 1,8-$(PhOCH_2)_2Np$, and 1,4-$(PhOCH_2)_2Np$ than those for 1-$BPOCH_2Np$, 2-$BPOCH_2Np$, 1-$PhOCH_2Np$, and 2-$PhOCH_2Np$ indicate that the C$-$O bond cleavage efficiency for $(ROCH_2)_2Np$ is higher than that for $ROCH_2Np$. The 2-fold larger Φ values for 1,8-$(ROCH_2)_2Np$ than those for 1-$ROCH_2Np$ indicate that the excitation energy of the T_n state is dispersed more efficiently including the C$-$O bond in 1,8-$(ROCH_2)_2Np(T_n)$. The dissipation of the T_n state energy in 1,8-$(ROCH_2)_2Np(T_n)$ is almost 2 times larger than that of 1-$ROCH_2Np(T_n)$. Because the two $ROCH_2$ groups at the 1- and 8-positions have an equivalent environment in 1,8-$(ROCH_2)_2Np$, two equivalent crossing points should exist between the two C$-$O bond dissociation surfaces and the T_n state potential surface. When 1,8-$(ROCH_2)_2Np(T_1)$ is excited to 1,8-$(ROCH_2)_2Np(T_n)$, the excitation energy is delocalized on the Np and one of the two $ROCH_2$ substituents leads to one C$-$O bond cleavage, giving 1,8-$ROCH_2NpCH_2^\bullet$ and $RO^\bullet$.

In the case of 1,8-$(HOCH_2)_2Np$, the π-electron delocalization between Np and $-CH_2OH$ is impossible in the T_n state, because only a hydrogen atom is bonded to the oxygen atom. Therefore, the C$-$O bond cleavage was not observed. In other words, a large ΔE value exists between the potential surfaces of 1,8-$(HOCH_2)_2Np(T_n)$ and the C$-$O bond dissociation.

Two-Step Cleavage of the Two C$-$O Bonds of $(BPOCH_2)_2Np$ during the Three-Color Three-Laser Flash Photolysis. The two-step cleavage of the two C$-$O bonds of $(BPOCH_2)_2Np$ was observed during the three-color three-laser (the first 308-nm, second 430-nm, and third 355-nm laser) photolysis of 1,8-$(BPOCH_2)_2Np$ and 1,4-$(BPOCH_2)_2Np$ in Ar-saturated acetonitrile at room temperature.[16] In the case of 1,8-$(BPOCH_2)_2Np$, most of the first 308-nm photons were absorbed by the BP group to give 1,8-$(^1BP^*OCH_2)_2Np(S_1)$. The excitation energy of the S_1 state is mainly localized on the BP moiety, from which

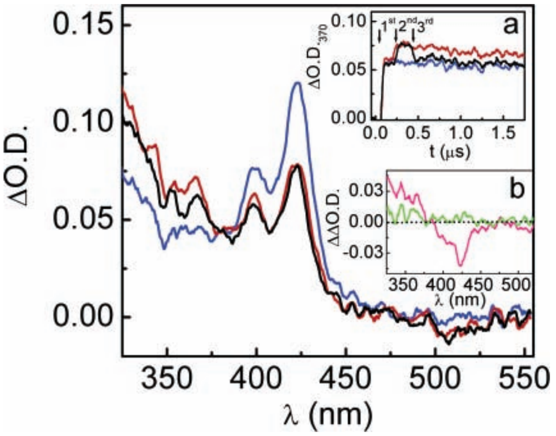


Figure 4. Three-color three-laser photolysis of 1,8-$(PhOCH_2)_2Np$ in Ar-saturated cyclohexane. The transient spectra observed during the 308-nm laser irradiation (at 500 ns after the laser flash) (blue line), successive irradiation with 308- and 430-nm lasers (at 300 ns after the second laser flash; delay time between the two lasers, 200 ns) (red line), and successive irradiation of 308-, 430-, and 355-nm lasers (at 100 ns after the third laser flash; delay time between the lasers, 200 ns and 200 ns) (black line). The time profiles of the transient absorption at 370 nm during irradiation with the one 308-nm laser (blue line), two 308- and 430-nm lasers (red line), and three 308-, 430-, and 355-nm lasers (black line) are shown in inset a of Figure 4, in which 1st, 2nd, and 3rd refer to the irradiation time of the 308-, 430-, and 355-nm lasers, respectively. The transient absorption spectral changes (ΔΔO.D.) are shown in inset b of Figure 4, where the pink line refers to the changes between the first 308-nm laser and second 430-nm laser irradiation which were obtained by subtraction of the red line from the blue line, and the green line refers to the changes between the second 430-nm laser and third 355-nm laser irradiation which were obtained by subtraction of the black line from the red line.

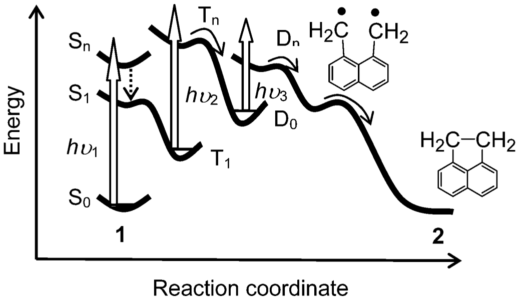
a very fast intersystem crossing (ISC) occurred with high quantum yield ($\Phi_{ISC} = 1.0$)[1,19] to give 1,8-$(^3BP^*OCH_2)_2Np$-(T_1) with the excitation energy mainly localized on the BP moiety. Subsequently, fast intramolecular energy transfer occurred from the BP(T_1) moiety to the Np moiety to give 1,8-$(BPOCH_2)_2{}^3Np^*(T_1)$ with the excitation energy mainly localized on the Np moiety.[14−16] 1,8-$BPOCH_2NpCH_2^\bullet$ was not observed from 1,8-$(BPOCH_2)_2{}^3Np^*(T_1)$. The selective excitation of the Np(T_1) moiety of 1,8-$(BPOCH_2)_2{}^3Np^*(T_1)$ by the second 430-nm laser gave 1,8-$(BPOCH_2)_2Np(T_n)$ whose excitation energy delocalized including the C−O bonds, and the ground state 1,8-$BPOCH_2NpCH_2^\bullet(D_0)$ is generated from the first C−O bond cleavage. The third 355-nm laser excitation of the $NpCH_2^\bullet$ moiety of 1,8-$BPOCH_2NpCH_2^\bullet$ gave excited 1,8-$BPOCH_2$-$NpCH_2^\bullet(D_n)$, from which the final product acenaphthene is produced from a biradical [1,8-$(^\bullet CH_2)_2Np$] generated by the second C−O bond cleavage.[16]

Two-Step Cleavage of the Two C−O Bonds of $(PhOCH_2)_2$-Np during the Three-Color Three-Laser Flash Photolysis. One C−O bond cleavage of 1,8-$(PhOCH_2)_2Np(T_n)$ occurred to give 1,8-$PhOCH_2NpCH_2^\bullet$ with larger Φ than that from 1,8-$(BPOCH_2)_2Np(T_n)$. Similar stepwise photocleavage of two C−O bonds to that of 1,8-$(BPOCH_2)_2Np$ was expected for 1,8-$(PhOCH_2)_2Np$ during the three-color three-laser photolysis. Because the solubilities of 1,4-$(PhOCH_2)_2Np$ and 1,8-$(PhOCH_2)_2$-Np in acetonitrile are low, the three-color three-laser photolysis experiments were done in cyclohexane. The experimental results of the three-color three-laser photolysis of 1,8-$(PhOCH_2)_2Np$ in Ar-saturated cyclohexane at room temperature are shown in Figure 4.

In contrast to the results of 1,8-$(BPOCH_2)_2Np$, the absorption of the 1,8-$PhOCH_2NpCH^\bullet$ radical in the region of 330−380 nm was observed together with that of 1,8-$(PhOCH_2)_2{}^3Np^*(T_1)$ at 425 and 400 nm during the first 308-nm laser irradiation of 1,8-$(PhOCH_2)_2Np$. This is most likely due to the presence of two competitive paths from 1,8-$(PhOCH_2)_2{}^1Np^*(S_1)$ with the excitation energy mainly localized on the Np moiety; one path is a C−O bond cleavage to give 1,8-$PhOCH_2NpCH_2^\bullet(D_0)$, and the other is an intersystem crossing to 1,8-$(PhOCH_2)_2{}^3Np^*(T_1)$. This result can be explained by the lower Φ_{ISC} value of 1,8-$(PhOCH_2)_2Np$ than that of 1,8-$(BPOCH_2)_2Np$. Since no C−O bond cleavage occurred from 1,8-$(PhOCH_2)_2{}^3Np^*(T_1)$, the increase of the transient absorption in the region of 330−380 nm was not observed during the decay of 1,8-$(PhOCH_2)_2{}^3Np^*$-(T_1). When 1,8-$(PhOCH_2)_2{}^3Np^*(T_1)$ was excited to 1,8-$(PhOCH_2)_2Np(T_n)$ with the excitation energy delocalized including the C−O bonds during the second 430-nm laser irradiation, cleavage of one C−O bond occurred from 1,8-$(PhOCH_2)_2Np(T_n)$. The decrease of the transient absorption at 425 nm ($\Delta\Delta O.D._{425}$) and the increase of the transient absorption in the region of 330−380 nm gave strong evidence for the C−O bond cleavage from 1,8-$(PhOCH_2)_2Np(T_n)$ to 1,8-$PhOCH_2$-$NpCH_2^\bullet(D_0)$. In the case of 1,8-$(PhOCH_2)_2Np$, 1,8-$PhOCH_2$-$NpCH_2^\bullet(D_0)$ can be selectively excited to 1,8-$PhOCH_2NpCH_2^\bullet$-(D_n) with the third 355-nm laser irradiation, in contrast to 1,8-$(BPOCH_2)_2Np$. Clear bleaching of the transient absorption in the region of 330−380 nm was observed upon the third laser irradiation. Ionization of 1,8-$PhOCH_2NpCH_2^\bullet(D_0)$ did not occur during the 355-nm laser excitation, because transient absorptions of 1,8-$PhOCH_2NpCH_2^+$ which are expected to be similar to that of 1-$NpCH_2^+$ at 481, 614, 667, and 735 nm were not observed.[21] Therefore, the bleaching is due to the occurrence of the second C−O bond cleavage from 1,8-$PhOCH_2NpCH_2^\bullet(D_n)$. These experimental results for 1,8-$(PhOCH_2)_2Np$ are similar to those of 1,8-$(BPOCH_2)_2Np$.[16] Formation of the 1,8-$(^\bullet CH_2)_2Np$ biradical from 1,8-$PhOCH_2NpCH_2^\bullet(D_n)$ to give acenaphthene as the final product is expected. Similar experimental results to those of 1,4-$(BPOCH_2)_2Np$ were observed for 1,4-$(PhOCH_2)_2Np$ (Supporting Information Figure S2), indicating that the second C−O bond cleavage occurred from 1,4-$PhOCH_2NpCH_2^\bullet(D_n)$.[16]

The transient absorption of 1,8-$(^\bullet CH_2)_2Np$ at 500 nm was not observed during the three-color three-laser flash photolysis of 1,8-$(BPOCH_2)_2Np$ and 1,8-$(PhOCH_2)_2Np$ probably due to the small absorption coefficient ($\epsilon_{500} \approx 200$ M^{-1} cm^{-1})[23] and fast cyclization of 1,8-$(^\bullet CH_2)_2Np$ within the laser duration (5 ns). It should be noted that the formation mechanism of the 1,8-$(^\bullet CH_2)_2Np$ biradical in the present study is different from that reported by Wirz et al.[23] In the case of Wirz's experiments, the diazo compound 1-(diazomethyl)-8-methylnaphthalene was used as the starting compound to give the 1,8-$(^\bullet CH_2)_2Np$ biradical. Upon the irradiation of 1-(diazomethyl)-8-methylnaphthalene, the 1,8-$(^\bullet CH_2)_2Np$ biradical with triplet multiplicity is generated via a carbene intermediate that was formed by the initial N_2 elimination. The cyclization of the 1,8-$(^\bullet CH_2)_2Np$ biradical with a triplet multiplicity to acenaphthene is a spin forbidden process. Therefore, the lifetime of the 1,8-$(^\bullet CH_2)_2Np$ biradical with triplet multiplicity is long (102 ± 5 μs), and transient absorption of the 1,8-$(^\bullet CH_2)_2Np$ biradical was detected. However, in the present study, the 1,8-$(^\bullet CH_2)_2Np$ biradical was produced from 1,8-$BPOCH_2NpCH_2^\bullet(D_n)$ and 1,8-$PhOCH_2NpCH_2^\bullet(D_n)$ during the third 355-nm laser irradiation. This 1,8-$(^\bullet CH_2)_2Np$ biradical should have singlet multiplicity, from which the cyclization of the 1,8-$(^\bullet CH_2)_2Np$ biradical to acenaphthene(S_0) is a spin allowed process. Therefore, the lifetime of the 1,8-$(^\bullet CH_2)_2Np$ biradical is short (<5 ns), and transient absorption of the 1,8-$(^\bullet CH_2)_2Np$ biradical cannot be detected. Another possibility for

SCHEME 2: Potential Energy Diagram and Reaction Coordinates of Photoexcitation during the Three-Color Three-Laser Flash Photolysis of 1,8-$(BPOCH_2)_2Np$ (1) Giving the Final Product Acenaphthene (2) through the T_1 and T_n States of 1 and the D_0 and D_n States[a]



[a] $h\nu_1$, the first 308-nm laser excitation; $h\nu_2$, the second 430-nm laser excitation; $h\nu_3$, the third 355-nm laser excitation.

not detecting the transient absorption of the 1,8-$(^{\bullet}CH_2)_2Np$ biradical may be due to the low concentration of the 1,8-$(^{\bullet}CH_2)_2$-Np biradical in the solution, which could be calculated according to the concentration of 1,8-$ROCH_2NpCH_2^{\bullet}(D_0)$ disappeared during the third laser irradiation ($[1,8\text{-}ROCH_2NpCH_2^{\bullet}(D_0)] = (\Delta\Delta O.D._{365} \approx 0.02)/(\epsilon_{365} = 10\,000\ M^{-1}\ cm^{-1}) = 2.0 \times 10^{-6}$ M). It is very difficult to detect the transient absorption of 1,8-$(^{\bullet}CH_2)_2Np$ at such low concentration because of the small value $\epsilon_{500} \approx 200\ M^{-1}\ cm^{-1}$. Although the 1,8-$(^{\bullet}CH_2)_2Np$ biradical shows an absorption band in the range 300−340 nm ($\epsilon_{337} \approx 20\,000\ M^{-1}\ cm^{-1}$),[23] which is stronger than the absorption band at 500 nm, the absorption band in the range 300−340 nm should overlap with the absorptions of 1,8-$(BPOCH_2)_2Np(T_1)$ or 1,8-$(PhOCH_2)_2Np(T_1)$. Therefore, absorption of the 1,8-$(^{\bullet}CH_2)_2Np$ biradical cannot be separated from the absorption spectra in the range 300−340 nm.

The mechanism of the three-color three-laser photochemistry of 1,8-$(BPOCH_2)_2Np$ is shown in Scheme 2.

The first 308-nm laser selective excitation of the BP moiety of 1,8-$(BPOCH_2)_2Np$ causes an intramolecular triplet energy transfer from $BP(T_1)$ to the Np moiety, giving 1,8-$(BPOCH_2)_2{}^3$-$Np^*(T_1)$. The second selective excitation of the $Np(T_1)$ moiety of 1,8-$(BPOCH_2)_2{}^3Np^*(T_1)$ causes formation of 1,8-$BPOCH_2$-$NpCH_2^{\bullet}$ through the first C−O bond cleavage. The third selective excitation of 1,8-$BPOCH_2NpCH_2^{\bullet}$ causes the formation of the 1,8-$(^{\bullet}CH_2)_2Np$ biradical through the second C−O bond cleavage. Because of the lower Φ_{ISC} value than that of 1,8-$(BPOCH_2)_2Np$, the low yield of 1,8-$PhOCH_2NpCH_2^{\bullet}(D_0)$ was observed during the first 308-nm laser excitation of 1,8-$(PhOCH_2)_2Np$.

Conclusions

Photocleavage of one C−O bond of $ROCH_2Np$ and $(ROCH_2)_2$-Np through the T_n states was observed to give $NpCH_2^{\bullet}$ and $ROCH_2NpCH_2^{\bullet}$ radicals in almost 100% yield, respectively, during the two-color two-laser flash photolysis. The Φ values of the C−O bond cleavage of 1-$PhOCH_2Np$, 2-$PhOCH_2Np$, 1,8-$(PhOCH_2)_2Np$, and 1,4-$(PhOCH_2)_2Np$ were calculated to be higher than those of 1-$BPOCH_2Np$, 2-$BPOCH_2Np$, 1,8-$(BPOCH_2)_2Np$, and 1,4-$(BPOCH_2)_2Np$. No C−O bond cleavage occurred from 1,8-$(HOCH_2)_2Np(T_n)$ and 2-$CH_3OCH_2Np(T_n)$. The results show that the C−O bond cleavage is regulated by the position and the type of the substituents on Np. Higher efficiency in the C−O bond cleavage of 1-$ROCH_2Np$ than the efficiency in that of 2-$ROCH_2Np$ was observed. Stepwise cleavage of the two C−O bonds of 1,8- and 1,4-$(ROCH_2)_2Np$ (R = BP and Ph) was observed during the three-color three-laser flash photolysis. 1,8- and 1,4-$ROCH_2NpCH_2^{\bullet}$ were formed by the first C−O bond cleavage of 1,8- and 1,4-$(ROCH_2)_2Np$ (R = BP and Ph) in the T_n states, which was generated by the selective excitation of 1,8- and 1,4-$(ROCH_2)_2{}^3Np^*(T_1)$ using the 430-nm second laser. The intermediates 1,8- and 1,4-$(^{\bullet}CH_2)_2$-Np were obtained by the second C−O bond cleavage of 1,8- and 1,4-$ROCH_2NpCH_2^{\bullet}(D_n)$, which was generated by the selective excitation of 1,8- and 1,4-$ROCH_2NpCH_2^{\bullet}(D_0)$ using the 355-nm third laser.

Acknowledgment. This work has been partly supported by a Grant-in-Aid for Scientific Research on Priority Area (417), 21st Century COE Research, and others from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japanese Government.

Supporting Information Available: Figures showing two-color two-laser photolysis of 1-CH_3OCH_2Np and three-color three-laser photolysis of 1,4-$(PhOCH_2)_2Np$. 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., Inc.: Menlo Park, CA, 1978.

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

(3) Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2002**, *67*, 6117.

(4) Gupta, S. N.; Gupta, I.; Neckers, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 103.

(5) Fleming, S. A.; Pincock, J. A. *Mol. Supramol. Photochem.* **1999**, *3*, 211.

(6) Appleton, D. C.; Bull, D. C.; Givens, R. S.; Lillis, V.; McKenna, J.; McKenna, J. M.; Thackeray, S.; Walley, A. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 77.

(7) Foster, B.; Gaillard, B.; Mathur, N.; Pincock, A. L.; Pincock, J. A.; Sehmbey, C. *Can. J. Chem.* **1987**, *65*, 1599.

(8) Yamaji, M.; Yoshihara, T.; Tachikawa, T.; Tero-Kubota, S.; Tobita, S.; Shizuka, H.; Marciniak, B. *J. Photochem. Photobiol., A* **2004**, *162*, 513.

(9) Slocum, G. H.; Kaufmann, K.; Schuster, G. B. *J. Am. Chem. Soc.* **1981**, *103*, 4625.

(10) Johnston, L. J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 6368.

(11) Johnston, L. J. *Chem. Rev.* **1993**, *93*, 251.

(12) Ito, O.; Alam, M. M.; Koga, Y.; Ouchi, A. *J. Photochem. Photobiol., A* **1996**, *97*, 19.

(13) Ouchi, A.; Koga, Y.; Alam, M. M.; Ito, O. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1705.

(14) Adam, W.; Schneider, K.; Steenken, S. *J. Org. Chem.* **1997**, *62*, 3727.

(15) Cai, X.; Sakamoto, M.; Hara, M.; Tojo, S.; Fujitsuka, M.; Ouchi, A.; Majima, T. *Chem. Commun.* **2003**, 2604.

(16) 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.

(17) Cai, X.; Hara, M.; Kawai, K.; Tojo, S.; Majima, T. *Chem. Commun.* **2003**, 222.

(18) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(19) Murov, S. L.; Carmichael, I.; Hug, G. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1993.

(20) Watanabe, S.; Nagano, M.; Suzuki, T.; Ichimura, T. *J. Photochem. Photobiol., A* **2000**, *137*, 125.

(21) Habersbergerova, A.; Janovsky, I.; Kourim, P. *Radiat. Res. Rev.* **1972**, *4*, 123.

(22) Ishida, A.; Fukui, M.; Ogawa, H.; Tojo, S.; Majima, T.; Takamuku, S. *J. Phys. Chem.* **1995**, *99*, 10808.

(23) Biewer, M. C.; Platz, M. S.; Roth, M.; Wirz, J. *J. Am. Chem. Soc.* **1991**, *113*, 8069.