# Triplet-Sensitized Photolysis of the Photoisomer of a 2,11-Diaza[3,3](9,10)anthracenoparacyclophane: An Adiabatic Cycloreversion and a $[2\pi a + 2\pi a + 2\sigma s]$ Rearrangement in a Triplet State of the Biplanophane System[†]

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The triplet-sensitized photoreactions of the title biplanophane system **6**, the photoisomer of a 2,11-diaza[3,3](9,10)anthracenoparacyclophane derivative **5**, were investigated by stationary and laser-flash photolyses using xanthone (**XT**) and benzophenone (**BP**) as triplet sensitizers. When photoisomer **6** underwent **XT**-sensitized irradiation, a triplet cyclophane **5** and a novel polycyclic product **7** were obtained via an adiabatic cycloreversion and a formal $[2\pi a + 2\pi a + 2\sigma s]$ rearrangement, respectively. The maximum quantum yield for the formation of cyclophane **5** (0.69) and the upper-limit efficiency for the formation of polycycle **7** (0.31) were determined by laser photolysis techniques. For **BP**-sensitized photolysis of photoisomer **6**, oxetane **8**, in addition to triplet cyclophane **5** and polycycle **7**, was formed by a Paterno−Büchi reaction. The quenching rate constant ($k_q$) of triplet **BP** by photoisomer **6** ($3.4 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$) was found to be 1 order of magnitude smaller than that for **XT** ($5.0 \times 10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$). On the basis of the relationship between $k_q$ and the triplet donor−acceptor energy gap, the triplet energy level of photoisomer **6** was estimated to be ~71 kcal mol$^{-1}$. The photochemical and the photophysical processes involved in the sensitized photolyses are summarized in an energetic reaction diagram and discussed in detail.

## Introduction

Photocycloaddition of aromatic molecules and photocycloreversion of the adducts have become increasingly attractive processes to scientists from aspects of light-energy storage by the formation of photocycloadducts and the release of the stored energy through facile and clean cycloreversion of the adducts to their starting aromatic units.[1,2] These reactions have been applied to an energy storage system,[3] optical memories,[4] and a novel chemiluminescent system without the involvement of any oxidation process.[5,6] In addition to these potential applications, experimental and theoretical investigations of cycloaddition and reversion of aromatic molecules have been extensively directed toward the photoreaction mechanisms,[7,8] the intermediates involved,[9] and the significance of adiabatic photoprocesses.[10−15]

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[†] Biplanemer is a nickname for $[4\pi + 4\pi]$-type cycloadducts of aromatic molecules.[20] Here, we denote, for convenience, the bridged biplanemer skeleton of the title photoisomer of an anthracenoparacyclophane as a *biplanophane*.

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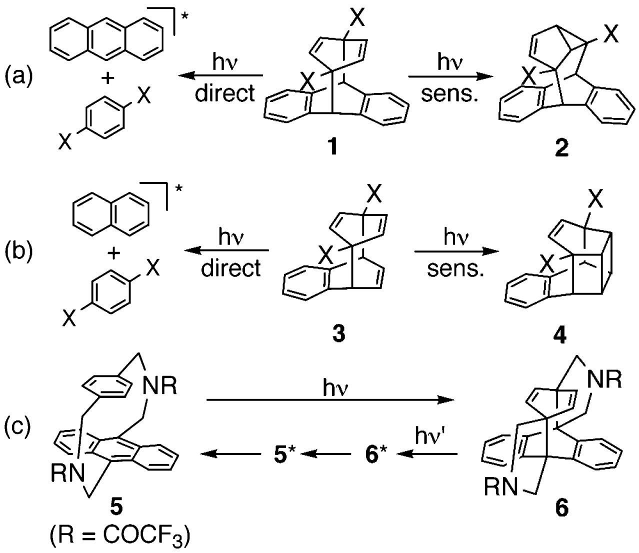
**SCHEME 1. Photoreactions of Biplanemers 1 and 3 and the 5−6 Cyclophane System**



In contrast to such widespread studies on the photochemistry of aromatic molecules in excited singlet states, much less effort has been addressed to the elucidation of reactivities of aromatic compounds and their cycloadducts in the triplet state. However, it has been confirmed that triplet species play significant roles in the photocycloadditions of aromatics, and that triplet cycloadducts display interesting reactions, which are significantly different from those observed in their excited singlet states.[2,12,16−19] Anthracene chromophores, bound by an ethylene linker, undergo a $[4\pi + 4\pi]$ intramolecular cycloaddition by direct photoreaction, while they afford $[4\pi + 2\pi]$ intramolecular cycloadducts through the triplet manifold.[16] In some derivatives of 1,3-dianthrylpropane, an efficient $[4\pi + 4\pi]$ intramolecular cycloaddition between their two anthracene chromophores occurs in the triplet state.[2,17] For a $[4\pi + 4\pi]$ photocycloaddition of amide-linked naphthalene and anthracene chromophores, a triplet biradical was confirmed as the intermediate.[18]

It has been suggested that anthracene photodimers and an anthracene−naphthacene biplanemer[20] undergo cycloreversion in the triplet state.[13] Interestingly, photoreactions of some biplanemers in the triplet state have been shown to afford novel polycyclic or cage molecules which are not accessible by direct irradiation.[12,19] Anthracene−benzene biplanemers **1** provide an electronically excited anthracene through an adiabatic pathway on direct irradiation.[6,11,12] In contrast, they undergo di-$\pi$-methane rearrangement[21] upon triplet-sensitized photolysis, giving tetracyclic product **2** (Scheme 1a).[19] Also, photoexcited naphthalene−benzene biplanemer **3** affords both singlet- and triplet-excited naphthalene, whereas triplet **3** undergoes intramolecular $[2\pi + 2\pi]$ cycloaddition, affording a cage compound, **4** (Scheme 1b).[12]

The title compound **6** is the photoisomer of the 2,11-diaza[3,3](9,10)anthracenoparacyclophane **5**. Cyclophane system **5** has been developed as a photochromic molecular device based on interconversion with photoisomer **6**.[4b,22] Since photoisomer **6** possesses a bridged biplanemer skeleton (*biplanophane*), we have been interested in its photoreactions in comparison with those of nonbridged analogues **1**. We have found that the photocycloreversion of photoisomer **6** adiabatically occurs to give an excited singlet cyclophane **5** efficiently on direct photolysis, as in the case of the nonbridged analogue **1** (Scheme 1c).[23]

Considering the results of the triplet-sensitized photolyses of biplanemers **1** and **3**, the triplet photochemistry of photoisomer **6** would be of interest since triplet **6** is expected to display reactions different than those of excited singlet **6**. However, photoexcited **6** essentially reverts on a singlet adiabatic surface to afford an excited singlet **5**, while photoexcitation of cyclophane **5** results in the intramolecular cycloaddition exclusively through a singlet manifold. Thus, very little information has been available so far regarding the triplet state of the **5**−**6** cyclophane system. These facts motivated us to investigate the triplet-sensitized photoreaction of the **5**−**6** cyclophane system in order to characterize their nature in the triplet states.

In the present work, we have studied the sensitized photoreactions of photoisomer **6** by means of stationary and laser-flash photolyses, using xanthone (**XT**) and benzophenone (**BP**) as triplet sensitizers. Herein, we describe the results of the product studies and the kinetic analyses for the photochemical and photophysical processes.

## Results and Discussion

**Xanthone-Sensitized Photolysis of the Biplanophane.** When a 1:1 mixture of photoisomer **6** and **XT** was irradiated at 350 nm, cyclophane **5** and polycyclic compound **7** were obtained as the photoproducts (Scheme 2). A di-$\pi$-methane-rearranged product **9**, which was expected from the triplet reactions of biplanemers **1**,[19] was not observed. To understand the course of the reaction, the time dependence of the product formation was followed by $^1$H NMR spectroscopy (Figure 1a). In the early stage of the photolysis (<5 min), starting photoisomer **6** was consumed rapidly, and the formation of cyclophane **5** and polycycle **7** was observed. Since polycycle **7** was not detected in the photolysis of cyclophane **5** in the presence of **XT**, both polycycle **7** and cyclophane **5** were considered to be the primary products in the **XT**-sensitized photoreaction. As cyclophane **5** (formed in the photolysis) absorbed the incident light, it was consumed through intramolecular $[4\pi + 4\pi]$ cycloaddition as a secondary photoprocess affording photoisomer **6**, which

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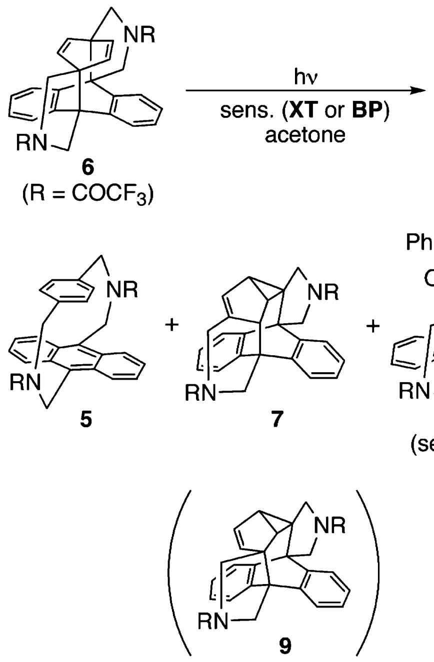
**SCHEME 2. Triplet-Sensitized Photoreaction of Photoisomer 6**



underwent further **XT** sensitization under the photolysis conditions. Therefore, at a longer irradiation time (~20 min), polycycle **7** was detected as the major component. With prolonged irradiation (>20 min), polycycle **7** was gradually lost due to further photoreactions. These results indicate that photoisomer **6** has a significantly different reactivity depending on the spin multiplicities of the excited state.

Polycyclic product **7** was characterized by $^1$H NMR spectra on the basis of $^1$H−$^1$H COSY and NOESY methods and variable-temperature techniques. Also, mass spectrum and elemental analysis support the assigned structure **7**. Photoproduct **7** was found to be a mixture of two exchanging isomers, and the observed $^1$H NMR signals were assigned to each isomer, as shown in Figure 2 (vide infra). In the higher field of the $^1$H NMR spectrum, characteristic peaks that were assigned to protons in the cyclopropane moiety appear at $\delta$ 1.63 ($H^a$) and 2.35 ppm ($H^b$).[24] With the structure of **7**, one can expect 12, nonequivalent protons rather than aromatic ones; however, 21 signals were actually observed for product **7**. Temperature dependence of product **7** in the $^1$H NMR spectrum was examined, as shown in Figure 3. The complex spectrum observed at 24 °C (Figure 3a) was simplified by an increase in temperature. At 120 °C, the multiplet signals assigned to $H^a$ and $H^b$ on the cyclopropane ring were merged into a triplet and a broad doublet pattern, respectively, which can be expected from structure **7** (Figure 3c). Additionally, at the higher temperature, the bridgehead ($H^e$, $\delta$ 3.50 ppm) and the olefinic ($H^q$, $H^r$, $\delta$ 4.78 ppm) protons appeared as doublet signals, which is consistent with structure **7**.[24] These results suggest that product **7** is a mixture of isomers, which are exchanging with each other. The NOESY spectrum of product **7** (Figure S1 in the Supporting Information) shows negative NOE values for the following pairs of methylene protons on the C−N−C bridges: $H^c$−$H^g$, $H^d$−$H^h$, $H^f$−$H^i$, $H^j$−$H^n$, $H^l$−$H^t$, and $H^s$−$H^u$ (for the assignment of each proton, see Figure 2), indicating that these pairs of protons undergo chemical exchange.[25,26] Thus, there are two indivisible isomeric structures in product **7**, as suggested by the temperature effects. The ratio of the major and the minor isomers was determined to be 1.5:1 by the $^1$H NMR integrals (Figure 2). Considering the high rotational barrier of the C−N bond in the amide group,[28] the observed isomers for polycycle **7** are able to be assigned as rotamers, which are interconvertible through rotation of the amide C−N bonds on the side chains. Such a rotational isomerism has also been observed for an *N*-formyl derivative of cyclophane **5** (R = CHO).[22a]

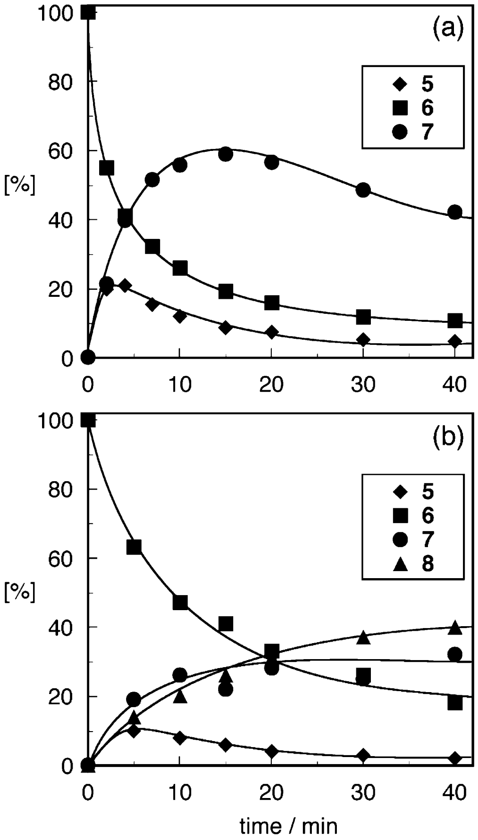


**FIGURE 1.** Time course of the sensitized irradiation (300 nm) of photoisomer **6** in acetone-$d_6$ monitored by $^1$H NMR spectroscopy (500 MHz) in the presence of (a) **XT** and (b) **BP**.

**Benzophenone-Sensitized Photolysis of the Biplanophane.** When photoisomer **6** was irradiated in the

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[24] The assigned chemical shifts are similar to those observed for the corresponding protons of the bicyclo[3.1.0]hexane moiety in the nonbridged analogue **2** [X = H, Scheme 1; 1.20 ($H^a$), 2.13 ($H^b$), 3.59 ($H^e$), and 5.09 ppm ($H^{q,r}$) in CDCl$_3$], suggesting that photoproduct **7** possesses the same bicyclic substructure as compound **2**.[19]

[25] Derome, A. E. *Modern NMR Techniques for Chemistry Research*; Pergamon Press: Oxford, 1987; pp 239−244.

[26] Using the phase-sensitive NOESY spectroscopy technique, a negative NOE is observed for exchanging pairs of protons. Thus, the NOE and the chemical exchange in polycycle **7** were unambiguously observed as the positive and the negative cross-peaks, respectively (shown in Figure S1 of the Supporting Information).[27]

[27] *One-Dimensional and Two-Dimensional NMR Spectra by Modern Pulse Techniques* (Japanese edition); Nakanishi, K., Ed.; Kodansha Scientific: Tokyo, 1986.

[28] Stewart, W. E.; Siddall, T. H., III. *Chem. Rev.* **1970**, *70*, 517−551.

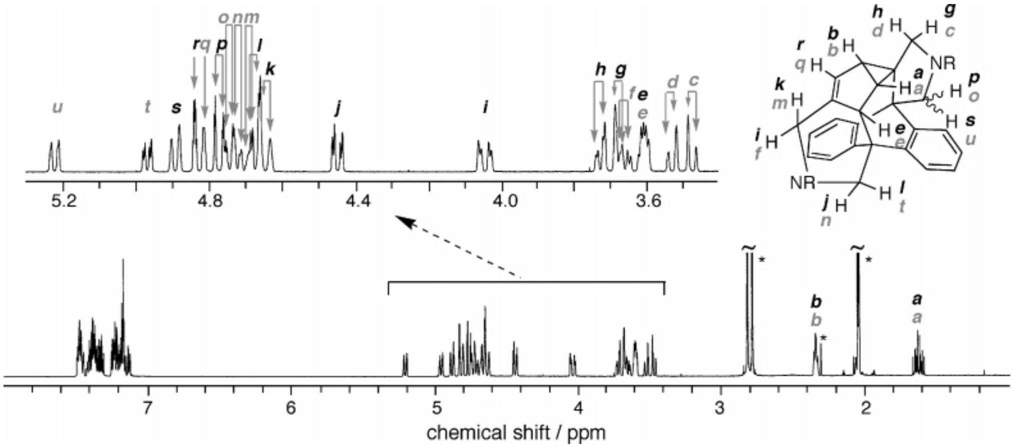

**FIGURE 2.** $^1$H NMR spectrum of polycycle **7** in acetone-$d_6$ at 600 MHz (the asterisked signals are due to the solvent used). The peaks depicted in black and gray letters are assigned to the major and the minor isomers of **7**, respectively.

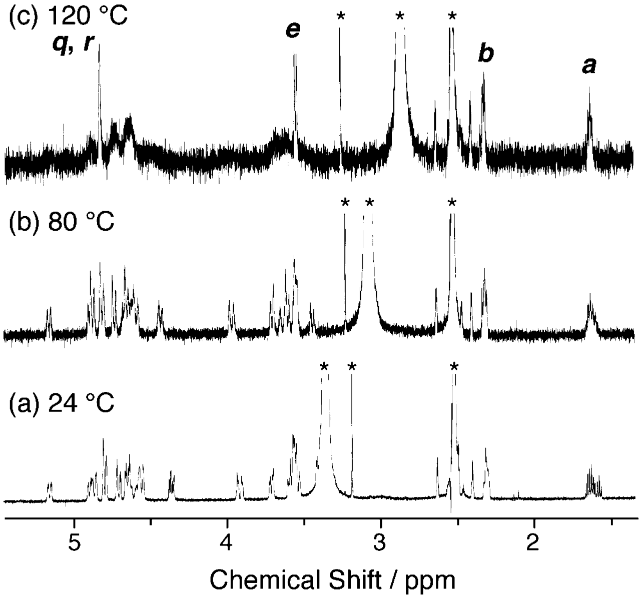

**FIGURE 3.** Temperature effects on the $^1$H NMR spectra of polycycle **7** in DMSO-$d_6$ at 600 MHz (the asterisked peaks are due to the solvent used).

presence of benzophenone (**BP**) as a triplet sensitizer, novel oxetane **8** was obtained in addition to cyclophane **5** and polycycle **7** (Scheme 2). The structure of oxetane **8** was confirmed by $^1$H and $^{13}$C NMR spectra using $^1$H−$^1$H COSY, NOESY, HMQC, and HMBC techniques. Furthermore, mass spectra and elemental analyses support the structure of **8**. The formation of oxetane **8** is well rationalized as a Paterno−Büchi reaction[29] between the 1,4-cyclohexadiene moiety of photoisomer **6** and triplet **BP**. In the case of the **XT**-sensitized photolysis of photoisomer **6**, such an oxetane was not obtained. Thus, the formation of oxetane **8** may be ascribed to a stronger n,$\pi^*$ character of triplet **BP** compared to that of triplet **XT** in the polar solvent used (acetone) where the electronic character of triplet **XT** is of a mixture of n,$\pi^*$ and $\pi,\pi^*$.[30] The time course of the **BP**-sensitized photolysis is shown in Figure 1b. Within a shorter irradiation period (<10 min), cyclophane **5**, polycycle **7**, and oxetane **8** were observed as the photoproducts. As in the case of the **XT**-sensitized irradiation, cyclophane **5**, once formed in the photolysis, was consumed through the secondary [4$\pi$ + 4$\pi$] photoprocess, and photoproducts **7** and **8** were, thus, observed in the mixture after prolonged irradiation (>30 min).

**Proposed Mechanism for the Formation of Polycycle 7.** A plausible mechanism for the rearrangement of photoisomer **6**, affording polycycle **7** in the triplet state, is shown in Scheme 3. With **XT**-sensitized irradiation, nonbridged **1** undergoes di-$\pi$-methane rearrangement within the 1,4-cyclohexadiene (CHD) moiety (Scheme 3a).[19,21] In the rearrangement of triplet photoisomer **6**, as in the case of biplanemer **1**, the cyclopropane ring is formed in the 1,4-CHD part of photoisomer **6** (A, Scheme 3b). Subsequent rupture of the central $C^1-C^2$ bond followed by the formation of the double bond and the new bridge $C^2-C^3$ bonding (B, Scheme 3b) affords polycycle **7**. These processes may be merged into a formal [2$\pi$a + 2$\pi$a + 2$\sigma$s] rearrangement (C, Scheme 3), which proceeds in a concerted manner. Different from that of the di-$\pi$-methane rearrangement of the nonbridged analogue **1**, the $C^1-C^2$ $\sigma$ bond significantly participates in the rearrangement of photoisomer **6**. This may be due to enhanced through-bond orbital interaction[31] between the $C^1-C^2$ $\sigma$ bridge and the $\pi$ system of photoisomer **6** through perturbation by the C−N−C side chains.

**Triplet Sensitization by Laser-Flash Photolysis.** Figure 4 shows transient absorption spectra obtained 100 ns and 1.2 $\mu$s after a 355 nm laser pulsing in an **XT**−**6** system. The absorption band at 630 nm is due to triplet **XT**.[32] The intensity of the absorption for triplet **XT** decreases with a first-order rate ($k_{\mathrm{obsd}} = 5.0 \times 10^6$ s$^{-1}$; see top inset in Figure 4), while the absorption at 417 nm increases with the same rate ($5.0 \times 10^6$ s$^{-1}$, bottom inset in Figure 4). The absorption band at 417 nm is due

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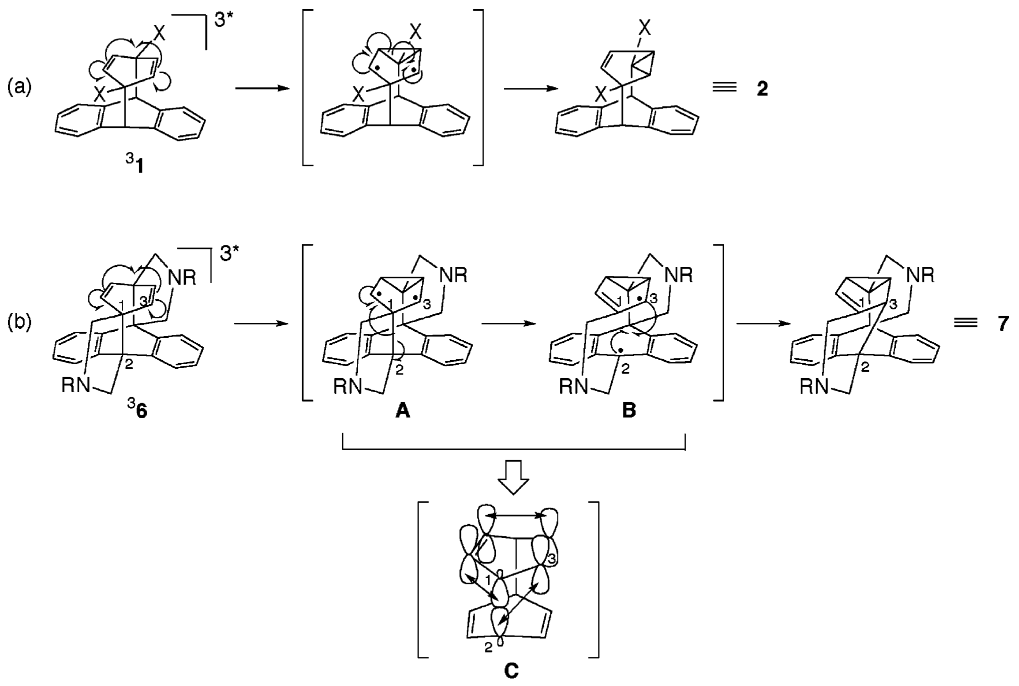
[32] Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747−7753.

**SCHEME 3. Proposed Mechanism for the Rearrangement of Triplet Photoisomer 6**



to neither the ketyl nor the anion radicals of **XT**, but the shape of the absorption spectrum resembles that of the triplet−triplet absorption of anthracenes.[33] The decay rate ($k_{\mathrm{obsd}}$) of triplet **XT** was found to increase proportionally to the concentration of **6**, [**6**] (Figure 5). These observations indicate that an unknown intermediate **X**, with an absorption band at 417 nm, should be produced via triplet **6**, which was formed by the triplet energy transfer from triplet **XT**. Since the plots of $k_{\mathrm{obsd}}$ show a straight line, the $k_{\mathrm{obsd}}$ can be formulated with a quenching rate constant, $k_{\mathrm{q}}$, by eq 1

$$k_{\mathrm{obsd}} = k_0 + k_{\mathrm{q}}[\mathbf{6}] \qquad (1)$$

where $k_0$ is the decay rate of triplet **XT** in the absence of **6**. From the slope and the intercept of the line, the values of $k_{\mathrm{q}}$ and $k_0$ were determined to be 5.0 × $10^9$ dm$^3$ mol$^{-1}$ s$^{-1}$ and 2.0 × $10^6$ s$^{-1}$, respectively. The obtained $k_{\mathrm{q}}$ value, which is smaller than the diffusion limit of acetone (2.0 × $10^{10}$ dm$^3$ mol$^{-1}$ s$^{-1}$ at 20 °C),[34] is typical of the exothermic triplet energy transfer having a triplet energy gap ($\Delta E_{\mathrm{T}}$) of >2 kcal mol$^{-1}$.[35] Since the triplet energy of **XT** is known to be 74.0 kcal mol$^{-1}$,[33] that of photoisomer **6** can be readily estimated to be <72 kcal mol$^{-1}$.

To characterize intermediate **X**, the absorption profiles at 417 nm were investigated in detail. Figure 6 shows the absorbance at 417 nm ($\Delta A_{417}$) for intermediate **X**, observed after depletion of triplet **XT** (see bottom inset in Figure 4), plotted as a function of [**6**]. With an increase of [**6**], the $\Delta A_{417}$ value increases, leveling off at higher regions of [**6**]. The $\Delta A_{417}$ can be formulated by using kinetic parameters $k_0$ and $k_{\mathrm{q}}$ as

$$\Delta A_{417} = \alpha_{\mathrm{TET}}\eta_{\mathrm{X}}\epsilon_{417}^{\mathrm{X}}\Phi_{\mathrm{ISC}}I_{\mathrm{abs}}k_{\mathrm{q}}[\mathbf{6}](k_0 + k_{\mathrm{q}}[\mathbf{6}])^{-1} \qquad (2)$$

where $\alpha_{\mathrm{TET}}$, $\eta_{\mathrm{X}}$, $\epsilon_{417}^{\mathrm{X}}$, and $\Phi_{\mathrm{ISC}}$ are the efficiency of the triplet energy transfer from triplet **XT** to **6**, the efficiency for the formation of intermediate **X** from triplet **6**, the molar absorption coefficient of **X** at 417 nm, and the

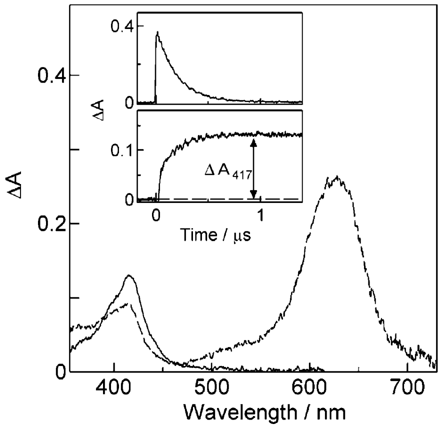


**FIGURE 4.** Transient absorption spectra obtained at 100 ns (- - -) and 1.2 $\mu$s (—) upon 355 nm laser pulsing in an **XT** (6.0 × $10^{-3}$ dm$^3$ mol$^{-1}$)−**6** (6.0 × $10^{-4}$ dm$^3$ mol$^{-1}$) system. Insets: the temporal absorbance changes at 630 nm for triplet **XT** (top) and at 417 nm for intermediate **X** (bottom).

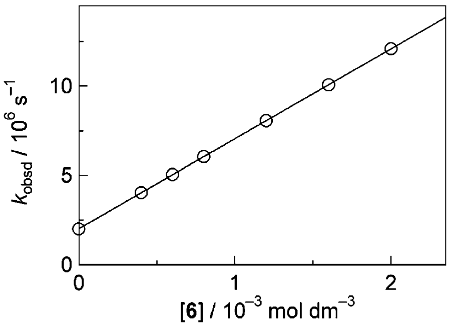


**FIGURE 5.** Decay rates ($k_{\mathrm{obsd}}$) of triplet **XT** plotted as a function of [**6**].

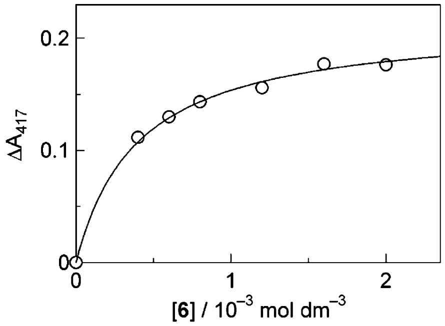


**FIGURE 6.** Transient absorbance change ($\Delta A_{417}$) observed after depletion of triplet **XT** plotted as a function of [**6**]. The solid curve was calculated by eq 2.

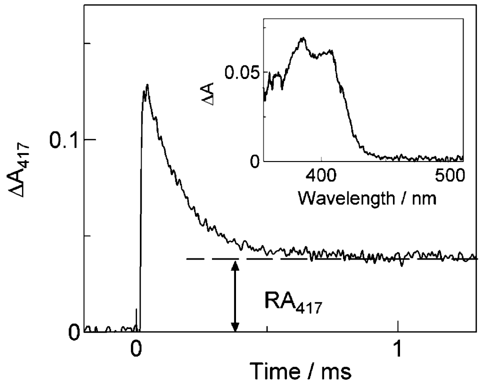


**FIGURE 7.** Time profile of the absorbance change at 417 nm for the decay of **X** obtained after 355 nm laser pulsing in the **XT** ($6.0 \times 10^{-3}$ dm$^3$ mol$^{-1}$)–**6** ($6.0 \times 10^{-4}$ dm$^3$ mol$^{-1}$) system. Inset: the transient absorption spectrum obtained at 1.0 ms for the above system.

triplet yield of **XT** (1.0), respectively.[34] The quantity of $I_{abs}$, the number of the photon flux of a laser pulse absorbed by **XT**, was determined by using the absorption of triplet benzophenone in acetonitrile as an actinometer.[36] By best-fitting eq 2 to the $\Delta A_{417}$ values obtained experimentally, the product value of $\alpha_{TET}\eta_{X}\epsilon_{417}^{X}$ was determined to be 9500 dm$^3$ mol$^{-1}$ cm$^{-1}$. The absorption spectrum of **X** was found to decay according to the first-order kinetics (Figure 7) with a lifetime of 180 μs, which was independent of [**6**] ($\leq 2.0 \times 10^{-3}$ mol dm$^{-3}$). In the millisecond time region (>1 ms) after the depletion of **X**, the residual absorbance ($RA_{417}$) at 417 nm was unchanged. The absorption spectrum at 1 ms, obtained after laser photolysis, was identical to that of cyclophane **5** (inset in Figure 7), indicating that intermediate **X** gave cyclophane **5** efficiently. By using the molar absorption coefficient of **5** at 417 nm ($\epsilon_{417}^{\mathbf{5}} = 3800$ dm$^3$ mol$^{-1}$ cm$^{-1}$ in acetone), the quantum yield, $\Phi_{\mathbf{5}}$, for the formation of cyclophane **5** is obtained by eq 3

$$\Phi_{\mathbf{5}} = \mathrm{RA}_{417}{\epsilon_{417}^{\mathbf{5}}}^{-1}{I_{\mathrm{abs}}}^{-1} \qquad (3)$$

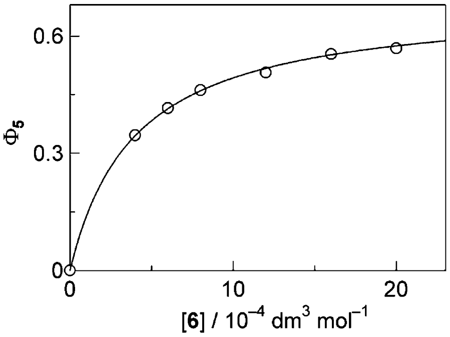


**FIGURE 8.** Quantum yields ($\Phi_{\mathbf{5}}$) for the formation of **5** obtained upon 355 nm laser photolysis of **XT** ($6.0 \times 10^{-3}$ dm$^3$ mol$^{-1}$)–**6** systems plotted as a function of [**6**]. The solid curve was drawn according to eq 4.

The obtained $\Phi_{\mathbf{5}}$ values are plotted as a function of [**6**] in Figure 8. The plots show a negative curve. On the other hand, with the use of kinetic parameters, $\Phi_{\mathbf{5}}$ can be expressed by eq 4

$$\Phi_{\mathbf{5}} = \Phi_{\mathbf{5}}^{\infty}k_{\mathrm{q}}[\mathbf{6}](k_0 + k_{\mathrm{q}}[\mathbf{6}])^{-1} \qquad (4)$$

where $\Phi_{\mathbf{5}}^{\infty}$ represents the ultimate quantum yield for the formation of **5** at infinite [**6**]. By best-fitting eq 4 to the $\Phi_{\mathbf{5}}$ values obtained experimentally, $\Phi_{\mathbf{5}}^{\infty}$ was determined to be 0.69 (±0.03). The estimated value is close to the yield for the formation of **5** upon direct excitation of **6** (0.61 ± 0.02).[37] The term $\Phi_{\mathbf{5}}^{\infty}$ can be interpreted by eq 5.

$$\Phi_{\mathbf{5}}^{\infty} = \alpha_{\mathrm{TET}}\eta_{\mathbf{X}}\Phi_{\mathrm{ISC}} \qquad (5)$$

Since the value of the product $\alpha_{TET}\eta_{X}\epsilon_{417}^{X}$ was determined to be 9500 dm$^3$ mol$^{-1}$ cm$^{-1}$ (Figure 6), that of $\epsilon_{417}^{X}$ is estimated to be 14 000 dm$^3$ mol$^{-1}$ cm$^{-1}$.

The following spectroscopic and photochemical properties of intermediate **X** were found: (1) **X** is a precursor of cyclophane **5**, (2) the absorption spectrum resembles that of triplet anthracene, and (3) the lifetime is 180 μs, which could be responsible for an excited state of triplet electronic character of $\pi,\pi^*$ in solution at room temperature. Therefore, from the above facts, we infer that intermediate **X** is assigned to the triplet state of **5** produced by an adiabatic cycloreversion from triplet **6**, which was photosensitized by triplet **XT**. Also, the estimated $\epsilon_{417}^{X}$ value resembles that of triplet anthracenes in order of magnitude ($1 \times 10^4$ dm$^3$ mol$^{-1}$ cm$^{-1}$).[33]

The efficiency, $\alpha_{TET}$, is less than unity; thus, the efficiency for the adiabatic cycloreversion, $\eta_X$, can be evaluated to be >0.69. Considering the estimated $\eta_X$ value (>0.69), the adiabatic conversion in the triplet manifold seems to be very efficient as is that in the excited singlet state, with an efficiency of 0.71.[23a] Therefore, the excited states of **6**, irrespective of the spin multiplicity, are fated to be converted to those of **5** by adiabatic processes with large efficiencies.

Furthermore, triplet sensitization was examined by using **BP** ($E_T = 69.2$ kcal mol$^{-1}$)[33] as a triplet sensitizer,

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[37] The quantum yield for cycloreversion of photoisomer **6** to give cyclophane **5** upon direct irradiation (266 nm laser pulsing) was determined in acetonitrile at 20 °C. The photon flux of the laser source used was determined by using the absorption of triplet benzophenone in acetonitrile as an actinometer.[36]

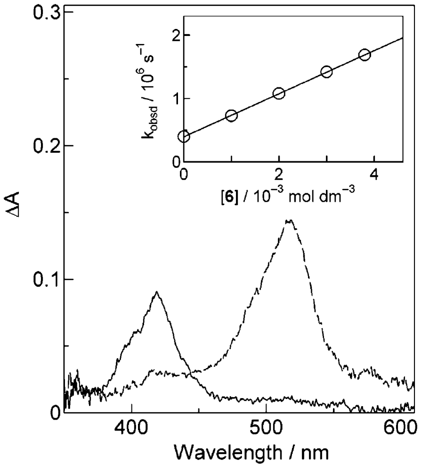

**FIGURE 9.** Transient absorption spectra obtained 100 ns (- - -) and 4.8 μs (—) after a 355 nm laser photolysis of a **BP** ($1.0 \times 10^{-2}$ dm$^3$ mol$^{-1}$)–**6** ($1.0 \times 10^{-3}$ dm$^3$ mol$^{-1}$) system. Inset: the decay rates ($k_{obsd}$) of triplet **BP** plotted as a function of [**6**].

whose $E_T$ value is smaller than that of **XT** ($E_T = 74.0$ kcal mol$^{-1}$), to characterize triplet **6** in more detail. Figure 9 shows the transient absorption spectra obtained by 355 nm laser pulsing in a **BP**–**6** system in acetone. The transient absorption band at 520 nm, which is due to triplet **BP**,[39] decays with a rate of $7.3 \times 10^5$ s$^{-1}$, giving the absorption spectrum of triplet **5** (417 nm) 4.8 μs after a laser pulse. The change in absorption spectra indicates that triplet energy transfer occurs from triplet **BP** to **6**, from which triplet **5** is produced by adiabatic cycloreversion.

As well as that in the case of the **XT**-sensitized photolysis, the absorption spectrum of triplet **5** was observed to decay according to first-order kinetics, resulting in the formation of cyclophane **5**. The quenching rate constant, $k_q$, of triplet **BP** by **6** was determined from the slope of the plots of the decay rates versus [**6**] (see inset in Figure 9) to be $3.4 \times 10^8$ dm$^3$ mol$^{-1}$ s$^{-1}$. The order of magnitude of the obtained value for $k_q$ indicates the occurrence of endothermic triplet energy transfer having a triplet energy gap, $\Delta E_T$, of 1.5–2.0 kcal mol$^{-1}$.[40] The energy level of triplet **6** is, thus, evaluated to be close to 71 kcal mol$^{-1}$, which is smaller than that of **XT** (74.0 kcal mol$^{-1}$) by more than 2.0 kcal mol$^{-1}$. The mechanism of such endoergonic energy transfer is interpreted in terms of the thermally activated crossing of potential surfaces and the absence of back energy transfer due to fast deactivation of the acceptor molecule,[40] which corresponds to the adiabatic transformation from triplet **6** to triplet **5** for the present system. When the apparent activation energy ($\Delta E_a$) is larger than the endothermic $\Delta E_T$, energy transfer will proceed.[40] The $\Delta E_a$ value for the **BP**–**6** system was obtained from the Arrhenius plots of $k_q$, as shown in Figure 10. Since the plots give a straight line, $k_q$ is expressed by eq 6. The $\Delta E_a$ value was determined to be $2.3 \pm 0.1$ kcal mol$^{-1}$, which is clearly larger than the estimated $\Delta E_T$ of the **BP**–**6** system (~2 kcal mol$^{-1}$), as expected.

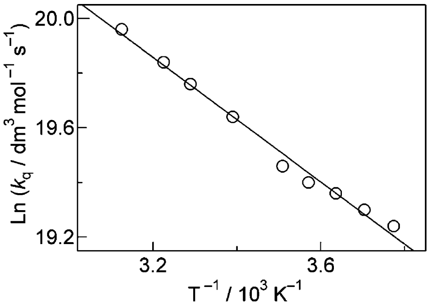

**FIGURE 10.** Arrhenius plots for the quenching rate constants, $k_q$, for the **BP** ($1.0 \times 10^{-2}$ dm$^3$ mol$^{-1}$)–**6** system.

$$k_q = (1.6 \times 10^{10}) \exp(-1140T^{-1}) \qquad (6)$$

Although the formations of photoproducts **7** and **8** were observed in the steady-state photolyses (Figure 1), we were unable to follow the formation profiles of these new compounds through transient absorption measurements because the absorption of photoproducts **7** and **8** is absent in the wavelength region >350 nm.

**Overview of the Sensitized Photolysis of the Biplanophane.** Figure 11 outlines an energetic diagram for the photochemical and photophysical processes upon triplet sensitization of photoisomer **6**, including the chemical products. The relative heats of formation of compounds **6**–**8**, compared to that of cyclophane **5**, were computed by the AM1 method:[41] **5** (0 kcal mol$^{-1}$), **6** (20.6 kcal mol$^{-1}$), **7** (39.7 kcal mol$^{-1}$), and **8** (55.9 kcal mol$^{-1}$). Although photoisomer **6** is known to revert to cyclophane **5** exclusively on an excited singlet adiabatic surface, its triplet features have not been revealed. By means of the present quenching experiments using **XT** and **BP** as triplet sensitizers, the triplet energy level was determined for the first time to be 71 kcal mol$^{-1}$. The energy transfer from triplet **XT** to photoisomer **6** is exoergonic by ~3 kcal mol$^{-1}$, while that from triplet **BP** to the substrate is endoergonic by 1.5–2 kcal mol$^{-1}$. In the case of the **BP** sensitization, triplet **6** vanishes by both the adiabatic cycloreversion and the rearrangement faster than the back energy transfer to **BP**. Therefore, triplet energy transfer is irreversible in the **BP**–**6** system. The triplet level of photoisomer **6** (71 kcal mol$^{-1}$) is unambiguously lower than those of *o*-xylene (82 kcal mol$^{-1}$) and 9,10-dihydroanthracene (82.4 kcal mol$^{-1}$),[33] which are involved as aromatic chromophores in photoisomer **6**, and comparable to that of norbornadiene (~72 kcal mol$^{-1}$), which has a 1,4-CHD chromophore.[35,42] From these considerations, it is inferred that the triplet exciton in triplet **6** is localized on the 1,4-CHD moiety of photoisomer **6**.

When it is assumed that the triplet level of cyclophane **5** is similar to that of 9,10-disubstituted anthracenes (~40

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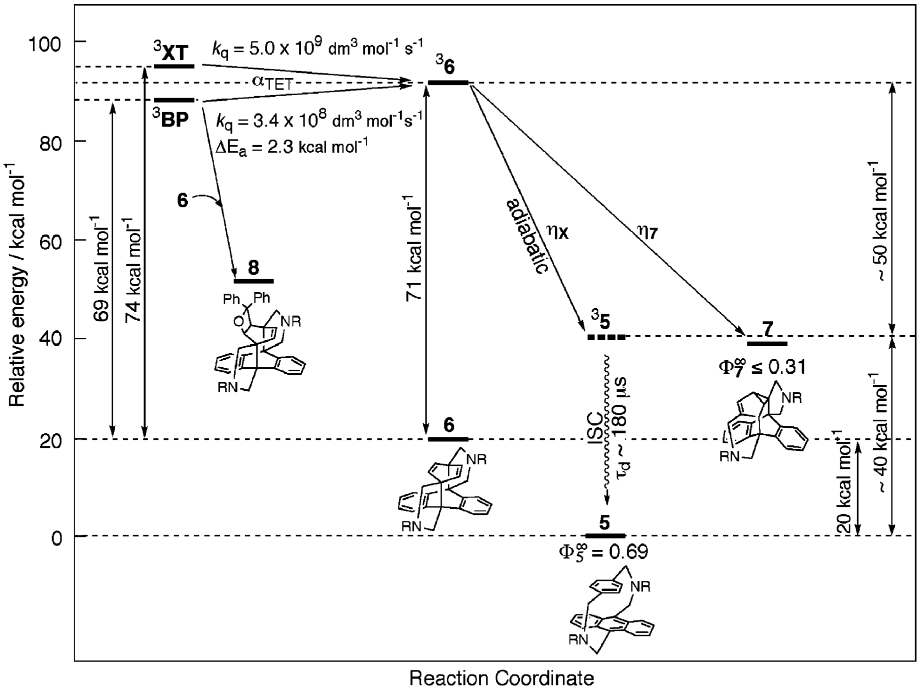

**FIGURE 11.** Schematic reaction diagram for the **XT**- and **BP**-sensitized photolysis of photoisomer **6** (in acetone at 295 K; the relative heats of formation of **5**–**8** were calculated by the AM1 method).[41] $\alpha_{TET}$ is the efficiency for the triplet energy transfer. $\eta_X$ is the fraction of the adiabatic cycloreversion from triplet **6** to triplet **5**. $\eta_7$ is the fraction of the rearrangement of triplet **6** to **7**. $\Phi_5^\infty$ and $\Phi_7^\infty$ are the limiting quantum yields for the formations of **5** and **7**, respectively; $\tau_d$ is the lifetime of triplet **5**, and ISC is the intersystem crossing.

kcal mol$^{-1}$),[33] the adiabatic process from triplet **6** to triplet **5** is expected to be highly exoergonic (~50 kcal mol$^{-1}$). The rate for such an exothermic process would be as large as that for the adiabatic cycloreversion of photoisomer **6**[23] or the nonbridged biplanemers **1**[11] in the excited singlet states. Therefore, the intersystem crossing from triplet **6** to the ground state is negligible in the decay pathways of triplet **6**. In fact, the evaluated efficiency for the adiabatic cycloreversion, $\eta_X$, is quite large (>0.69). From the above considerations, it is reasonable to assume that photoisomer **6** adiabatically reverts on a triplet surface efficiently, as in the case of direct photoexcitation.[23] Additionally, the rearrangement of triplet photoisomer **6** to provide polycycle **7** is expected to be a highly exothermic process and could compete with the adiabatic process. In the present work, triplet cyclophane **5** is found to be deactivated only by the intersystem crossing to the ground state, with a lifetime of ~180 $\mu$s at room temperature (Figure 4), and the limiting quantum yield for the formation of cyclophane **5** ($\Phi_5^\infty = 0.69$) upon **XT** sensitization. Consequently, considering that the sum of the quantum yields, $\Phi_5^\infty$ and $\Phi_7^\infty$, does not exceed unity, the upper-limit value of $\Phi_7^\infty$ is estimated to be 0.31.

## Summary

The detailed features of biplanophane system **6** in the triplet state have been clarified by the sensitized photolysis using **XT** and **BP** as triplet sensitizers on the basis of the results of the stationary and the laser-flash photolyses. The reaction processes of the triplet sensitization for photoisomer **6** are summarized in Figure 11. Triplet **6** provides triplet **5** through an adiabatic pathway, and the unknown polycycle **7** is formed by a formal [$2\pi a + 2\pi a + 2\sigma s$] rearrangement, which is a novel reaction mode of the anthracene–benzene biplanemer system. Oxetane **8** is obtained via a Paterno–Büchi reaction of photoisomer **6** and triplet **BP**. The observed reactivities of photoisomer **6** are quite different from those of the nonbridged analogue **1**, presumably due to enhanced through-bond interaction between the central C–C $\sigma$ bonds with the $\pi$ system in photoisomer **6** by participation of the side bridges in the triplet state. By means of the quenching experiments of triplet **XT** and **BP** by photoisomer **6**, the triplet energy level of **6** was determined to be ~71 kcal mol$^{-1}$, which was comparable to that of the 1,4-CHD chromophore in norbornadiene. When photoisomer **6** underwent **XT**-sensitized photolysis, the limiting quantum yield for the adiabatic cycloreversion, $\Phi_5^\infty = 0.69$, was determined, and that for the upper limit of the rearrangement, $\Phi_7^\infty$, was estimated to be 0.31. These values indicate that triplet photoisomer **6** is mainly deactivated through these reaction pathways rather than by intersystem crossing.

## Experimental Section

**Materials.** Cyclophane **5** and photoisomer **6** were prepared according to Usui's procedure.[22] Acetone, used for steady-state and laser-flash photolyses, was purified by distillation. **XT** and **BP** were purified by repeated recrystallizations from ethanol.

**Xanthone-Sensitized Photolysis of Photoisomer 6. Preparative Study.** An argon-purged solution of photoisomer **6** (50 mg, 94 mmol) and **XT** (18.5 mg, 94 mmol) in 30 mL of acetone was irradiated at 350 nm for 1 h. Acetone was evaporated under reduced pressure, and the residue was separated by preparative thin-layer chromatography (silica gel, $CHCl_3$) to give product **7** (28 mg, 56%). Recrystallization from a $CHCl_3$/acetone mixture gave colorless fine needles: mp 276–

278 °C dec; $^1$H NMR (600 MHz, acetone-$d_6$, cf. Figure 2) **Isomer a** (major isomer) $\delta$ 1.63 (m, 1H), 2.35 (m, 1H), 3.62 (m, 1H), 3.68 (d, 1H, $J$ = 11.4 Hz), 3.73 (d, 1H, $J$ = 11.4 Hz), 4.05 (d, 1H, $J$ = 16.2 Hz), 4.45 (d, 1H, $J$ = 13.2 Hz), 4.64 (d, 1H, $J$ = 16.2 Hz), 4.68 (d, 1H, $J$ = 13.2 Hz), 4.77 (d, 1H, $J$ = 12.6 Hz), 4.84 (m, 1H), 4.89 (d, 1H, $J$ = 12.6 Hz); **Isomer b** (minor isomer) $\delta$ 1.63 (m, 1H), 2.35 (m, 1H), 3.47 (d, 1H, $J$ = 13.2 Hz), 3.53 (d, 1H, $J$ = 13.2 Hz), 3.62 (m, 1H), 3.64 (1H),[43] 4.69 (1H),[43] 4.72 (d, 1H, $J$ = 10.8 Hz), 4.75 (1H),[43] 4.82 (m, 1H), 4.96 (d, 1H, $J$ = 10.8 Hz), 5.22 (d, 1H, $J$ = 11.4 Hz). Peaks of the aromatic protons in both isomers appear in a $\delta$ 7.2−7.5 ppm region as multiplet signals (Figure 2): $^{19}$F NMR (282 MHz, acetone-$d_6$) **Isomer a** $\delta$ 90.86 (s), 93.43 (s); **Isomer b** $\delta$ 91.22 (s), 93.00 (s); IR (KBr) $\nu_{\max}$ 1686 (C═O), 1180 (C−F) cm$^{-1}$; UV−vis (CHCl$_3$) $\lambda_{\max}$ (log $\epsilon$) 272 (sh, 3.02), 276 (sh, 2.94), 295 (2.24); MS (FAB) *m/e* 531 (M + H). Anal. Calcd for $C_{28}H_{20}F_6N_2O_2$: C, 63.40; H, 3.80; N, 5.28. Found: C, 63.50; H, 3.47; N, 5.35. **Analytical Experiments.** An argon-purged solution of photoisomer **6** ($5 \times 10^{-3}$ mol dm$^{-3}$) and **XT** ($1.5 \times 10^{-2}$ mol dm$^{-3}$) in acetone-$d_6$ was irradiated at 300 nm in an NMR tube, and the reaction mixture was analyzed by $^1$H NMR spectroscopy (500 MHz).

**Benzophenone-Sensitized Photoreaction of Photoisomer 6.** An argon-purged solution of photoisomer **6** (106 mg, 200 mmol) and **BP** (276 mg, 2 mmol) in 75 mL of acetone was irradiated at 300 nm for 2 h. Acetone was evaporated under reduced pressure, and the residue was separated by MPLC (silica gel, 5:1 hexane/AcOEt) and followed by reversed-phase chromatography (MeCN) to give oxetane **8** (45 mg, 32%). Recrystallization from CHCl$_3$/MeOH gave colorless needles: mp 286−288 °C; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 3.18 (d, 1H, $J$ = 12.3 Hz), 3.45 (d, 1H, $J$ = 6.3 Hz), 3.52 (d, 1H, $J$ = 12.3 Hz), 3.76 (d, 1H, $J$ = 12.3 Hz), 4.21 (d, 1H, $J$ = 12.3 Hz), 4.36 (d, 1H, $J$ = 12.3 Hz), 4.43 (dd, 1H, $J$ = 6.3, 1.8 Hz), 4.70 (d, 1H, $J$ = 13.5 Hz), 4.79 (d, 1H, $J$ = 13.5 Hz), 4.83 (d, 1H, $J$ = 9.3 Hz), 4.97 (d, 1H, $J$ = 13.5 Hz), 5.30 (dd, 1H, $J$ = 9.3, 1.8 Hz), 7.13 (m, 6H), 7.20−7.27 (m, 10H), 7.28−7.36 (m, 3H), 7.41 (d, 1H, $J$ = 7.8 Hz), 7.46 (d, 1H, $J$ = 7.8 Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 50.1, 50.6, 54.1, 54.9, 56.7, 56.9, 58.0, 59.3, 60.5, 78.5, 86.7, 116.0 ($J_{CF}$ = 286 Hz), 116.2 ($J_{CF}$ = 286 Hz), 123.3, 123.9, 124.8, 125.2, 125.4, 126.9, 127.1, 127.2, 127.5, 127.6, 127.9, 128.2, 128.4, 134.1, 137.6, 139.9, 140.4, 141.4, 141.5, 143.0, 146.9, 154.2 ($J_{CF}$ = 37.0 Hz), 154.6 ($J_{CF}$ = 38.0 Hz); IR (KBr) $\nu_{\max}$ 1690 (C═O), 1183 (C−F) cm$^{-1}$; UV−vis (CHCl$_3$) $\lambda_{\max}$ (log $\epsilon$) 262 (sh, 3.14), 272 (sh, 3.02), 282 (2.85); MS (FAB) *m/e* 713 (M + H). Anal. Calcd for $C_{41}H_{30}F_6N_2O_3$: C, 69.10; H, 4.24; N, 3.93. Found: C, 68.99; H, 3.90; N, 4.04.

**Laser-Flash Photolysis.** All of the samples in a quartz cell with a 1 cm path length were degassed by several freeze−pump−thaw cycles on a high-vacuum line. Transient absorption measurements were carried out at room temperature (295 K), unless noted, or in the temperature range from −43 to 45 °C. The temperature of the sample in a quartz dewar was maintained with hot water (>295 K) or a mixture of methanol and liquid nitrogen (<295 K) within a precision of ±0.5 °C during the measurement. Third harmonics (355 nm) of an Nd$^{3+}$:YAG laser (pulse width 8 ns) was used for flash photolysis. The details of the detection system for the time profiles of the transient absorption have been reported elsewhere.[44] The transient data obtained by laser-flash photolysis were analyzed using the least-squares best-fitting method. The transient absorption spectra were taken with a USP-554 system, with which one can take a transient absorption spectrum with a one-shot laser pulse.

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**Supporting Information Available:** General experimental methods and NMR spectra of polycycle **7** (NOESY and COSY) and oxetane **8** (NOESY and HMBC). This material is available free of charge via the Internet at http://pubs.acs.org.

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(43) Coupling constants were not determined due to the overlap of signals with the neighboring peaks (see Figure 2).

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