Selected Papers

Cyclization Reaction of Diarylethene through the Triplet Excited State

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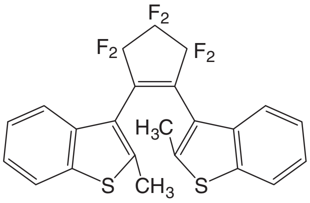
Photocyclization reaction of 1,2-bis(2-methyl-3-benzothienyl)perfluorocyclopentene (BT) in methanol was studied by using nanosecond laser flash photolysis at 296 K. When xanthone was used as a triplet sensitizer, the triplet energy transfer occurred efficiently and the closed-ring product of BT was observed.

Photochromism has attracted much attention because of potential application in optoelectronic devices, memories, and switches.[1–4] Diarylethene derivatives are a representative organic photochromic system, undergoing very efficient, thermally irreversible, and fatigue resistant cyclization–cycloreversion reactions.[1,5–10] Their primary photochemical processes have been well investigated by fs and ps time-resolved spectroscopy. Very recently, Miyasaka et al. reported that cyclization reactions of 1,2-bis(2-methyl-3-benzothienyl)perfluorocyclopentene (BT) (Chart 1) in nonpolar alkane solutions occurred via the singlet excited state of antiparallel form BT, but did not occur through its triplet state.[11] The cyclization reaction of diarylethene via the triplet state has scarcely been studied.[12,13] In previous studies, diarylethene has had some chromophores such as transition-metal complexes and perylenebisimide. To the best of our knowledge, cyclization via the triplet excited state of naked diarylethene has not been reported. To increase the efficiency of photochromic reaction, control of the cyclization via the triplet excited state is considered to be important. Thus in this paper, direct and triplet sensitization reactions of BT in methanol were studied by ns laser flash photolysis.

The laser flash photolysis apparatus was essentially the same as an apparatus described elsewhere.[14] The forth (266 nm) and third (355 nm) harmonics of a Nd:YAG laser were used as the excitation light source. All laser flash photolysis experiments were performed at 296 K.



1,2-bis(2-methyl-3-benzothienyl)perfluorocyclopentene (BT)

Chart 1.

Upon irradiation of BT (1.4×10^{-4} mol dm^{-3}) with the forth harmonics (266 nm), the transient absorption spectra observed under argon atmosphere at delay times of 0.3 and 30 µs after laser irradiation are shown in Figure 1a. The observed spectra have transient absorption peaks at 360 and 520 nm. The time profile of the transient absorption, $A(t)$, observed at 520 nm is shown in Figure 1b. The observed $A(t)$ curve has a decay component (rate constant (k_{decay}(520 nm)) = 1.4×10^5 s^{-1}) and an almost constant component. The later component can safely be assigned to the closed-ring product, because its transient absorption spectrum was observed at a delay time of 30 µs after laser irradiation and is in good agreement with the reported spectrum for the closed-ring product.[15]

From the difference spectrum between the spectra observed at delay times of 0.3 and 30 µs after laser irradiation, the fast decay component has a broad transient absorption band around 450 and 600 nm. Since this transient absorption was efficiently

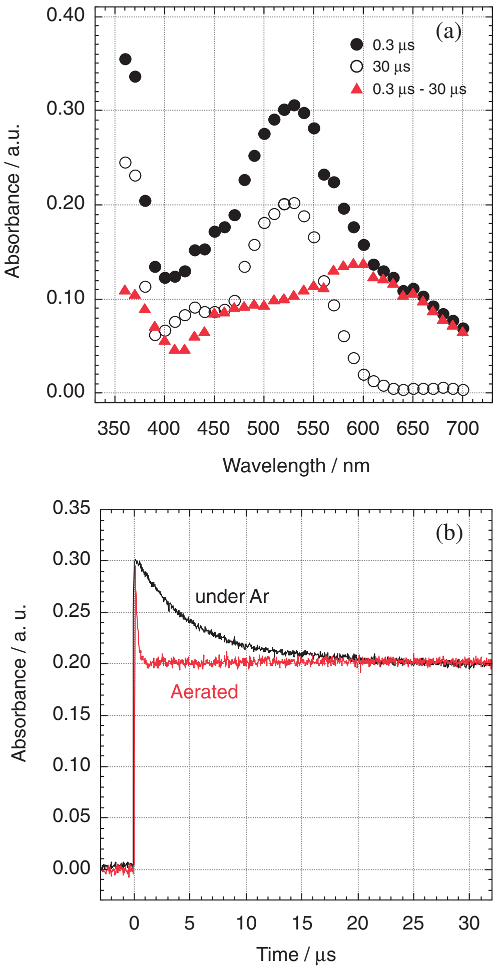


Figure 1. (a) Transient absorption spectra observed for the direct excitation of BT (1.4×10^{-4} mol dm^{-3}) under argon atmosphere at delay times of 0.3 (●) and 30 µs (○) after laser irradiation and difference spectrum (▲). (b) The $A(t)$ curves observed for the reaction of BT at 520 nm under argon atmosphere and aerated.

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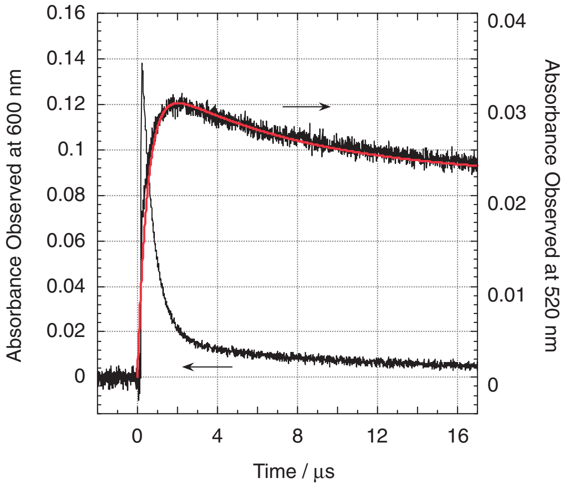


Figure 2. The $A(t)$ curves observed for the reaction of BT (1.6×10^{-4} mol dm^{-3}) with Xn (2.6×10^{-3} mol dm^{-3}) in methanol at 520 and 600 nm under argon atmosphere. $A(t)$ curve (red line) calculated by eq 9.

quenched by oxygen, as shown in Figure 1b, it can be assigned to the T–T absorption of BT (^{3}BT*). It is noteworthy that the yield of the almost constant component was not affected by oxygen, although the fast decay component (^{3}BT*) was efficiently quenched. Thus, we concluded that the formation of the closed-ring product does not occur through the triplet state generated from the direct excitation of BT.

Next, triplet sensitization of BT with xanthone (Xn) was carried out with the third (355 nm) harmonics of Nd:YAG laser. The concentration of BT was $0.056–0.32 \times 10^{-3}$ mol dm^{-3}. $A(t)$ curves were measured at 600 nm, because the triplet excited state of Xn has a T–T absorption around 600 nm.[16]

$$\mathrm{Xn} + h\nu(355\,\mathrm{nm}) \rightarrow {}^1\mathrm{Xn}^* \rightarrow {}^3\mathrm{Xn}^* \qquad (1)$$

$$^3\mathrm{Xn}^* + \mathrm{BT} \rightarrow \mathrm{Xn} + {}^3\mathrm{BT}^* \qquad (2)$$

Here, ^{1}Xn* and ^{3}Xn* represent the singlet and triplet excited states of Xn, respectively. The $A(t)$ curve observed for the reaction of BT with Xn (2.6×10^{-3} mol dm^{-3}) at 600 nm is shown in Figure 2 and its decay rate constant (k_{decay}(600 nm)) is obtained to be 1.6×10^6 s^{-1}. The decay of ^{3}Xn* accelerated with increasing concentration of BT. The BT concentration dependence of k_{decay}(600 nm) has a good linear relationship between k_{decay} and concentration of BT, and the quenching rate constant was determined to be 5×10^9 s^{-1} mol^{-1} dm^3. From these results, the triplet energy transfer was found to efficiently occur from ^{3}Xn* to BT.

The transient absorption spectra observed at delay times of 0.2, 0.5, 1.0, 2.0, and 5.0 µs after laser irradiation are shown in Figure 3. Strong T–T absorption due to ^{3}Xn* observed at 600 nm disappeared quickly and then a new transient absorption band appeared around 520 nm. This new band does not show any decrease in the later time range of 15 µs.

The $A(t)$ curve observed at 520 nm is also shown in Figure 2. The observed $A(t)$ curve has a rise component ($0 < t \leq 2.0$ µs), a decay component ($2.0 < t \leq 15$ µs) and an almost constant component (15 µs $\leq t$). The rate constant of the rise component (k_{rise}(520 nm)) was obtained to be 1.6×10^6 s^{-1}. This value shows good agreement with k_{decay}(600 nm) of ^{3}Xn*. Thus the

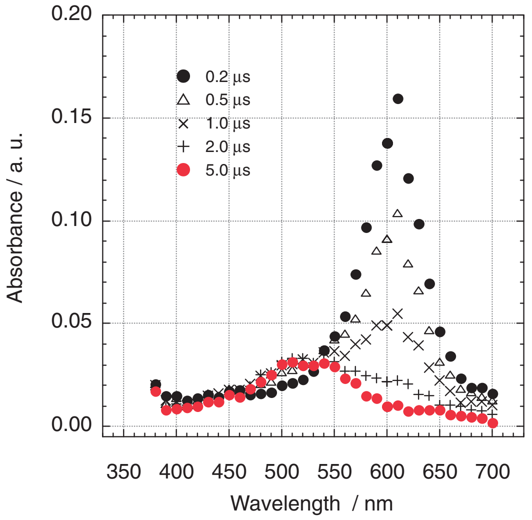
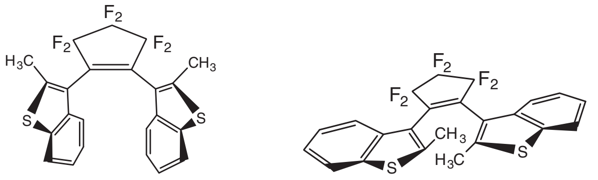


Figure 3. Transient absorption spectra observed for the triplet sensitization reaction of BT (1.6×10^{-4} mol dm^{-3}) with Xn (2.6×10^{-3} mol dm^{-3}) in methanol at delay times of 0.2 (●), 0.5 (△), 1.0 (×), 2.0 (+), and 5.0 µs (●) after laser irradiation under argon atmosphere.



parallel form (p-BT) antiparallel form (ap-BT)

Chart 2.

rise component and ^{3}Xn* has a relationship between daughter and parent. Moreover, the rate constant of the decay component (k_{decay}(520 nm)) was obtained to be 1.4×10^5 s^{-1} and showed good agreement with the decay rate constant of ^{3}BT* (k_{decay}(520 nm)) obtained from the direct excitation of BT. From these results, the component which has rise and decay is ascribable to ^{3}BT*. On the other hand, the almost constant component may be assigned to the closed-ring product.

The ground state of BT has two conformers; parallel form and antiparallel form (Chart 2).[15] In the present study, formation and disappearance of ^{3}BT* were directly observed at 520 nm by the triplet sensitization reaction. The triplet energy transfer should occur in both p-BT and ap-BT. Miyasaka et al. reported that the ^{3}BT* observed for the direct excitation of BT was p-BT and the cyclization reaction of BT did not occur through the triplet excited state of p-BT (^{3}p-BT*).[11] In the preset study, k_{decay}(520 nm) observed from the sensitization reaction is almost the same as that observed from the direct excitation of BT. Thus formation of ^{3}p-BT* is at least concluded.

The cyclization reaction of BT, however, was suggested from the transient absorption spectra. We then carried out stationary UV spectrum measurements upon irradiation of a degassed methanol solution containing BT (1.6×10^{-4} mol dm^{-3}) and Xn (2.6×10^{-3} mol dm^{-3}). The spectra observed before and after 40 s irradiation (355 nm, 10 mJ/pulse, 10 Hz) are shown in Figure 4 together with the spectra observed for the solution containing BT only. We can see

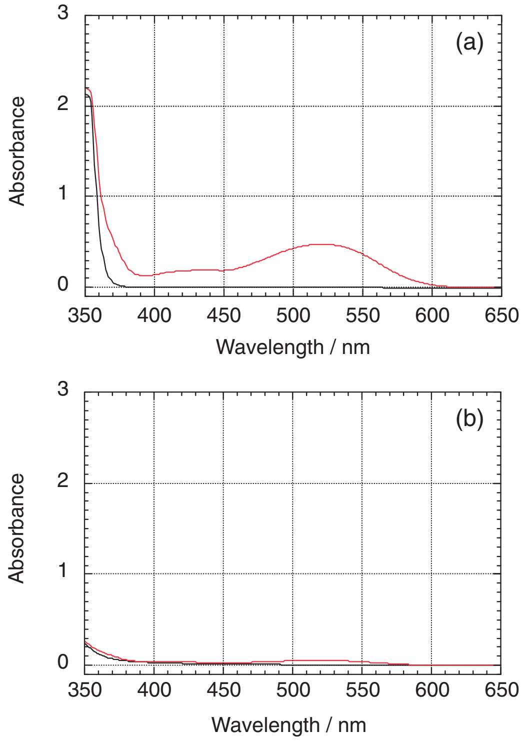


Figure 4. UV spectra observed before (—) and after 40 s laser irradiation (—) of the degassed methanol solution containing (a) BT (1.6×10^{-4} mol dm^{-3}) with Xn (2.6×10^{-3} mol dm^{-3}) and (b) BT only.

from Figure 4a that the spectrum for the closed-ring product[15] was clearly observed and its overall quantum yield (Φ), eqs 3–6, was obtained to be ca. 0.3.[17] The obtained Φ value is almost the same as the value of direct excitation of BT ($\Phi = 0.35$).[15] On the other hand, the formation of the closed-ring product was scarcely observed for the solution without Xn (Figure 4b). These results indicate that the cyclization reaction via the triplet excited state certainly occurs and it may occur through the triplet excited state of ap-BT (^{3}ap-BT*).

From these results, a reaction scheme is proposed as follows:

$$\text{p-BT} + {}^3\text{Xn}^* \xrightarrow{k_1} {}^3\text{p-BT}^* + \text{Xn} \tag{3}$$

$$ {}^3\text{p-BT}^* \xrightarrow{k_2} \text{p-BT} \tag{4}$$

$$\text{ap-BT} + {}^3\text{Xn}^* \xrightarrow{k_3} {}^3\text{ap-BT}^* + \text{Xn} \tag{5}$$

$$ {}^3\text{ap-BT}^* \xrightarrow{k_4} \text{closed-ring product} \tag{6}$$

Here, k_1, k_2, k_3, and k_4 are the rate constants of each reaction, respectively. Thus the time profile of ^{3}p-BT* can be expressed by

$$[{}^3\text{p-BT}^*] = A_1 \frac{k_1}{k_2 - k_1}(\exp(-k_1 t) - \exp(-k_2 t)) \tag{7}$$

Since the concentration of BT is as low as $0.056\text{–}0.32 \times 10^{-3}$ mol dm^{-3}, k_4 is believed to be much larger than k_3 (10^5–10^6 s^{-1}). Thus the time profile of closed-ring product can be expressed by

$$[\text{closed-ring product}] = A_2(1 - \exp(-k_3 t)) \tag{8}$$

At 520 nm, ^{3}p-BT* and closed-ring product have transient absorption and ^{3}ap-BT* may display the absorption. However, the time profile of ^{3}ap-BT* may be negligible because k_4 is thought to be much larger than 10^9 s^{-1}. Thus $A(t)$ can be expressed by

$$A(t) = a_1 \frac{k_1}{k_2 - k_1}(\exp(-k_1 t) - \exp(-k_2 t)) + a_2(1 - \exp(-k_3 t)) \tag{9}$$

Here, a_1 and a_2 represent the pre-exponential factors. Using eq 9, $A(t)$ curve observed at 520 nm was analyzed. The $A(t)$ calculated with $k_1 = k_3 = 2.0 \times 10^6$ s^{-1}, $k_2 = 1.3 \times 10^5$ s^{-1}, $a_1 = 0.011$, and $a_2 = 0.022$ is plotted in Figure 2 (red line). As clearly shown in this figure, the observed $A(t)$ curve can be reproduced fairly well by using this model.

In the present study, the cyclization reaction via the triplet excited state of naked diarylethene was studied by the ns laser flash photolysis and an alternative cyclization pathway via the triplet excited state of BT was found to occur with a triplet sensitizer Xn. To establish the cyclization of diarylethene via the triplet excited state, it is desirable to clarify the nature of the triplet state of BT.

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17 The overall quantum yield was obtained from the UV spectra observed for the methanol solution containing BT (2.0×10^{-4} mol dm^{-3}) and Xn (9.0×10^{-4} mol dm^{-3}).