

Large Substituent Effect on the Photochemical Rearrangement of 1,6-(*N*-Aryl)aza-[60]fulleroids to 1,2-(*N*-Arylaziridino)-[60]fullerenes

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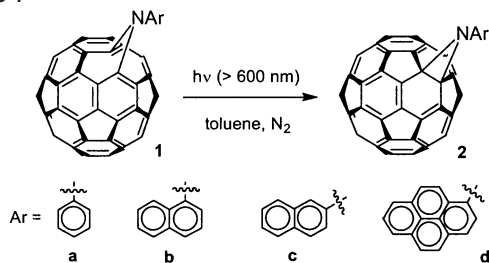
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Since the discovery of fullerene, reactions of C_{60} with various compounds,¹ such as organic azides,² have been conducted to extend the utility of C_{60} .³ Photochemical reactions are also important, one being the rearrangement of 1,6-(*N*-substituted)aza-[60]fulleroids (**1**) to 1,2-(*N*-substituted)aziridino-[60]fullerenes (**2**). It is reported that although **1a** undergoes photochemical rearrangement into **2a**,^{2h} 1,6-(*N*-methoxyethoxymethyl)aza-[60]fulleroid is photochemically stable.^{2f} This example indicates that *N*-substituents play a crucial role in remotely controlling the reactivities of fullerene centers. However, systematic studies of *N*-substituent effects on the photochemical reactivity of fullerene derivatives have not previously been reported.

We report here a large *N*-substituent effect on the photochemical rearrangement **1** → **2** for a series of *N*-aryl substituents **a–d** shown in Scheme 1. The difference in the photochemical rearrangement rates was more than 2000-fold between the fastest **1b** and the slowest **1c**.

Scheme 1



Absorption spectra of **1a–d** and **2a–d** were similar to that of parent C_{60} except for a considerable increase of their molar extinction coefficients (ϵ) at >430 nm.⁴ In analogy with the absorptions of C_{60} ,⁵ those of **1a–d** and **2a–d** at <430 nm can be assigned to the allowed transitions, and the weak absorptions at >430 nm, to the orbital-forbidden electronic transitions.

Figure 1 shows the time profiles of photochemical rearrangement **1** → **2** by >600 nm light under a nitrogen atmosphere. The figure shows the decrease of **1a–d** and the increase of **2a–d** as a function of irradiation time. The light is mainly absorbed by the forbidden transitions of **1a–d**.

As seen in Figure 1A, the reaction took 20 h (**1a**) and >30 h (**1c**) for completion; the consumption of **1a,c** and the formation of **2a,c** showed single exponential-like decay and rise, which is an indication for a unimolecular process. On the other hand, Figure 1B shows a very fast reaction for **1b**, which only took 50 s for completion. The reaction rate of **1b** in the initial stage was slower

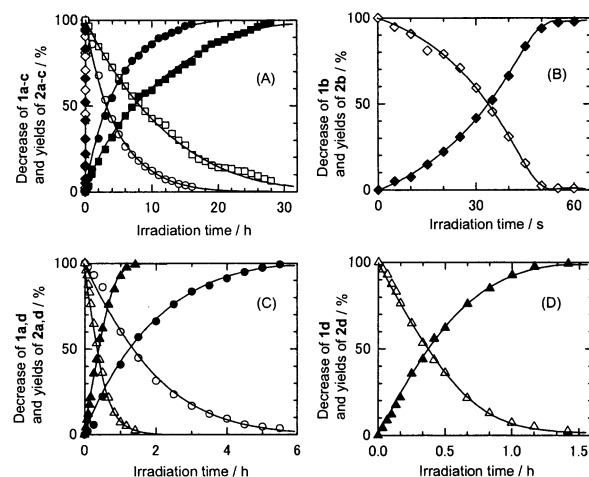


Figure 1. Decrease and formation of (A) **1a–c** and **2a–c**, (B) **1b** and **2b**, (C) **1a,d** and **2a,d**, and (D) **1d** and **2d** as a function of irradiation time. Substrates and products: **1a**: \circ , **2a**: \bullet , **1b**: \diamond , **2b**: \blacklozenge , **1c**: \square , **2c**: \blacksquare , **1d**: \triangle , **2d**: \blacktriangle . Initial concentration: (A, B) 5×10^{-4} M and (C, D) 1×10^{-5} M **1** in toluene; irradiated light: >600 nm.⁴

than that in the latter stage, showing nonexponential curves for the consumption of **1b** and the formation of **2b**. The photolyses of **1d** were conducted at lower concentration because of its low solubility; therefore, the photolysis of **1a** was also conducted in the same concentration for comparison. The photolysis of **1d** proceeded faster than that of **1a** (Figure 1C) with an exponential-like decay and rise of **1d** and **2d**, respectively (Figure 1D). The ratios of the required reaction time for the completion of the reactions of **1a**:**1b**:**1c**:**1d** was 1440:1: >2160 :360.

The photolyses of **1a–d** in air-saturated solutions showed a large decrease in the rate of rearrangement **1** → **2**, indicating that the rearrangement occurs via triplet states of **1**. This conclusion is consistent with the report that the intersystem crossing of C_{60} and its derivatives from their singlet to triplet excited states is very fast and efficient.⁶

The nonexponential nature of rearrangement **1b** → **2b**, shown in Figure 1B, was interpreted as a triplet sensitization by product **2b**. The energy level of the triplet state of **2** is reported to be slightly higher than that of **1**⁷ so that the triplet sensitization by **2b** for conversion **1b** → **2b** seems to be reasonable.

Figure 2 shows the consumption of **1b** and the formation of **2b** as a function of the ratio of the amount of initially added **2b** to **1b**. As seen in the figure, an increase in the consumption of **1b** and the formation of **2b** was observed, which was proportional to the

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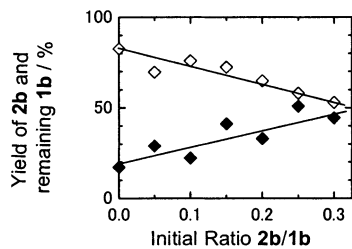


Figure 2. Yield of **2b** and remaining **1b** as a function of the initial ratio of additive **2b** to **1b**. Substrates and products, **1b**: ◇, **2b**: ◆. Irradiation time: 20 s. Initial concentration: 5×10^{-4} M **1** in toluene. Irradiated light: >600 nm.⁴

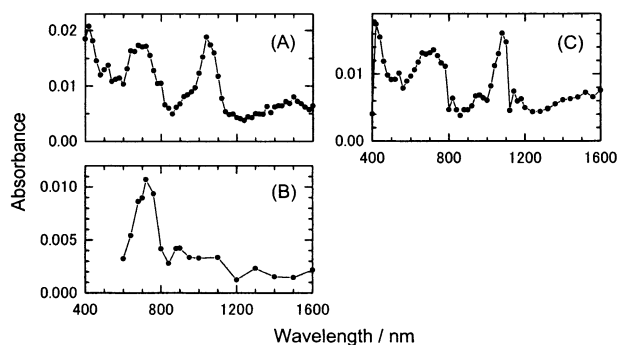


Figure 3. Nanosecond transient absorption spectra of (A) **1a**, (B) **1b**, and (C) **1c**. Excitation wavelength: 530 nm. Concentration: 1×10^{-4} M in toluene. Measured at (A, C) 200 ns and (B) 100 ns after the laser pulse.

amount of initially added **2b**. This means that the rate of the reaction increases with the progress of the reaction, which is consistent with the result obtained for rearrangement **1b** \rightarrow **2b** (cf. Figure 1B). In the case of **1a,c**, the addition of **2a,c** showed no effect on the reaction, while for **1d**, the addition of **2d** showed slight retardation.⁴

The different photochemical reactivities among **1a–d** cannot be explained by the difference of their ϵ values because the order of the ϵ values has no relevance to that of the reaction rates at >600 nm. Although participation of triplet states was expected in all photochemical rearrangements, different reactivities among **1a–d** suggested a large difference in the nature of their excited states.

Figure 3 shows the transient spectra of **1a–c**. Figure 3B only shows a peak at 700 nm, which can be assigned to the normal triplet–triplet absorption of fullerene derivatives. On the other hand, panels A and C of Figure 3 show that **1a,c** have strong absorptions at 420, 650, and 1050 nm, and a broad absorption at >1300 nm, which are different from the normal triplet–triplet absorptions.⁸ Therefore, the slow reaction of **1a,c** can be rationalized by the participation of the excited states different from the pure triplet states, which are not responsible for the rearrangement, in addition to the small contribution of the triplet states. However, the transient absorption spectrum could not be observed for **1d**, which is due to the very weak transient absorption of **1d** that may be rationalized by a fast decay of the triplet state.

Figure 4 shows the transient spectra of **2a–d**. The trend of the spectra is similar to that of **1a–c**. Compounds **2a,c** show the absorptions at 450, 650, and 900 nm, which are different from those of the pure triplet states. This implies that **2a,c** cannot act as triplet sensitizers, which is consistent with the fact that rearrangement **1** \rightarrow **2** was not affected by the addition of **2a,c**. On the other hand, **2b,d** show a typical triplet absorption, which indicates that these compounds can be used as sensitizers. The acceleration of

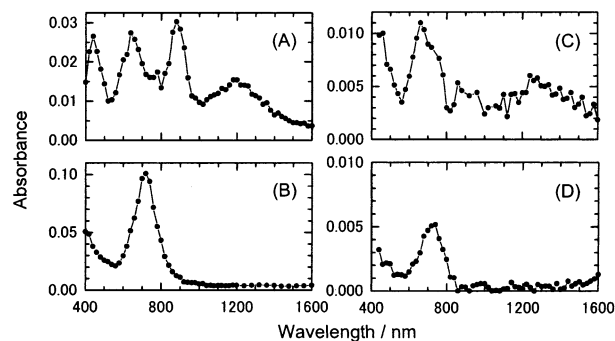


Figure 4. Nanosecond transient absorption spectra of (A) **2a**, (B) **2b**, (C) **2c**, and (D) **2d**. Excitation wavelength: (A, C, D) 530 nm and (B) 532 nm. Concentration: 1×10^{-4} M in toluene. Measured at 200 ns after the laser pulse.

rearrangement **1b** \rightarrow **2b** can be rationalized by this sensitization. The reason for the small effect on the addition of **2d** in rearrangement **1d** \rightarrow **2d** might be due to the very short triplet lifetime of **2d**.

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Supporting Information Available: Experimental details, UV spectra of **1a–d** and **2a–d**, effect of the addition of **2** on rearrangement **1** \rightarrow **2**, and time profiles of the transient species (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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