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Tetrahedron Letters 46 (2005) 6713–6716
Tetrahedron Letters

Drastic change in the rate of photochemical rearrangement of 1,6-(*N*-phenyl)aza-[60]fulleroids by switching the excited states through simple methyl substitution on the phenyl group

Akihiko Ouchi,[a,*] Bahlul Z. S. Awen,[a] Hongxia Luo,[b] Yasuyuki Araki[b] and Osamu Ito[b,*]

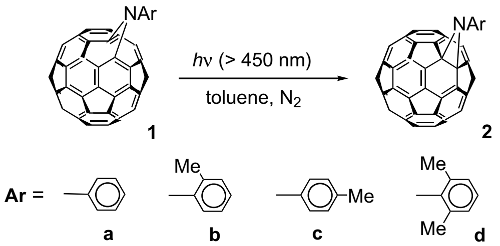
[a] *National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan*
[b] *Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi 980-8577, Japan*

Received 17 June 2005; revised 20 July 2005; accepted 26 July 2005
Available online 10 August 2005

Abstract—The reaction rate for the photochemical rearrangement of 1,6-*N*-(substituted-phenyl)aza-[60]fulleroid **1** to 1,2-*N*-(substituted-phenyl)aziridino-[60]fullerene **2** differed ca. 3000-fold depending on the position and number of methyl substituents on the *N*-phenyl group. The required time for the completion of the reaction decreased in the order 2,6-dimethylphenyl (**1d**) < 2-methylphenyl (**1b**) < phenyl (**1a**) < 4-methylphenyl (**1c**). The difference was mainly due to switching of the excited states between normal (fast reactions) and charge-separated (slow reactions) triplet states, which was induced by steric interactions between the *N*-phenyl group and the C_{60} moiety.

Molecules showing twisted intramolecular charge transfer (TICT) have been well studied and it is known that their spectroscopic properties are largely affected by small structural modifications of the molecules.[1] An explanation for this phenomenon is the switching between two excited states by intramolecular steric interactions. If this switching is linked to a chemical reaction in which the rate of the reaction is very different between the two excited states, a molecule that amplifies a small structural difference into a large chemical reactivity can be constructed.

We report here a photochemical rearrangement of 1,6-(*N*-phenyl)aza-[60]fulleroids (**1**) to 1,2-(*N*-phenyl)aziridino-[60]fullerenes (**2**)[2,3] with different substitutions on the phenyl group (**1a–d**) (Scheme 1), which provides an example for the above mentioned amplification systems; a small difference in the methyl substitution on the phenyl group is found to induce an approximate 3000-fold acceleration in the reaction rates between the slowest (**1c**) and the fastest (**1d**) photochemical rearrangement **1** → **2**.



Scheme 1. Photochemical rearrangement **1** → **2**.

Absorption spectra of **1a–d** and **2a–d** were similar to that of parent C_{60}, though a slight difference among their molar absorption coefficients (ε) was observed.[4] The absorptions of **1a–d** and **2a–d** at <430 nm can be assigned to allowed transitions and the weak absorptions at >430 nm to orbital forbidden electronic transitions, by analogy with those of C_{60}.[5]

Figure 1 shows the time profiles of photochemical rearrangement **1** → **2** by >450 nm light irradiation under a nitrogen atmosphere. The light is mainly absorbed by the forbidden transitions of **1a–d**. The reactions were very sensitive to oxygen and a significant retardation of the reactions was observed in the presence of even a small amount of oxygen. As seen in Figure 1, the conversion of **1** to **2** was quantitative and Figure 1A

Keywords: Amino compounds; Fullerenes; Photochemical reactions; Reactivity; Rearrangements.

[*] Corresponding authors. Tel.: +81 29 861 4550; fax: +81 29 861 4511 (A.O.); e-mail: ouchi.akihiko@aist.go.jp

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doi:10.1016/j.tetlet.2005.07.133

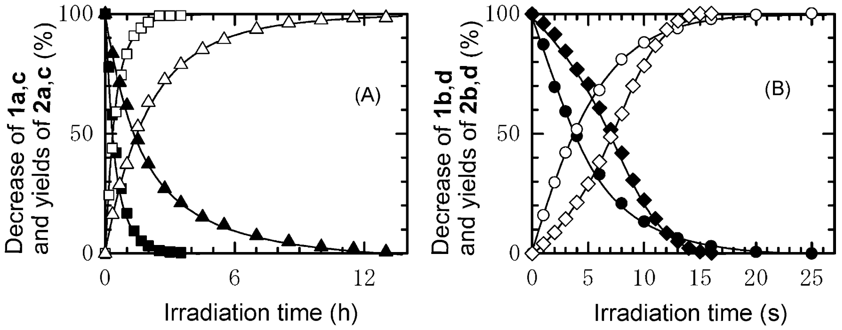


Figure 1. Decrease of **1** and yield of **2** for (A) **1a**,**c** and **2a**,**c**, and (B) **1b**,**d** and **2b**,**d** as a function of irradiation time. Substrates and products; **1a**: ■, **2a**: □, **1b**: ●, **2b**: ○, **1c**: ▲, **2c**: △, **1d**: ◆, **2d**: ◇. Initial concentration: 10^{-5} M **1** in toluene; irradiated light: >450 nm.[6]

shows that the required times for complete consumption of **1a** and **1c** were 3.5 and 13 h, respectively, whereas Figure 1B demonstrates a very fast reaction of **1b** and **1d** which only took 25 and 15 s, respectively. The ratio of the required time for the complete consumption of **1** was **1a**/**1b**/**1c**/**1d** = 790:1.6:2930:1.

Figure 2 shows nanosecond transient absorption spectra of **1a**–**d** and **2a**–**d**. The transient absorption spectra of fast reacting **1b** and **1d** show a main absorption band at 720 nm (Fig. 2, B1 and D1), which is characteristic of the excited triplet state of C_{60} derivatives.[7,8] In contrast, the transient absorption spectra of slow reacting **1a** and **1c** show absorption bands at <420, 680, 1050 nm, and a broad absorption at >1300 nm (Fig. 2, A1 and C1), which can be attributed to a charge-separated triplet state.[3b,8–10] Interestingly, the transient spectrum of **1b** also shows absorptions corresponding to the charge-separated triplet state in addition to the normal triplet absorptions.

These results indicate a switching of the excited states between the normal and charge-separated triplet states, which leads to the fast and slow reactions, respectively.

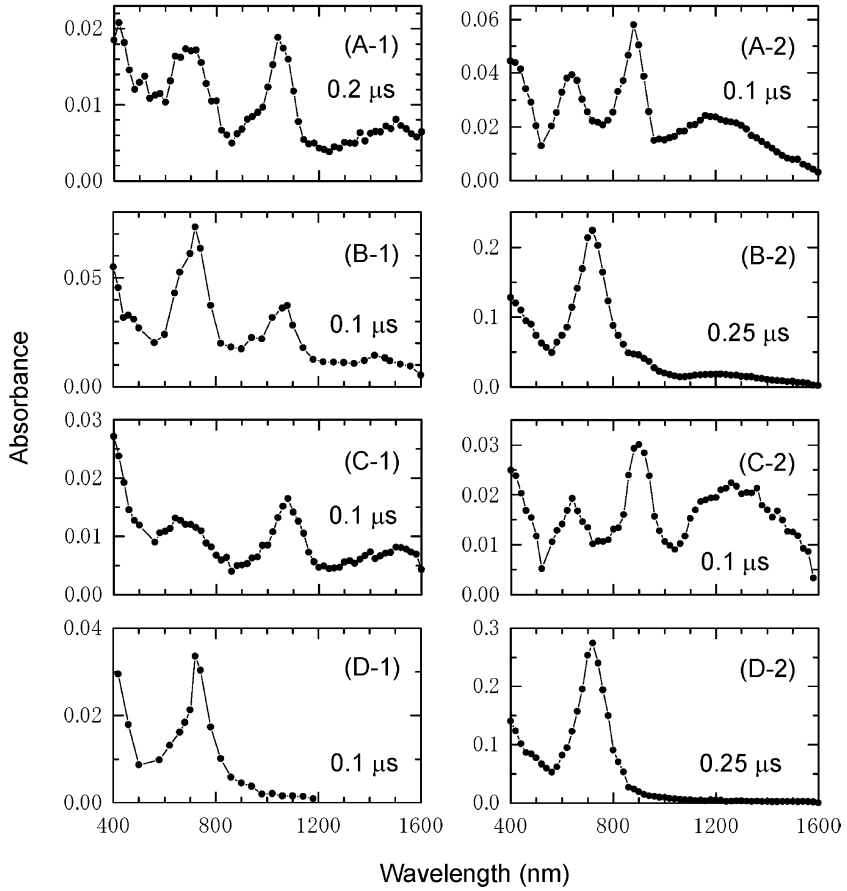
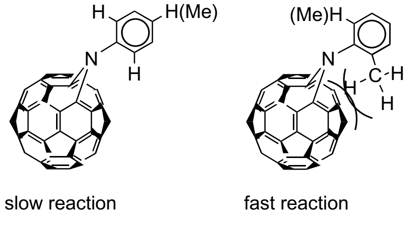


Figure 2. Nanosecond transient absorption spectra of (A1) **1a**,[3] (A2) **2a**,[3] (B1) **1b**, (B2) **2b**, (C1) **1c**, (C2) **2c**, (D1) **1d**, and (D2) **2d**. Excitation wavelength: 530 (A1) and 532 (A2, B–D) nm. Concentration: 10^{-4} M in toluene. Measured times of the spectra after the laser pulse are shown in the figures.

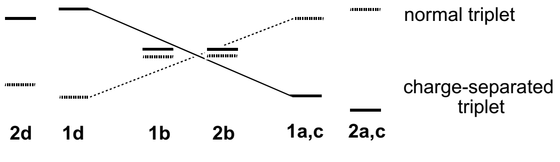
Scheme 2 indicates the presence of a large steric interaction between the *ortho*-methyl-substituted phenyl group and C_{60} moiety in the case of fast reactions (**1b**,**d**), particularly when the phenyl group rotates around the N–Ph bond, whereas smaller interactions are expected for the slow reactions (**1a**,**c**). The Ar group without the *ortho*-methyl-substituent may give the best angle with respect to the *N*-lone pair that enables facile electron transfer of the lone pair electron to the C_{60} moiety, which is most probably due to the rupture of efficient delocalization between the lone pair electrons and the π-electrons of the phenyl ring. The generation of the positive charge on the nitrogen atom might be the reason for the decrease in the rate of the rearrangement in the case of charge-separated triplet states.

Besides rearrangement rates, Figure 1 also demonstrates a difference in the reaction mechanisms. The consumption of **1a**–**c** and the formation of **2a**–**c** showed single exponential-like decay and rise, which is an indication of a unimolecular process. However, the reaction of **1d** shows nonexponential curves for the consumption of **1d** and the formation of **2d**. This is explained by the triplet sensitization of the reaction by product **2d**.[3] To determine the contribution of the unimolecular and sensitized processes, the rate constants of both processes were obtained similar to the reported procedure[3b] with consideration of the difference in ε values of **1a**–**d** and **2a**–**d**.[4] Thus, the rate constants (normalized with ε) obtained for the unimolecular (k_d) and the sensitized (k_s) processes are 1.5×10^{-7} cm M s^{-1} and 7.3×10^{-3} cm s^{-1} for **1a**, 1.4×10^{-4} cm M s^{-1} and 5.8 cm s^{-1} for **1b**, 4.7×10^{-8} cm M s^{-1} and 6.3×10^{-17} cm s^{-1} for **1c**, and 1.2×10^{-5} cm M s^{-1} and 2.6×10 cm s^{-1} for **1d**.[4]

The result of the sensitized reactions can be explained by the relative triplet energies of **1a**–**d** and **2a**–**d** (Scheme 3). The transient spectra of **2a**–**d** are similar to those of **1a**–**d** so that those of **2a** and **2c** are assigned to the charge-separated triplet state and **2b** and **2d** to the normal triplet state. As the triplet energy of charge-separated **2** is estimated to be lower than that of **1**,[3b] **2a** and **2c** cannot act as triplet sensitizers, which is consistent with the fact that rearrangement **1** → **2** proceeded by a unimolecular process. In contrast, it is reported that the triplet energy of **2d** is higher than that of **1d**[11] so that **2d** can act as a triplet sensitizer showing a large k_s value and nonexponential feature in the rearrangement. Although **2b** has a normal triplet character, the sensitization effect is not apparently observed in the reaction; this is due to the fact that the k_s value was 1/4.5 but the k_d value was 11.7-fold larger than that of **1d**. This inefficient triplet sensitization of **2b** can be rationalized by **2b** having similar triplet energy to that of **1b**.



Scheme 2. Steric interaction between *N*-aryl and C_{60} moieties.



Scheme 3. Schematic diagram for the relative triplet energy of **1a**–**d** and **2a**–**d**.

Although the rearrangement rate is mostly controlled by the steric effect, the electronic factor of the substituents also affected the rate of the reaction. In the case of the unimolecular process, k_d values decreased with the introduction of the electron-donating group to the phenyl group; the rate decreased to 1/3.2 with *para*-methyl (**1c** vs **1a**) and to 1/11.7 with *ortho*-methyl (**1b** vs **1d**) substitutions. The result on the *para*-methyl substitution can be explained by the facilitation of charge transfer from the electron-donating *N*-lone pair to the electron-accepting C_{60} moiety due to the increase in the electron density of the *N*-lone pair. In contrast, a 4.5-fold increase in k_s value was observed with *ortho*-methyl substitution (**1b** vs **1d**), which is rationalized by the facilitation of the triplet energy transfer from **2** to **1** due to the increase in triplet energy of **2d**.

In summary, the reaction rate of the photochemical rearrangement **1** → **2** differed ca. 3000-fold depending on the position and number of the methyl substituents on the *N*-phenyl group. The required time for the completion of the reaction decreased in the order **1d** < **1b** < **1a** < **1c**. The difference was mainly due to a switching of the excited states between normal (fast reactions) and charge-separated (slow reactions) triplet states, which was caused by steric interactions between the *N*-phenyl group and the C_{60} moiety. The large difference in the reaction rates can be considered as an amplification of small structural differences into large chemical reactivities by the switching between the two different excited states, which may be extended to the development of molecular switches.

Acknowledgements

We thank Mr. Shin-ichirou Kawabata and Mr. Akio Tominaga, Shimadzu Co., for MALDI-TOFMS measurements, Dr. Y. Xiao for the preparation of **1b**–**d** and **2b**–**d**, and Dr. T. Oishi for the purification and spectroscopic measurements of **1** and **2**.

Supplementary data

Experimental details for the synthesis, analytical data, spectral data, steady-state photolyses, and flash photolyses of **1** and **2**. UV spectra of **1a**–**d** and **2a**–**d**, and determination of rate constants k_d and k_s. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.tetlet.2005.07.133.

References and notes

1. (a) Rettig, W. *Top. Curr. Chem.* **1994**, *169*, 253–299; (b) Herbich, J.; Brutschy, B. In *TICT Molecules*; Balzani, V., Ed.; Electron Transfer in Chemistry; Wiley-VCH: Weinheim, 2001; Vol. 4, pp 697–741.
2. (a) Hirsch, A. The Chemistry of the Fullerenes; George Thieme: Stuttgart, 1994; (b) Taylor, R. Lecture Notes on Fullerene Chemistry: A Handbook for Chemists; Imperial College Press: London, 1999; (c) Kleineweischede, A.; Mattay, J. In *CRC Handbook of Organic Photochemistry and Photobiology*, 2nd ed.; Horspool, W., Lenci, F., Eds.; Photochemical Reaction of Fullerenes and Fullerene Derivatives; CRC Press: Boca Raton, 2003, Chapter 28.
3. (a) Ouchi, A.; Hatsuda, R.; Awen, B. Z. S.; Sakuragi, M.; Ogura, R.; Ishii, T.; Araki, Y.; Ito, O. *J. Am. Chem. Soc.* **2002**, *124*, 13364–13365; (b) Ouchi, A.; Awen, B. Z. S.; Hatsuda, R.; Ogura, R.; Ishii, T.; Araki, Y.; Ito, O. *J. Phys. Chem. A* **2004**, *108*, 9584–9592.
4. Details are given as Supplementary data.
5. Leach, S.; Vervloet, M.; Desprès, A.; Bréheret, E.; Hare, J. P.; Dennis, T. J.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Chem. Phys.* **1992**, *160*, 451–466.
6. Average of three independent runs.
7. (a) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; Macghie, A. R.; McCauley, J. P.; Smith, A. B., III, Jr.; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075–6081; (b) Greaney, M. A.; Gorun, S. M. *J. Phys. Chem.* **1991**, *95*, 7142–7144.
8. (a) Thomas, K. G.; Biju, V.; Guldi, D. M.; Kamat, P. V.; George, M. V. *J. Phys. Chem. B* **1999**, *103*, 8864–8869; (b) Konishi, T.; Fujitsuka, M.; Ito, O.; Toba, Y.; Usui, Y. *J. Phys. Chem. A* **1999**, *103*, 9938–9942; (c) Martín, N.; Sánchez, L.; Herranz, Ma. A.; Guldi, D. M. *J. Phys. Chem. A* **2000**, *104*, 4648–4657; (d) Bhasikuttan, A. C.; Shastri, L. V.; Sapre, A. V. *J. Photochem. Photobiol. A: Chem.* **2001**, *143*, 17–21; (e) Imahori, H.; El-Khouly, M. E.; Fujitsuka, M.; Ito, O.; Sakata, Y.; Fukuzumi, S. *J. Phys. Chem. A* **2001**, *105*, 325–332.
9. Shida, T. *Electronic Absorption Spectra of Radical Ions*; Elsevier: Amsterdam, 1988.
10. (a) Guldi, D. M.; Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1997**, *119*, 974–980; (b) Fujitsuka, M.; Ito, O.; Yamashiro, T.; Aso, Y.; Otsubo, T. *J. Phys. Chem. A* **2000**, *104*, 4876–4881; (c) Fukuzumi, S.; Ohkubo, K.; Imahori, H.; Shao, J.; Ou, Z.; Zheng, G.; Chen, Y.; Pandey, R. K.; Fujitsuka, M.; Ito, O.; Kadish, K. M. *J. Am. Chem. Soc.* **2001**, *123*, 10676–10683.
11. (a) Guldi, D. M.; Carmichael, I.; Hungerbühler, H.; Asmus, K.-D.; Maggini, M. *Proc.–Electrochem. Soc.* **1998**, *98-8*, 268–272; (b) Guldi, D. M.; Hungerbühler, H.; Carmichael, I.; Asmus, K.-D.; Maggini, M. *J. Phys. Chem. A* **2000**, *104*, 8601–8608.