Controlling electronic states and photochemical reactivities of C_{60} by chemical functionalization: *Ortho*-substituent effect of 1,6-*N*-(phenyl)aza-[60]fulleroids and 1,2-(*N*-phenyl)aziridino-[60]fullerenes

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Abstract

The reaction rate of the photochemical rearrangement 1,6-*N*-(2-substituted)aza-[60]fulleroids (**1**) → 1,2-(*N*-substituted)aziridino-[60]fullerenes (**2**) differed ca. 3.1-fold as the *ortho*-substituent of the *N*-phenyl group changed from 2-methylphenyl (**b**), 2-ethylphenyl (**c**), to 2-*iso*-propylphenyl (**d**). The retardation of the rearrangement is due to the contribution of charge-separated triplet state in the excited states in addition to the normal triplet state, which was confirmed by transient absorption measurements. A semi-empirical calculations on the ground state conformation of **1** and **2** showed that **1** with phenyl (**a**) and 2,6-dimethylphenyl (**e**) *N*-substituents and **2a,e** have C_{2v} symmetry but the rotation of the phenyl group along the N–Ph bond occurs with the increase of steric hindrance between the phenyl group and C_{60} moiety (**1b–d** and **2b–d**). These results indicate that the rate of the rearrangement, i.e., the nature of the excited states, is probably controlled by the conformation of the molecules at their excited states rather than that of their ground states. The generation of charge-separated triplet state in the excited state can be explained by the occurrence of phenyl group rotation along the N–Ph bond.
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1. Introduction

Several methods for chemical modifications of fullerenes, particularly of C_{60} molecules, have been developed in order to introduce some new properties to the C_{60} molecules [1]. One of the modifications is the introduction of aziridine group to C_{60} molecule to form 1,2-(*N*-substituted)aziridino-[60]fullerenes (**2**). The synthesis was a three-step reaction, in which the third step was a photochemical rearrangement of 1,6-*N*-(2-substituted)aza-[60]fulleroids (**1**) to **2** (*cf*. Scheme 1) [2].

It is reported that this photochemical rearrangement proceed when the substituent on the nitrogen atom was phenyl or 4-cyanophenyl groups [2] but the reaction did not proceeded when the substituent was methoxyethoxymethyl group [3]. These results indicate that phtochemical rearrangement **1** → **2** can be
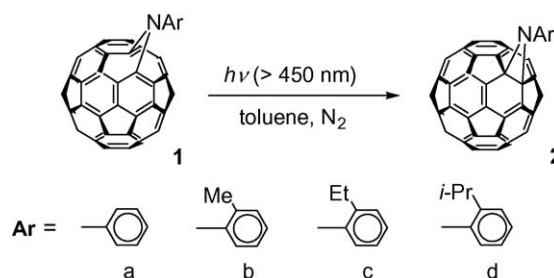
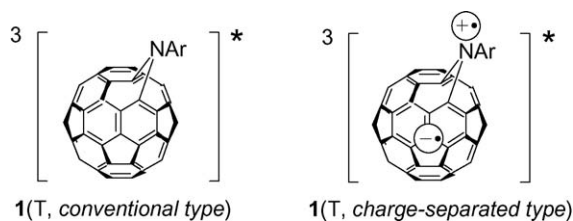Scheme 1. Photochemical rearrangement **1** → **2**.

controlled by changing the substituent on the nitrogen atom, which should be a result of some change in their excited states.

To investigate the *N*-substituent effect on the photochemical rearrangement, we have conducted a series of experiments using different aromatic substituents, namely, phenyl (**a**), 1-naphthyl, 2-naphthyl, and 1-pyrenyl groups [4].
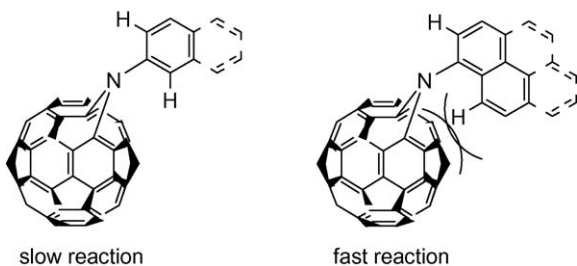
In these reactions, the substituents were classified into two groups. The first group (1-naphthyl and 1-pyrenyl) gave fast

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Scheme 2. Different electronic states in the excited states.

Scheme 3. Steric interaction between *N*-aryl and C_{60} moieties.

photochemical rearrangement and transient spectra of **1** and **2** showed normal triplet absorptions that are generally observed in C_{60} and its derivatives. In contrast, the second group (phenyl and 2-naphthyl) gave very slow photochemical rearrangement and showed transient spectra that were much different from the triplet states of conventionally reported C_{60} derivatives. We have assigned the absorptions to intramolecular charge separated triplet states [4] and it was later confirmed by time-resolved ESR spectroscopy (Scheme 2) [5]. The difference of the photochemical rearrangement rate between the two groups was approximately 3000-fold.

The origin of the switching of the excited states by the type of the *N*-aryl groups can be explained by steric and electronic effects. As seen in Scheme 3, a larger steric interaction is expected between the aryl group and C_{60} moiety for the fast reacting compounds (1-naphthyl and 1-pyrenyl) than that for the slow reacting compounds (phenyl and 1-naphtyl). A significant contribution of both effects, particularly the steric effect, in the switching of the excited states is confirmed by the introduction of methyl substituent(s) to the *N*-phenyl group; [6] it was revealed that the excited state of **1a** and **2a** changed from the intramolecular charge separated triplet state to the normal triplet state by the introduction of methyl group(s) to the *ortho*-position(s) of the *N*-phenyl group.

However, it is still not clear how the steric effect is affecting the structure of the excited state of the molecule. Therefore, we have herein conducted a series of experiments by changing the size of the *ortho*-substituent, i.e., phenyl (**a**), 2-methylphenyl (**b**), 2-ethylphenyl (**c**), and 2-*iso*-propylphenyl (**d**), as shown in Scheme 1.

2. Results and discussion

Fig. 1 shows the absorption spectra of **1a–d** and **2a–d**, which are similar to those of **1** and **2** with different *N*-aryl substituents reported previously except for the small molar absorption coef-
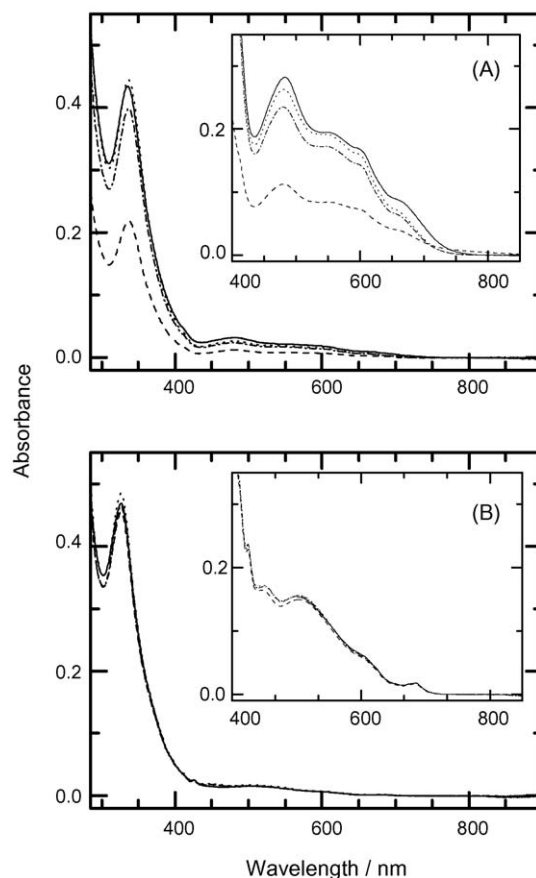

Fig. 1. Absorption spectra of: (A) **1a–d** and (B) **2a–d**. Concentration: 10^{-5} M and 10^{-4} M (inset) in toluene. Optical path: 10 mm. **1a**, **2a**: [6] (—); **1b**, **2b**: [6] (– – –); **1c**, **2c**: (· · ·); **1d**, **2d**: (- - -).

ficient of **1b** [6]. The absorptions of **1a–d** and **2a–d** at <430 nm correspond to allowed transitions and the weak absorptions at >430 nm to symmetrically forbidden electronic transitions [4,6].

The time profiles of photochemical rearrangement of **1b–d** are shown in Fig. 2. The utilized light was >450 nm, which was mainly absorbed by the forbidden transitions of **1a–d**. Similar to the photolysis of other azafulleroids, even a small amount
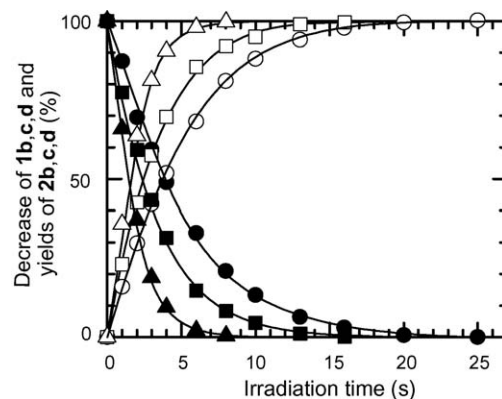

Fig. 2. Decrease of **1** and yield of **2** as a function of light-irradiation time. Substrates and products: **1b**: [6] (●), **2b**: [6] (○), **1c**: (■), **2c**: (□), **1d**: (▲), **2d**: (△). Initial concentration: 10^{-5} M **1** in toluene; irradiated light: >450 nm; [11] under nitrogen atmosphere.

Table 1
Rate constants of direct and sensitized photochemical rearrangement $1 \rightarrow 2$

Substituent	Direct process			Sensitized process		
	k_d (cm M s^{-1})	ε_1[a] (cm^{-1} M^{-1})	$k_d\varepsilon_1$ (s^{-1})	k_s (cm s^{-1})	ε_2[a] (cm^{-1} M^{-1})	$k_s\varepsilon_2$ (s^{-1} M^{-1})
a[b]	1.523×10^{-7}	2824	0.00043	7.267×10^{-3}	1532	11
b[b]	1.375×10^{-4}	1126	0.15486	5.861	1495	8762
c	9.003×10^{-5}	2631	0.23687	8.704	1558	13560
d	1.457×10^{-4}	2353	0.34283	2.906×10	1552	45097

[a] Molar absorption coefficient of **1** and **2** at λ_{max} in >450 nm region.

[b] Ref. [6].

of oxygen resulted in a significant retardation of the reactions. As seen in Fig. 2, the conversion of **1** to **2** was quantitative and the reaction of **1b–d** was accelerated with the increase of the size of the *ortho*-substituent on the phenyl group, which took 25, [6] 16, and 8 s, respectively, for the complete consumption of the starting materials whereas **1a** took 3.5 h [6]. The ratio of the required time for the completion of the reactions was **1a/1b/1c/1d** = 1575:3.1:2:1.

Although the consumption of **1a–d** and the formation of **2a–d** showed single exponential-like decay and rise, which is an indication for a unimolecular process, the photochemical rearrangement $1 \rightarrow 2$ is known to proceed by both direct and triplet sensitized (sensitized by product **2**) processes [4,6]. Therefore, to clarify the contribution of each process, the rate constants (normalized with ε) of direct (k_d) and sensitized (k_s) processes were obtained similar to the reported procedures [6]. The results are summarized in Table 1 [7].

The apparent reaction rates for the direct and sensitized processes are shown by $k_d\varepsilon_1$ and $k_s\varepsilon_2$, respectively. For both processes, the apparent reaction rates increased with the increase of the size of the *ortho*-substituent on the phenyl group. The value k_s increased with the increase of the size of the *ortho*-substituent of the phenyl group. However, the value k_d showed irregular order relative to the size of the substituent, **a < c < b < d**, but as the value of ε_1 also showed irregular order, **b < d < c < a**, the apparent reaction rate $k_d\varepsilon_1$ resulted in the order **a < b < c < d**.

Fig. 3 shows nanosecond transient absorption spectra of **2a–d**. The transient absorption spectrum of slow reacting **1a** show absorption bands at <420, 680, 1050 nm, and a broad absorption at >1300 nm, which was assigned to a charge-separated triplet state(s), whereas the absorption spectrum of fast reacting **1b** shows absorptions corresponding to the normal triplet state at 720 nm in addition to the charge-separated triplet state [6,7]. The transient absorption spectra of **2a,b** also showed the similar trend as seen in Fig. 3; the absorption of **2a** is attributed to the charge-separated triplet species and that of **2b** to the mixture of both normal and charge-separated triplet states [6]. However, contribution of charge-separated triplet state of **2b** was smaller than that of **1b** [7]. Fig. 3 shows that the transient absorption spectra of **2c,d** is similar to that of **2b** and the contribution of charge-separated triplet state seems to decrease with the increase of the size of the *ortho*-substituent on the phenyl group.

These results indicate that steric factor has a large influence on the electronic states of **1** and **2**. To understand the feature of the steric effect in more details, semi-empirical calculations were conducted for **1a–d** and **2a–d**; some of the calculated results are shown in Table 2. The results on *N*-2,6-dimethylphenyl derivatives (**e**) are also included in the table.
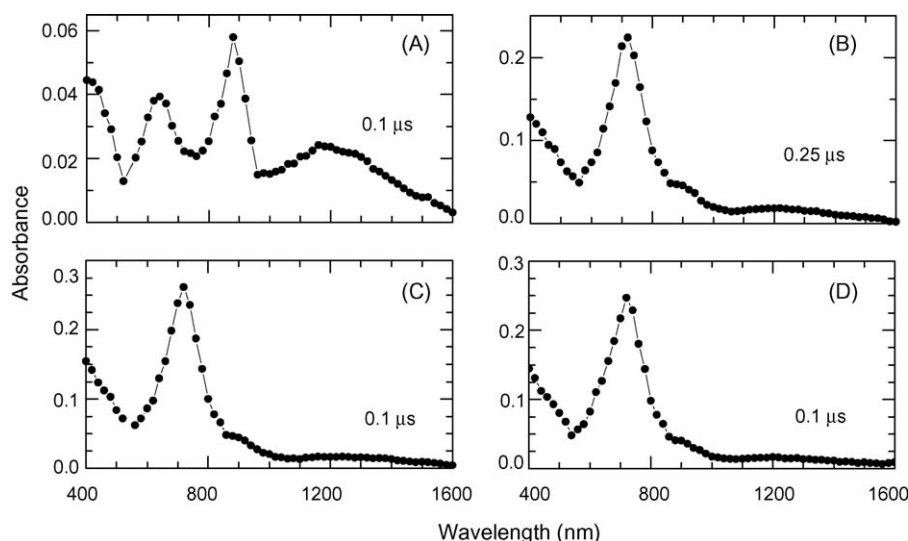

Fig. 3. Nanosecond transient absorption spectra of: (A) **2a** [6], (B) **2b** [6], (C) **2c**, and (D) **2d**. Excitation wavelength: 532 nm. Concentration: 10^{-4} M in toluene. Measured times of the spectra after the laser pulse are shown in the figures.

Table 2
Heats of formation, charges on the nitrogen atom, bond angles, and dihedral angle for the ground-state 1,6-N-(2-alkylphenyl)aza-[60]fulleroid (**1**) and 1,2-N-(2-alkylphenyl)aziridino-[60]fullerene (**2**)[a]

Substituent	ΔH_f[b] (kJ/mol)	Charge[c]	Bond angle 1[d] (°)	Bond angle 2[e] (°)	Dihedral angle[f] (°)
Azafulleroids **1**					
a	3548	0.137	98	119 (119)	30
b	3521	0.134	98	120 (119)	57
c	3505	0.131	98	121 (120)	60
d	3487	0.128	98	121 (120)	63
e	3505	0.138	97	121 (121)	33
Aziridinofullerenes **2**					
a	3558	0.121	63	125 (124)	41
b	3526	0.124	63	120 (124)	68
c	3509	0.123	63	121 (125)	69
d	3490	0.122	63	121 (125)	71
e	3526	0.124	63	126 (126)	54

[a] Calculated by MOPAC2000 using PM3 Hamiltonian.
[b] Heat of formation.
[c] Charge on the nitrogen atom.
[d] Bond angle $\angle C_2$–N_1–C_3.
[e] Bond angle $\angle C_3$–N_1–C_4 and the bond angles in brackets are those of $\angle C_2$–N_1–C_4.
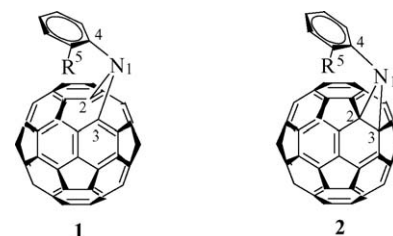[f] Dihedral angle $\angle C_3$–N_1–C_4–C_5.

Table 2 shows that photochemical rearrangement **1** → **2** is an endothermic reaction and the difference of ΔH_f decreased with the increase of the size of the *ortho*-substituent of the phenyl group; $\Delta\Delta H_f$ of the reaction **1** → **2** was **e** (21 kJ/mol) > **a** (10 kJ/mol) > **b** (5 kJ/mol) > **c** (4 kJ/mol) > **d** (3 kJ/mol). The endothermic nature of the reaction is probably due to the formation of aziridine ring that introduces some strain in the molecule. The charges on the nitrogen atoms did not show considerable difference among **1a**–**e** and also among **2a**–**e**. The bond angles 1 ($\angle C_2$–N_1–C_3) were almost the same among **1a**–**e** (97–98°) and among **2a**–**e** (63°). The bond angles 2 ($\angle C_3$–N_1–C_4 and $\angle C_2$–N_1–C_4) of **1a**–**d** have almost the same angle (119–121°) but the bond angles 2 of **2a**,**e** were slightly larger than those of angle 1 and a small distortion of the molecules is observed for monosubstituted phenyl groups, **2b**–**d**.

In contrast to the cases of bond angles, a significant difference was seen for the dihedral angles ($\angle C_3$–N_1–C_4–C_5) of both **1** and **2**. From Table 2, we can see that the conformation of **1a**,**e** and **2a**,**e** has very close to C_{2v} symmetry, in which the plane of symmetry and phenyl plane are almost perpendicular to each other. However, for the monosubstituted phenyl groups, phenyl plane rotates along the N_1–C_4 bond with the increase of the size of the *ortho*-substituent. Comparison of the degree of the rotation, which seems to reflect the degree of the steric interaction, showed that the steric interaction of **2** is larger than that of **1**.

From the ground state conformation of the molecules and the rate of the rearrangement, it was found that (i) compounds having C_{2v} symmetry (**a** and **e**) gave both slow (**a**) and fast (**e**) rearrangements and (ii) the rearrangement rate increased with the increase of the phenyl group rotation along N_1–C_4 bond. These results indicate that the rate of the rearrangement, i.e.,

the nature of the excited states, is probably controlled by the conformation of the molecules at their excited states rather than that of their ground states because the ground state conformation of the molecules seems to have no connection with the rate of the rearrangement. The rate of the rearrangement is expected to increase with the increase of steric hindrance between the N-phenyl group and C_{60} moiety that prevent rotation of the phenyl group along N_1–C_4 axis in their excited states and makes the molecule to have normal triplet states that facilitate photochemical rearrangement.

The charge-separated triplet states that give slow rearrangement should be generated by the rotation of the phenyl group in the excited state (cf. Scheme 4). This is supported by the fact that fluorescence spectra of the molecules that give charge-separated triplet state show considerable change in their fluorescence spectra compared with parent C_{60} and the molecules that show normal triplet in their excited state [4b]. This change of the fluorescence spectra can be explained by the difference

fast reaction
2(T, *conventional-type*)

slow reaction
2(T, *ion-pair*)
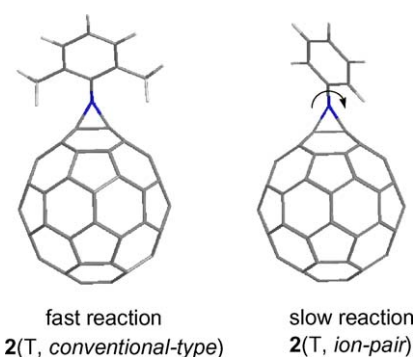
Scheme 4. Expected excited state conformations of **2**.

in the molecular conformation between ground and excited states.

3. Experimental

3.1. Synthesis of 1,6-N-(2-alkylphenyl)aza-[60]fulleroid (*1a-d*) and 1,2-N-(2-alkylphenyl)aziridino-[60]fullerene(*2a–d*)

3.1.1. General aspects

NMR spectra were recorded on a JEOL JNM-LA500 (^{1}H NMR: 499.10 MHz; ^{13}C NMR: 125.40 MHz) with CS_2:acetone-d_6 (10:1) as solvent. As internal standards, acetone-d_6 was used for ^{1}H NMR (δ: 2.05 ppm) and ^{13}C NMR (δ: 29.9 ppm) analyses. UV absorption spectra were recorded on a Shimadzu UV-2400PC spectrophotometer and infrared spectra were measured on a Shimadzu IRPrestige-21 spectrophotometer. LCMS spectra were measured on a Shimadzu LCMS-2010A spectrophotometer using APCI ionization method. Elemental analyses were carried out at the analytical center of the National Institute of Advanced Industrial Science and Technology. Fullerene C_{60} (99.5%) was purchased from Southern Chemical Group, LLC, toluene from Wako Chemicals, sodium azide and sodium nitrite from Nakarai Chemicals Ltd., 2-ethylaniline, 2-isopropylaniline, and 2-chloronaphthalene from Tokyo Kasei Kogyo Co. Ltd., spectral grade toluene from Kanto Chemical Co., Inc. Solvents and commercially available chemicals were purified and dried by standard procedures or used as bought.

3.2. Synthesis of 2-alkylphenyl azides

3.2.1. General procedure

2-Alkylphenyl azides were synthesized from corresponding arylamines according to the reported procedure [8] and purified by silica gel column chromatography (hexane).

3.2.2. 2-Ethylphenylazide

Yield, 90%; pale yellow oil. ^{1}H NMR(δ): 1.17 (t, 3H, $J = 7.6$ Hz), 2.58 (q, 4H, $J = 7.6$ Hz), 7.05 (dd, 1H, $J = 7.6$, 7.6 Hz), 7.09 (d, 1H, $J = 7.6$ Hz), 7.15 (d, 1H, $J = 7.6$ Hz), 7.20 (dd, 1H, $J = 7.6$, 7.6 Hz) ppm; ^{13}CNMR(δ): 14.60, 24.39, 118.03, 124.82, 127.13, 129.65, 135.68, 137.84 ppm; IR(neat): 3400, 3267, 3223, 3071, 3024, 2968, 2934, 2874, 2565, 2432, 2390, 2253, 2124, 2099, 1937, 1902, 1786, 1582, 1489, 1450, 1371, 1287, 1202, 1150, 1105, 1055, 1031, 966, 934, 855, 822, 748, 652, 575, 532, 465 cm^{-1}.

3.2.3. 2-Iso-propylphenylazide

Yield, 60%; pale yellow oil. ^{1}H NMR (δ): 1.19 (d, 6H, $J = 7.0$ Hz), 3.20 (septet, 1H, $J = 7.0$ Hz), 7.08 (dd, 1H, $J = 7.3$, 7.9 Hz), 7.10 (d, 1H, $J = 7.9$ Hz), 7.19 (dd, 1H, $J = 7.3$, 7.9 Hz), 7.23 (d, 1H, $J = 7.9$ Hz) ppm; ^{13}C NMR (δ): 22.85, 27.91, 118.02, 124.94, 126.58, 126.92, 137.17, 139.99 ppm; IR (neat): 3387, 3262, 3071, 3026, 2963, 2870, 2565, 2430, 2363, 2126, 2095, 1944, 1904, 1597, 1582, 1489, 1447, 1383, 1362, 1348,

1294, 1159, 1140, 1109, 1078, 1036, 934, 814, 750, 656, 534, 478 cm^{-1}.

3.3. Synthesis of 1,6-N-(2-alkylphenyl)aza-[60]fulleroids (*1*)

3.3.1. General procedure

A sample of 500 mg of C_{60} was dissolved in 30 mL of 2-chloronaphthalene (CN) and 1.5 eq. of the aryl azide in CN was added dropwise to the stirred solution at room temperature under a nitrogen atmosphere. The reaction mixture was then stirred at 80 °C, after cooling to room temperature, 130 mL of acetonitrile was added, the precipitate was separated by centrifugation, and the solvent was passed through a PTFE membrane filter (pore size 0.45 μm) to collect any remaining small particles. The centrifuged and filtered precipitates were combined and then submitted to silica–gel chromatography (1:1 mixture of CS_2:*n*-hexane as eluent) to give pure *1* and recovered C_{60}.

3.3.2. 1,6-(N-2-ethylphenyl)aza-[60]fulleroid (*1c*)

Reaction time: 24 h; yield, 15% (recovered C_{60}: 20%) [9a]; black powder. ^{1}H NMR (δ): 1.38 (t, 3H, $J = 7.6$ Hz), 2.97 (q, 2H, $J = 7.6$ Hz), 7.09 (ddd, 1H, $J = 7.3$, 7.3, 1.0 Hz), 7.19 (ddd, 1H, $J = 8.1$, 7.3, 1.6 Hz), 7.29 (dd, 1H, $J = 7.3$, 1.6 Hz), 7.77 (dd, 1H, $J = 8.1$, 1.0 Hz) ppm; ^{13}CNMR(δHz): 14.65, 27.70, 117.39, 124.94, 127.02, 131.49, 134.55, 135.68, 137.15, 138.34, 138.47, 138.55, 139.30, 139.98, 140.49, 140.99, 141.89, 141.99, 142.34, 143.30, 143.34, 143.55, 143.58, 143.64, 143.67, 143.88, 143.91, 143.94, 144.15, 144.17, 144.33, 144.37, 144.46, 144.54, 144.56, 144.66, 144.80, 144.84, 145.13, 147.93 ppm; IR (KBr): 2963, 2924, 2864, 1597, 1528, 1508, 1487, 1460, 1449, 1427, 1342, 1306, 1277, 1244, 1229, 1186, 1117, 1088, 1076, 1061, 748, 712, 698, 673, 642, 629, 610, 583, 571, 559, 527, 473, 459, 419 cm^{-1}; LCMS (m/e, relative intensity): 720 (6), 721 (4), 839 (100, M$^+$), 840 (82), 841 (23), 842 (6); elemental analysis: C: 97.583%, H: 0.935%, N: 1.482% (observed); C: 97.252%, H: 1.080%, N: 1.668% (calculated).

3.3.3. 1,6-(N-2-iso-propylphenyl)aza-[60]fulleroid (*1d*)

Reaction time: 24 h; yield, 6% (recovered C_{60}: 9%) [9a]; black powder. ^{1}H NMR (δ): 1.36 (d, 6H, $J = 6.7$ Hz), 3.70 (septet, 1H, $J = 6.7$ Hz), 7.14 (ddd, 1H, $J = 7.3$, 7.3, 1.6 Hz), 7.18 (ddd, 1H, $J = 7.3$, 7.3, 1.8 Hz), 7.39 (dd, 1H, $J = 7.6$, 1.8 Hz), 7.81 (dd, 1H, $J = 7.9$, 1.6 Hz) ppm; ^{13}C NMR (δ): 24.25, 29.9, 117.91, 125.41, 126.83, 128.61, 132.98, 135.77, 137.24, 138.33, 138.54, 138.71, 139.34, 139.77, 140.00, 140.56, 141.02, 141.02, 142.01, 142.06, 142.40, 143.36, 143.37, 143.56, 143.63, 143.70, 143.84, 143.93, 143.97, 143.99, 144.18, 144.19, 144.41, 144.51, 144.58, 144.59, 144.70, 144.86, 144.87, 145.18, 147.96 ppm; IR (KBr): 2957, 2920, 1510, 1483, 1460, 1447, 1425, 1395, 1381, 1342, 1306, 1285, 1277, 1244, 1229, 1076, 1034, 974, 772, 746, 675, 664, 642, 629, 610, 583, 571, 559, 542, 525, 488, 478, 459 cm^{-1}; LCMS (m/e, relative intensity): 720 (26), 721 (10), 722 (5), 853 (100, M$^+$), 854 (44), 855 (9); elemental analysis: C: 97.380%, H: 1.215%, N: 1.405% (observed); C: 97.061%, H: 1.299%, N: 1.640% (calculated).

3.4. Synthesis of 1,2-N-(2-alkylphenyl)aziridino-[60]fullerenes (2)

3.4.1. General procedure

A sample of **1** was dissolved in toluene and nitrogen gas was passed through the stirred solution for an appropriate time. The stirred solution in a Pyrex vessel was then irradiated with a 500-W xenon lamp (USHIO Optical ModuleX SX-UI500XQ), supplied with an 18-cm water filter and a Toshiba UV-29 filter under a nitrogen-gas atmosphere. The reaction mixture was then submitted to silica–gel chromatography (1:1 mixture of CS_2:n-hexane as eluent) to give pure **2**.

3.4.2. 1,2-(N-2-ethylphenylaziridino)-[60]fullerene (2c)

Substrate: 120 mg of 1,6-(*N*-2-ethylphenyl)aza-[60]fulleroid (**1c**); toluene: 150 mL; irradiation time: 20 min. Yield, 90%; [9b] black powder. ^{1}H NMR (δ): 1.59 (t, 3H, $J = 7.3$ Hz), 3.39 (q, 2H, $J = 7.3$ Hz), 7.18 (ddd, 1H, $J = 7.3, 7.3, 1.1$ Hz), 7.28 (ddd, 1H, $J = 7.6, 7.3, 1.3$ Hz), 7.38 (dd, 1H, $J = 7.3, 1.3$ Hz), 7.52 (dd, 1H, 7.6, 1.1 Hz) ppm; ^{13}C NMR (δ): 14.28, 26.28, 83.46, 122.26, 125.23, 126.88, 130.01, 136.11, 141.10, 141.38, 142.59, 142.72, 142.95, 143.28, 143.52 (x2), 144.34, 144.54, 145.01, 145.05, 145.22, 145.33, 145.60, 145.71, 145.78 ppm; IR (KBr): 2963, 2926, 2866, 1599, 1510, 1485, 1458, 1450, 1427, 1387, 1315, 1304, 1296, 1263, 1252, 1223, 1182, 1171, 1119, 1055, 1034, 966, 932, 862, 835, 799, 783, 752, 741, 712, 704, 677, 667, 583, 573, 565, 550, 540, 527, 484, 453, 420 cm^{-1}; LCMS (m/e, relative intensity): 720 (19), 721 (15), 722 (8), 839 (100, M$^+$), 840 (82), 841 (38), 842 (8); elemental analysis: C: 97.688%, H: 0.910%, N: 1.402% (observed); C: 97.252%, H: 1.080%, N: 1.668% (calculated).

3.4.3. 1,2-(N-2-iso-propylaziridino)-[60]fullerene (2d)

Substrate: 60 mg of 1,6-(*N*-2-*iso*-propylphenyl)aza-[60]fulleroid (**1d**); toluene: 150 mL; irradiation time: 20 min. Yield, 85%; [9b] black powder. 1H NMR (δ): 1 53 (d, 6H, $J = 7.0$ Hz), 4.14 (septet, 1H, $J = 7.0$ Hz), 7.20 (ddd, 1H, $J = 7.6$, 7.6, 1.5 Hz), 7.26 (ddd, 1H, $J = 7.6, 7.6, 1.5$ Hz), 7.45 (dd, 1H, $J = 7.6, 1.5$ Hz), 7.53 (dd, 1H, $J = 7.6, 1.5$ Hz) ppm; ^{13}C NMR (δ): 24.26, 29.23, 83.75, 122.64, 125.57, 126.70, 127.52, 141.06, 141.22, 141.47, 142.21, 142.69, 142.82, 143.38, 143.61, 143.63, 144.44, 144.65, 145.11, 145.16, 145.33, 145.42, 145.70, 145.82, 145.90 ppm; IR (KBr): 3026, 2959, 2922, 2864, 1597, 1516, 1510, 1499, 1483, 1466, 1458, 1449, 1429, 1387, 1381, 1362, 1314, 1298, 1279, 1263, 1252, 1225, 1182, 1171, 1084, 1034, 889, 860, 833, 799, 750, 714, 704, 667, 648, 582, 573, 565, 540, 527, 484, 457, 419 cm^{-1}; LCMS (m/e, relative intensity): 720 (9), 721 (6), 853 (100, M$^+$), 854 (76), 855 (32); elemental analysis: C: 97.445%, H: 1.203%, N: 1.352% (observed); C: 97.061%, H: 1.299%, N: 1.640% (calculated).

3.5. Photolysis of 1

The toluene (spectral grade) solutions of **1** (1×10^{-5} M) were prepared and degassed by seven freeze–pump–thaw cycles. The photolysis of ca 3 mL **1** was conducted in a synthetic quartz cuvett (optical path: 10 mm, width: 10 mm) under a nitrogen-gas atmosphere while stirring. A 500-W xenon lamp (USHIO Optical ModuleX SX-UI500XQ), fitted with an 18-cm water filter, an IR cutoff filter (Edmund Industrial Optics, TECH SPEC^{TM}), and a Toshiba Y-45 filter, was used for the photolysis. The energy of the light at the position of the cuvett was set to 8.7 mW cm^{-2}. The light intensity of the xenon lamp was measured by an Ushio USR-40D Spectroradiometer. The consumption of **1** and the formation of **2** were determined by HPLC analysis [JASCO PU-980 Intelligent HPLC Pump and a JASCO UV-970 Intelligent UV–vis Detector (detection wavelength: 300 nm) fitted with a Merck Superspher 100 RP-18e column (4 mm i.d. $\times$ 250 mm)], relative to authentic samples.

3.6. Flash photolysis of 1 and 2

Transient absorption spectra in the visible/near-IR regions were observed by the laser-flash photolysis spectroscopy. The C_{60} derivatives were excited with 530–532 nm light from the OPO system, attached to a Nd: YAG laser (6 ns fwhm). A Si-PIN photodiode module (400–600 nm) and a Ge-APD module (600–1600 nm) were employed as detectors for monitoring the light from a pulsed Xe-lamp [10].

4. Conclusion

The reaction rate of the photochemical rearrangement $1 \rightarrow 2$ differed ca. 3.1-fold as the *ortho*-substituent of the *N*-phenyl group changed from 2-methylphenyl (**b**), 2-ethylphenyl (**c**), to 2-*iso*-propylphenyl (**d**). The retardation of the rearrangement is due to the contribution of charge-separated triplet state in the excited states in addition to the normal triplet state, which was confirmed by transient absorption measurements. A semi-empirical calculations on the ground state conformation of **1** and **2** showed that **1** with phenyl (**a**) and 2,6-dimethylphenyl (**e**) *N*-substituents and **2a,e** have C_{2v} symmetry but the rotation of the phenyl group along the N–Ph bond occurs with the increase of steric hindrance between the phenyl group and C_{60} moiety (**1b–d** and **2b–d**). These results indicate that the rate of the rearrangement, i.e., the nature of the excited states, is probably controlled by the conformation of the molecules at their excited states rather than that of their ground states. The generation of charge-separated triplet state in the excited state can be explained by the occurrence of phenyl group rotation along the N–Ph bond.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2006.06.011.

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[9] (a) The yields of **1** and recovered C_{60} are based on the amount of initially used C_{60}.;
(b) The yields of **2** are based on the amount of initially used **1**. The low synthetic yields of **2** are most likely due to the lack on the optimization of the synthetic conditions.

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