Fullerene Chemistry

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[2+1] Cycloaddition of Nitrene onto C_{60} Revisited: Interconversion between an Aziridinofullerene and an Azafulleroid**

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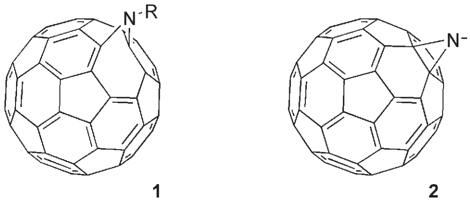
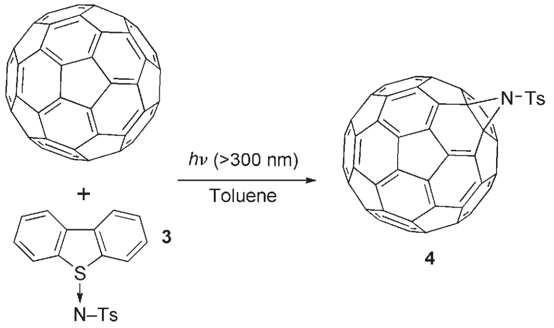
It is known that organic azides react with a [6,6] bond of C_{60} through a 1,3-dipolar [3+2] cycloaddition to afford triazolines.[1] Thermolysis of a triazoline, followed by concomitant loss of nitrogen, gives rise to a [1,6]azafulleroid **1** and a [1,2]aziridinofullerene **2** (Scheme 1).[2] Both **1** and **2** can also be obtained directly from the reaction of C_{60} and azides at higher temperatures, but the ratio of **1**:**2** depends on the nature of the substituent.[3] Furthermore, azides have major associated problems in regards to toxicity and explosibility.[4] Thus, new useful methods for the preparation of azafulleroids and aziridinofullerenes are expected.



Scheme 1. Structures of **1** and **2**.

Sulfilimines[5] are known to generate an *N*-substituted nitrene in thermal and photochemical reactions. Recently, it has been reported that *N*-sulfenylsulfilimine generates a sulfenylnitrene under mild conditions. Nitrenes readily react with alkenes to afford the corresponding three-membered aziridines.[6] In this context, a nitrene is expected to be a key intermediate, instead of an azide, in the aziridination of fullerene.

In the course of our study on the development of synthetic methodology for the preparation of [1,2]aziridinofullerene,[2] we carried out the photoreaction of C_{60} with an *N*-*p*-toluenesulfonylsulfilimine[7] having a dibenzothiophene structure (**3**; Scheme 2) to accomplish the regioselective synthesis of *N*-tosyl[1,2]aziridinofullerene ([6,6]-closed C_{60}NTs, **4**). It is well known that 1,6-azafulleroids **1** readily cyclize thermally and photochemically to afford [1,2]aziridinofullerenes **2**, while the reverse reaction hardly occurs.[8] This finding may indicate that **2** is more thermally stable than **1**. We examined the stability of the newly synthesized **4** and found that it thermally rearranges to a [1,6]azafulleroid ([5,6]-open C_{60}NTs, **5**) and that the photochemical reversible reaction also takes place.[9] Here we report for the first time the reversible interconversion between **1** and **2**. The structures of both adducts were successfully determined by single-crystal X-ray analyses.



Scheme 2. Photoreaction of C_{60} with *N*-tosylsulfilimine **3**. Ts = tosyl = *p*-toluenesulfonyl.

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

The photoreaction of C_{60} with one equivalent of sulfilimine **3** afforded the corresponding monoadduct (C_{60}NTs, **4**) as a major product with 80 % conversion. The absorption band at 430 nm in the UV/Vis spectrum of **4** is indicative of the formation of a 1,2-addition product of C_{60} (Figure 1).[10]

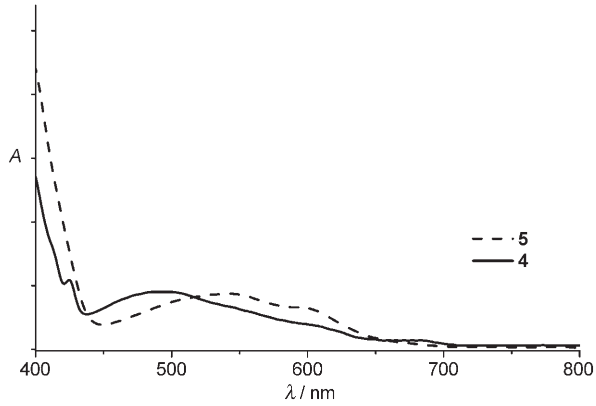
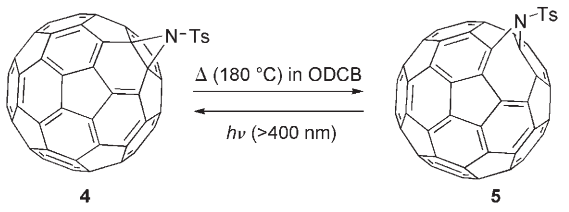


Figure 1. UV/Vis spectra of aziridinofullerene **4** and azafulleroid **5**.

To examine the thermal stability of the monoadduct, a solution of **4** in *o*-dichlorobenzene (ODCB) was heated at 180 °C for 10 hours (Scheme 3). HPLC analysis of the reaction mixture showed that the peak intensity of **4** decreased while that of a new peak increased in size. The MALDI-TOF mass spectrum of the product exhibited a molecular ion signal at *m/z* 889. A band at 430 nm, which is characteristic of a 1,2-addition product,[10] did not appear in its UV/Vis spectrum. These data reveal that **5** may be a regioisomer of **4** which has an open structure.[3] It was found that the isomerization of **4** occurs in good yield upon heating. A reverse isomerization of **5** to **4** was also observed photochemically (see the Supporting Information).



Scheme 3. Interconversion between **4** and **5**.

Although a [5,6]-open azafulleroid **1** has been shown to isomerize readily to a [6,6]-closed type aziridinofullerene **2**,[11] the single-crystal X-ray analysis of **1** had not been reported. We have succeeded in the structural determination of both [6,6]-closed aziridinofullerene **4** and [5,6]-open azafulleroid **5** by single-crystal X-ray analysis (Figure 2).[12,13] The dihedral angles of the *N*-tosyl ligand on C_{60} (ϕ(N-S-$C_{ipso}=C_{ortho}$)) in **4** and **5** are 95.6° and 104.0°, respectively, for the aryl sulfonamide conformations.[14]

To clarify the reversible rearrangement, the relative stabilities and HOMO/LUMO energies of **4** and **5** were calculated at the B3LYP/6-31G(d,p) level.[15] Azafulleroid **5** has two geometric isomers (**5a** and **5b**) with different conformations of the *N*-tosyl group (see the Supporting Information for the optimized structures of **5a** and **5b**). Both **5a** and **5b** are slightly more stable than **4** (Table 1). These results are consistent with the fact that **4** thermally rearranges to **5**. This situation is different from the known thermal isomerizaiton of **1** to **2**. This unusual phenomenon may originate from the introduction of a tosylated amine bridge.

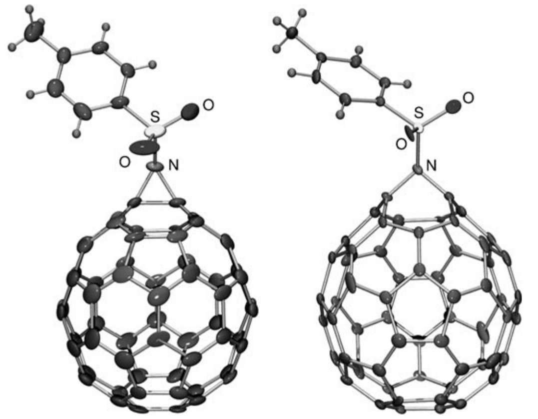


Figure 2. X-ray crystal structures of **4** (left) and **5** (right) with thermal ellipsoids at the 50 % probability level; only one orientation is shown and CS_2 is omitted for clarity.

Table 1: Relative energies (kcal mol^{-1}) and HOMO/LUMO energies (eV) of **4** and **5**.

Isomers	Relative energies	HOMO	LUMO	HOMO/LUMO gap
[6,6]-closed **4**	0.00	−5.82	−3.21	2.61
[5,6]-open **5a**	−0.04	−6.01	−3.32	2.69
[5,6]-open **5b**	−0.75	−5.93	−3.21	2.72

In conclusion, it has been shown that the addition of a nitrene generated by the photochemical reaction of sulfilimine **3** occurs at the [6,6] junction of C_{60} to afford the [1,2]aziridinofullerene **4**. It is found that **4** thermally rearranges to the [1,6]azafulleroid **5**, and is the first example for a monosubstituted fullerene.[16] Moreover, photochemical ring-closure of **5** also takes place to afford **4**. The structures of **4** and **5** have been characterized by NMR spectroscopy and X-ray crystallographic analyses.[17]

Experimental Section

General: Toluene was distilled over benzophenone sodium ketyl under argon prior to use in the reactions. ODCB was distilled over P_2O_5 under vacuum prior to use. CS_2 was distilled over P_2O_5 under argon prior to use. HPLC isolation was performed on a LC-908 system (Japan Analytical Industry Co., Ltd.). Toluene was used as the eluent. Mass spectrometric analysis was performed on a Bruker BIFLEX III spectrometer in the negative mode with 1,1,4,4-tetraphenylbutadiene used as the matrix. The UV/Vis spectra were measured between 400 and 800 nm in toluene solution on a

SHIMADZU UV-3150 spectrophotometer. NMR spectra were obtained on a Bruker AVANCE 500 spectrometer. The ^{1}H and ^{13}C shifts were calibrated with tetramethylsilane (TMS) as an internal reference ($\delta = 0.0$).

3: A solution of dibenzothiophene (2.0 g, 10.73 mol), chloramine-T (4.53 g, 16.10 mol), and $MgSO_4$ (1.93 g, 16.10 mol) in acetonitrile (20 mL) was stirred at 50 °C for 18 h. The reaction mixture was then cooled to room temperature and the $MgSO_4$ removed by filteration. The filtrate was extracted with $CHCl_3$ (20 mL × 3), and the organic layer then dried over $MgSO_4$ and evaporated under reduced pressure. The resulting solid was recrystallized from MeOH to give **3** (1.42 g, 38 %) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K): $\delta =$ 2.44 (s, 3 H), 7.26 (d, $J = 8.3$ Hz, 2 H), 7.44–7.47 (m, 2 H), 7.63–7.67 (m, 4 H), 7.83 (d, $J = 8.4$ Hz, 2 H), 7.87 ppm (d, $J = 8.3$ Hz, 2 H); ^{13}C NMR (75 MHz; $CDCl_3$, 293 K): $\delta = 21.7$, 122.7, 126.9, 127.8, 129.6, 130.3, 133.2, 137.5, 137.7, 141.5, 142.2 ppm; m.p. 171.5–173.0 °C; MALDI-TOF MS: m/z 353 $[M]^-$; UV/Vis: λ_{max} (ε) 320 (1313) nm.

Photoreaction of C_{60} with **3** (Scheme 2): A solution of C_{60} (15.0 mg, 2.8 × 10–3 M) and sulfilimine **3** (7.4 mg, 2.8×10^{-3} M) in toluene was placed in a pyrex tube and degassed by freeze-thaw cycles under reduced pressure before irradiating with a high-pressure mercury lamp (> 300 nm) at 20 °C for 30 min. The reaction mixture was analyzed by HPLC as follows: column, Buckyprep ϕ4.6 × 250 mm; eluent, toluene; flow rate, 1.0 mL min^{-1}; temperature, 40 °C; detector, UV 320 nm. **4**: ^{1}H NMR (300 MHz, [D$_6$]acetone in a capillary/CS_2, 293 K): $\delta = 1.95$ (s, 3 H), 6.81 (d, $J = 8.3$, 2 H), 7.44 ppm (d, $J = 8.3$, 2 H); ^{13}C NMR (125 MHz; [D$_6$]acetone in a capillary/CS_2, 293 K): $\delta = 22.47$, 80.10, 128.98, 130.35, 136.43, 141.18, 141.61, 142.14, 142.47, 143.05, 143.36, 143.42, 143.69, 144.18, 144.28, 144.46, 144.76, 145.21, 145.29, 145.37, 145.39, 145.54 ppm; MALDI-TOF MS: m/z 889 $[M^-]$, 734 $[M-(\text{tosyl})]^-$, 720 $[M-(N\text{-tosyl})]^-$.

Interconversion between **4** and **5**: Thermal rearrangement: A solution of **4** (4.2×10^{-4} M) in [D$_4$]ODCB was degassed by freeze-thaw cycles under reduced pressure and then heated at 180 °C in the dark for 10 h. Photochemical rearrangement: The solution was heated for 5 h and then photoirradiated with a halogen lamp fitted with a filter (cut-off < 400 nm) at 20 °C for 15 min. These reactions were monitored by ^{1}H NMR spectroscopy (500 MHz, [D$_4$]ODCB, 293 K) and HPLC as follows: column, Buckyprep Mϕ4.6 × 250 mm; eluent, toluene; flow rate, 1.0 mL min^{-1}; temperature, 25 °C; detector, UV 400 nm. **5**: ^{1}H NMR (300 MHz, [D$_6$]acetone in a capillary/CS_2, 293 K): $\delta = 1.82$ (s, 3 H), 6.65 (d, $J = 8.3$, 2 H), 7.24 ppm (d, $J = 8.3$, 2 H); ^{13}C NMR (125 MHz; [D$_6$]acetone in a capillary/CS_2, 293 K): $\delta =$ 22.35, 129.27, 130.08, 134.54, 135.12, 136.06, 136.52, 138.15, 138.23, 138.62, 138.87, 139.97, 140.31, 141.98, 143.01, 143.04, 143.29, 143.51, 143.72, 143.92, 143.97, 144.08, 144.23, 144.27, 144.36, 144.44, 144.53, 144.65, 144.98, 147.69, 148.54 ppm; MALDI-TOF MS: m/z 889 $[M]^-$.

Recrystallization of **4** and **5**: Black crystals of **4** and **5** were obtained by slow evaporation of CS_2 at 0 °C.

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[12] The X-ray diffraction data collection of [5,6]-open azafulleroid **5** was performed on beamline BL-1B at the Photon Factory, KEK, Japan.

[13] a) Crystal data for **4**·CS_2: $C_{136.53}H_{14}N_2O_4S_{7.06}$, $M_r = 1972.33$, black needles, 0.50 × 0.14 × 0.06 mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 18.572(2)$, $b = 21.376(2)$, $c = 10.0431(13)$ Å, $\alpha = 92.632(3)$, $\beta = 105.614(3)$, $\gamma = 94.808(2)°$, $V = 3816.7(8)$ Å^3, $Z = 2$; $\rho_{calcd} =$ 1.716 g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.88$ cm^{-1}, $\theta_{max} = 20.82°$, $T = 120$ K, 12 109 measured reflections, 5858 independent reflections, 1367 refined parameters, GOF = 1.128, $R_1 = 0.0906$ and $wR_2 = 0.2020$ for all data; $R_1 = 0.0905$ for 5850 independent reflections ($I > 2.0\sigma(I)$), min./max. electron density 0.89/−0.63 e Å^{-3}; b) crystal data for **5**·CS_2: $C_{68}H_7NO_2S_3$, $M_r = 965.99$, black plates, 0.20 × 0.15 × 0.10 mm, orthorhombic, space group *Pnma* (no. 62), $a =$ 18.2815(6), $b = 13.6431(5)$, $c = 14.5987(5)$ Å, $V = 3641.2(2)$ Å^3, $Z = 4$; $\rho_{calcd} = 1.762$ g cm^{-3}, wavelength = 0.68880 Å, $\mu =$ 2.71 cm^{-1}, $\theta_{max} = 35.71°$, $T = 123$ K, 30 606 measured reflections, 6656 independent reflections, 641 refined parameters, GOF = 1.186, $R_1 = 0.0954$ and $wR_2 = 0.1700$ for all data; $R_1 = 0.0791$ for 5738 independent reflections ($I > 2.0\sigma(I)$), min./max. electron density 1.05/−0.86 e Å^{-3}; c) CCDC 665365 (**4**) and 665366 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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[17] When this study was presented at the annual meeting of the Japan Chemical Society, in April, 2007, H. Hachiya and Y. Kabe informed us that they were also able for the first time to characterize a [5,6]-monoazafulleroid by X-ray crystallographic analysis.