Ionic Introduction of an N₁ Unit to C₆₀ and Unique Rearrangement of Aziridinofullerene

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Experimental Procedures

General Methods.

IR spectra were obtained on a Jasco FT/IR-410 infrared spectrophotometer. UV/Vis spectra were performed on a Shimadzu UV-265 spectrophotometer. ¹H and ¹³C-NMR spectra were recorded on a JEOL FT-NMR JNM EX 270 spectrometer (¹H-NMR, 270 MHz; ¹³C-NMR, 68 MHz) using tetramethylsilane as an internal standard. FAB-Mass spectra were measured with a JEOL TMS-700 spectrometer. Column chromatography was performed using silica gel 60 (0.063-0.200 mm, Merck). Analytical thin layer chromatography was performed using EM reagent 0.25 mm silica gel 60-F plates. Visualization was accomplished with UV light.
General procedure for preparation of ion-exchanged chloramines.

A suspension of chloramine (chloramines-T or chloramines-B) (1.1 mmol) and Aliquat® 336 (1 mmol) was stirred in CH₂Cl₂ (10 mL) for 5 min, quenched with water (10 mL), extracted with CH₂Cl₂ (10 mL x 3), dried over Na₂SO₄, and concentrated under reduced pressure. Ion-exchanged chloramine (1a or 1b) was obtained as yellow oil in good yield (85-90%).

N-(4-Methylbenzenesulfonyl)aziridinofullerene (2a)

A solution of C₆₀ (72 mg, 0.1 mmol) and chloramine 1a (76 mg, 0.1 mmol) was heated in toluene (50 mL) for 10 min under reflux and vigorous stirring. The solution was passed through a short column of silica gel and the solvent then was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: toluene/hexane = 6/4) to give 59 mg (81%) of unconverted C₆₀ (1st fraction) and 15 mg (17%) of the corresponding aziridinofullerene 2a (2nd fraction).

black crystalline solid; FT-IR (KBr) cm⁻¹ 3425, 2919 1641, 1352, 1169, 1090, 818, 527; ¹H NMR (270 MHz, CDCl₃): δ 2.55 (s, 3H, Ar-CH₃), 7.53 (d, 2H, J = 8.1 Hz, Ar-H), 8.25 (d, 2H, J = 8.1 Hz, Ar-H); ¹³C NMR (68 MHz, CDCl₃) δ 21.99, 79.88, 128.46, 130.19, 135.36, 140.85, 141.37, 141.81, 142.10, 142.73, 143.05, 143.09, 143.16, 143.84, 144.13, 144.48, 145.01, 145.11, 145.27, 145.76; UV-Vis (CH₂Cl₂) λ_max nm 321, 254, 229; FAB-MS m/z 889 ([M]+1), 720 (C₆₀); HR-MS: calcd for (C₆₇H₇NO₂S): 889.0198, found: 889.0203 R_f = 0.37 (TLC, SiO₂, hexane : toluene = 1 : 1)
**N-(4-Methylbenzenesulfonyl)azafulleroid**\(^1\) (3a)

A solution of C\(_{60}\) (72 mg, 0.1 mmol) and chloramine 1a (76 mg, 0.1 mmol) was heated in toluene (50 mL) for 10 min under reflux and vigorous stirring in the presence of 400 mg of MS4A. The solution was passed through a short column of silica gel and the solvent was then evaporated under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: toluene/hexane = 6/4) to give 50 mg (70%) of unconverted C\(_{60}\) (1st fraction), 9 mg (10%) of 2a (2nd fraction), and 15 mg (17%) of corresponding azafulleroid 3a. Spectroscopic data were in agreement with those for previously reported material.\(^1\)

![N-(Benzenesulfonyl)aziridinofullerene (2b)](image)

black crystalline solid; \(^1\)H NMR (270 MHz, CDCl\(_3\)): \(\delta\) 2.47 (s, 3H, Ar-CH\(_3\)), 7.37 (d, 2H, \(J = 8.2\) Hz, ArH), 8.06 (d, 2H, \(J = 8.2\) Hz, ArH); FAB-MS \(m/z\) 889 ([M\(^+\)+1], 720 (C\(_{60}\)); HR-MS: calcd for (C\(_{67}\)H\(_7\)NO\(_2\)S): 889.0198, found: 889.0206. \(R_f = 0.30\) (TLC, SiO\(_2\), hexane : toluene = 1 : 1)

**N-(Benzenesulfonyl)aziridinofullerene (2b) and N-(p-Benzenesulfonyl)azafulleroid (3b)** were synthesized using the procedure described above.

**N-(Benzenesulfonyl)aziridinofullerene (2b)

black crystalline solid; FT-IR (KBr) cm\(^{-1}\) 3413, 2920, 2852, 1350, 1084, 812, 528; \(^1\)H NMR (270 MHz, CDCl\(_3\)) \(\delta\) 7.77 (m, ArH) 8.31 (d, 2H, \(J = 7.0\) Hz, ArH); \(^{13}\)CNMR (68 MHz, CDCl\(_3\)) \(\delta\) 79.70, 128.24, 129.45, 134.37, 138.31, 140.77, 141.22, 141.70, 142.00, 142.63, 142.86, 142.95, 143.73, 143.99, 144.36, 144.89, 144.94, 145.00, 145.17 UV-Vis (CH\(_2\)Cl\(_2\)) \(\lambda_{\text{max}}\) nm 325, 255, 227; FAB-MS \(m/z\) 875 ([M\(^+\)+1], 720 (C\(_{60}\)); HR-MS: calcd for (C\(_{66}\)H\(_5\)NO\(_2\)S): 875.0041, found: 875.0047. \(R_f = 0.37\) (TLC, SiO\(_2\), hexane : toluene = 1 : 1)
N-(p-Benzenesulfonyl)azafulloidal (3b)

black crystalline solid; FT-IR (KBr) cm$^{-1}$ 3423, 2923 1652, 1367, 1170, 1088; $^1$H NMR (270 MHz, CDCl$_3$): δ 7.59 (dd, 2H, $J=7.0$ Hz, 7.6 Hz, Ph-CH$_2$), 7.67 (d, 1H, $J=7.6$ Hz, ArH), 8.19 (d, 2H, $J=7.0$ Hz, ArH); $^{13}$C NMR (68 MHz, CDCl$_3$) δ 78.02, 128.24, 128.85, 129.12, 133.08, 133.94, 134.67, 135.02, 137.78, 137.83, 138.17, 138.41, 138.98, 139.58, 139.92, 141.42, 141.51, 142.42, 142.49, 142.78, 142.84, 143.05, 143.28, 143.47, 143.51, 143.65, 143.80, 143.84, 143.97, 144.02, 144.19, 144.58, 147.09, 148.49; UV-Vis (CH$_2$Cl$_2$) $\lambda_{max}$ nm 326, 259, 229; FAB-MS $m/z$ 875 ([M]$^+$+1), 720 (C$_{60}$); HR-FAB-MS: calcd for (C$_{67}$H$_7$NO$_2$S): 875.0041, found: 875.0027. $R_f$= 0.29 (TLC, SiO$_2$, hexane : toluene = 1 : 1)

Reference