Title: First Isolation and Characterization of Eight Regioisomers for [60]Fullerene–Benzyne Bisadducts

Author: Yosuke Nakamura, Nobutoshi Takano, Tatsuya Nishimura, Eiji Yashima, and Jun Nishimura*

Supporting Information

Experimental Section

General

NMR spectra were recorded on a JEOL α-500 FT NMR spectrometer with tetramethylsilane as an internal standard in $CDCl_3$ at room temperature unless otherwise noted. Preparative HPLC for the separation of bisadduct regioisomers was performed with a Shimadzu LC-6AD pump, an SPD-6A UV spectrophotometric detector, an FCV-100B fraction collector, a C-R4A chromatopac, and a Develosil RPFULLERENE column (20 x 250 mm) purchased from Nomura Chemical Co., Ltd. GPC was performed with a JAI LC-918 using a JAIGEL-1H and 2H columns. FAB Mass spectra were taken by a JEOL JMS-HX110A mass spectrometer. Absorption spectra were recorded on a Hitachi U3210 spectrophotometer. CD spectra were taken by a JASCO J-720W spectropolarimeter. Precursor **4** is commercially available (Tokyo Chemical Industry Co., Ltd.).

Preparation of [60]fullerene bisadducts 5

A mixture of [60]fullerene (288 mg, 0.4 mmol), benzyne precursor **4** (316 mg, 1.6 mmol), and isoamyl nitrite (187 mg, 1.6 mmol) was refluxed in toluene (300 mL) for 30 min. After the reaction mixture was cooled to room temperature, the solvent was evaporated under reduced pressure. The residue was chromatographed on silica gel (eluent; toluene→toluene/ethyl acetate (9:1(v/v)), to give unchanged [60]fullerene (49 mg, 17%), monoadduct (68 mg, 20%), and regioisomeric mixture of bisadducts **5a–g** (71 mg, 18%) as brown-colored powder. These bisadducts were separated and isolated by HPLC using a Develosil RPFULLERENE column (20 x 250 mm) with an eluent of toluene/acetonitrile (1:3 (v/v)). The spectroscopic data of **5a–g** are as follows.

5a (*trans*-1). ^{1}H NMR (500 MHz) δ 7.69 (4H, s), 4.19 (12H, s); ^{13}C NMR (125 MHz, $CDCl_3/CS_2$) δ 152.49, 152.07, 146.10, 145.29, 143.96, 143.79, 142.92, 141.18, 141.05, 139.03, 106.98, 56.27; FAB MS *m/z* 992 (M^+).
5b (*trans*-2). ^{1}H NMR (500 MHz) δ 7.65 (2H, s), 7.56 (2H, s), 4.17 (6H, s), 4.14 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.34, 154.11, 152.09, 151.90, 151.45, 148.65, 148.28, 147.58, 147.14, 146.62, 146.21, 146.00, 145.75, 145.68, 145.09, 145.03, 144.97, 144.24, 143.71, 143.55, 142.85, 142.76, 142.47, 142.22, 141.94, 141.66, 141.23, 141.12, 139.76, 137.40, 136.92, 106.81, 106.75, 56.61, 56.58; (Acetone-d_6/CS_2) 77.15, 76.71 (Since the sp^3 carbon peaks overlap with those of $CDCl_3$, other solvents were employed for the detection of these peaks.); FAB MS *m/z* 992 (M^+).
5c (*trans*-3). ^{1}H NMR (500 MHz) δ 7.62 (2H, s), 7.37 (2H, s), 4.15 (6H, s), 4.04 (6H, s); ^{13}C NMR (125

MHz, $CDCl_3$) δ 158.11, 156.21, 156.19, 155.81, 151.73, 151.68, 149.11, 148.96, 148.56, 148.00, 147.87, 147.57, 147.06, 145.98, 145.10, 145.07, 144.98, 144.92, 144.75, 144.72, 144.07, 143.79, 143.72, 143.51, 142.58, 141.64, 141.15, 141.10, 141.04, 139.81, 139.10, 139.02, 106.73, 106.69, 56.58, 56.49; (Acetone-d_6/CS_2) 77.87, 77.47; FAB MS *m/z* 992 (M^+).

5d (*trans*-4). ^{1}H NMR (500 MHz) δ 7.48 (2H, s), 7.33 (2H, s), 4.09 (6H, s), 4.02 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.46, 153.46, 151.75, 151.70, 150.45, 149.34, 148.93, 148.75, 147.94, 147.86, 147.23, 147.03, 146.04, 146.01, 145.89, 145.80, 145.68, 145.40, 144.28, 142.85, 142.80, 142.24, 142.02, 141.55, 141.11, 140.71, 140.35, 139.91, 138.60, 138.25, 134.34, 106.50, 56.50, 56.44; (C_6D_6/CS_2) 76.98; FAB MS *m/z* 992 (M^+).

5e (*e*). ^{1}H NMR (500 MHz) δ 7.40 (1H, s), 7.33 (2H, s), 7.20 (1H, s), 4.05 (3H, s), 4.02 (6H, s), 3.96 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.21, 153.97, 153.33, 152.95, 151.63, 151.58, 151.53, 148.72, 148.56, 147.90, 147.82, 147.63, 147.42, 146.81, 146.65, 146.52, 145.72, 145.30, 144.98, 144.92, 144.59, 144.45, 143.82, 143.79, 143.51, 143.48, 143.09, 142.31, 142.04, 141.44, 141.39, 141.30, 141.10, 138.88, 137.36, 106.75, 106.44, 106.21, 56.49, 56.35; (C_6D_6/CS_2) 77.96, 77.65; FAB MS *m/z* 992 (M^+).

5f (*cis*-1). ^{1}H NMR (500 MHz) δ 7.33 (2H, s), 7.29 (2H, s), 4.05 (6H, s), 3.99 (6H, s); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 156.67, 152.49, 152.23, 151.40, 150.36, 149.76, 149.11, 148.27, 148.02, 146.93, 146.61, 146.28, 146.10, 146.03, 145.44, 145.08, 144.54, 144.44, 144.32, 144.31, 144.16, 143.24, 142.85, 142.69, 142.55, 142.31, 141.30, 140.70, 139.91, 139.10, 138.59, 137.40, 109.79, 107.44, 57.12, 56.86; FAB MS *m/z* 992 (M^+).

5g (*cis*-2). ^{1}H NMR (500 MHz) δ 7.50 (2H, s), 7.26 (2H, s), 4.16 (6H, s), 4.00 (6H, s); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$) δ 159.23, 157.00, 153.14, 152.70, 152.56, 150.15, 149.18, 149.04, 148.94, 148.83, 147.40, 147.00, 146.63, 146.54, 146.38, 146.02, 145.93, 145.81, 145.75, 144.68, 144.58, 144.44, 144.09, 143.97, 142.77, 142.04, 141.54, 141.21, 140.96, 136.88, 136.47, 134.68, 108.68, 107.41, 57.07, 57.03; FAB MS *m/z* 992 (M^+).

5h (*cis*-3). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.01 (6H, s), 3.99 (6H, s); (CD_2Cl_2) δ 7.35 (2H, s), 7.26 (2H, s), 3.96 (6H, s), 3.93 (6H, s) (CD_2Cl_2 was employed for the detection of the aromatic proton peaks, which overlap with the peaks of $CHCl_3$ in $CDCl_3$.); FAB MS *m/z* 992 (M^+).