Photooxidation and Intramolecular Reaction of the Anthryl Moiety in [60]Fullerene Derivatives

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Keywords: Fullerenes / Anthracene / Photooxidations / Photochemistry

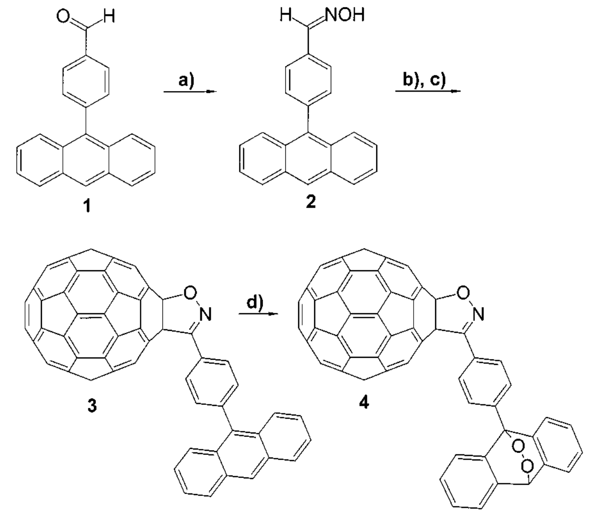
Anthracene groups have been linked to [60]fullerene by the [3+2] cycloaddition of the corresponding nitrile oxides or by esterification with a [60]fullerenol. The anthryl groups of the fullerene derivatives **3**, **7**, and **10** react readily with singlet oxygen to form the 9,10-epidioxides **4**, **8**, and **12** under photooxidation. The anthryl moiety of the fullerenol ester **10** also reacts with the fullerene skeleton to form the stable intramolecular Diels–Alder adduct **11**.

Introduction

Photophysical investigations of C_{60} and its derivatives have revealed that [60]fullerene and dihydro[60]fullerene derivatives produce singlet oxygen in high quantum yields.[1] The products synthesized by the reaction of singlet oxygen in the presence of fullerenes have previously been reported.[2] In Diels–Alder adducts of 9,10-dimethylanthracene with C_{60}, the anthracene moiety can be removed by irradiation with light in the presence of oxygen to yield the anthracene endoperoxide.[3] Oxidation of C_{60} cycloadducts with singlet oxygen results in ring opening[4] or epoxide formation,[5] although the proposed epidioxy intermediates could not be isolated. In this article we describe fullerene derivatives substituted by an anthracene group which produce well-defined epidioxy compounds by photooxidation. In the most favorable case the substituted anthracene group could be added to the fullerene moiety in an intramolecular thermal cycloaddition reaction. Cycloaddition reactions of anthracene to [60]fullerene have previously been reported in solution[6] and in the solid state.[7]

Results and Discussion

The anthracene moiety in compound **3** was covalently linked to the fullerene by a [3+2] cycloaddition of the corresponding nitrile oxide to C_{60}. For that purpose we converted the aldehyde **1** into the oxime **2** and, after chlorination with NCS, HCl was eliminated to form the nitrile oxide, which then reacted with [60]fullerene in situ. Since the product **3** could not be separated completely from C_{60} by chromatography, it was converted directly to the epidioxide **4** (Scheme 1). At room temperature, a toluene solution of compound **3** was exposed to oxygen and sunlight, and the produced epidioxide **4** could be isolated in a pure form. The oxidation product was analyzed by ^{1}H NMR, ^{13}C NMR, IR, UV/Vis and mass spectrometry. The NMR-spectroscopic data show the characteristic signals of the oxidized anthryl group. In the ^{1}H NMR spectrum the methine proton appears at $\delta = 5.98$. The signals of the two sp^3 hybridized carbon atoms at the addition site of oxygen appear at $\delta = 80.08$ and 83.14. The observed positions of these relevant signals are in agreement with that of 9,10-epidioxyanthracene ($\delta = 6.02$ and 79.4 for ^{1}H NMR and ^{13}C NMR, respectively).[8] Obviously the fullerene, or its derivative, operate as photosensitizers to generate singlet oxygen which then adds to the anthryl substituent.



Scheme 1. Synthesis of the epidioxide **4** by the addition of a nitrile oxide to C_{60} followed by photooxidation: a) $H_2NOH{\cdot}HCl$, Na_2CO_3/ethanol; b) NCS/chloroform; c) C_{60}, Na_2CO_3/toluene; d) O_2, hν/toluene

The fullerene derivative **6** could be utilized to attach 9-anthrylacetic acid by esterification with the DCC/DMAP method. Starting from the glycine ester hydroxytosylate **5** the alcohol **6** was synthesized by a procedure that we have described previously.[9] The initial fullerene derivative **7,** substituted by anthracene, converts rapidly into the epidioxide **8** under exposure to light and air; no spectra of the pure compound **7** could be obtained (Scheme 2). The ^{1}H NMR analysis indicates that 10% of compound **7** was already oxidized at the time of measurement. The signals of the anthryl moiety were detected at $\delta = 7.46$–8.44 and the signals of the three methylene groups also appear in the expected regions.

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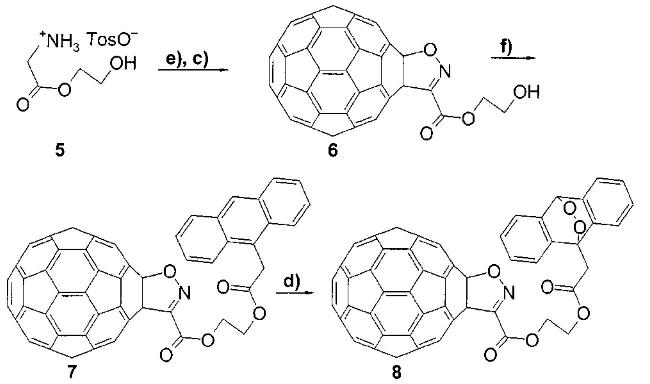
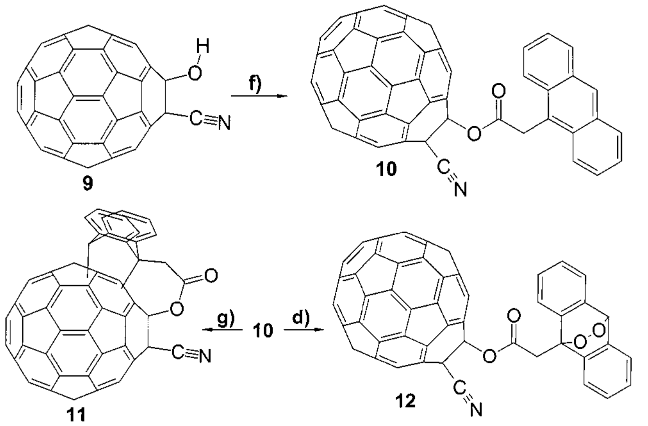


Scheme 2. Synthesis of the epidioxide **8** by esterification with the alcohol **6** followed by photooxidation: e) $NaNO_2$, HCl/H_2O; c) C_{60}, Na_2CO_3/toluene; f) 9-anthrylacetic acid, DCC, DMAP/toluene, acetonitrile; d) O_2, hν/toluene

The stable endoperoxide **8** was characterized by ^1H NMR, ^{13}C NMR, IR, UV/Vis and mass spectrometry. The NMR-spectroscopic data indicate that the anthryl group has been converted into the corresponding epidioxyanthryl group (^1H NMR: methine proton: $\delta = 5.97$; ^{13}C NMR: anthryl C9,10: $\delta = 79.8$ and 80.4). In the MALDI-TOF mass spectrum besides the molecular ion peak the $M^- - O_2$ peak could be observed.

The fullerenol **9** was used for the esterification with 9-anthrylacetic acid (Scheme 3). The product **10** turned out to be more stable against photooxidation than compound **7** and could be analysed by ^1H NMR, ^{13}C NMR, IR, UV/Vis and mass spectrometry.



Scheme 3. Synthesis of the epidioxide **12** and the intramolecular cycloadduct **11**: f) 9-anthrylacetic acid, DCC, DMAP/toluene, acetonitrile; d) O_2, hν/toluene; g) reflux/toluene

As observed for fullerene derivative **7**, compound **10** converts into the stable epidioxide **12** by photooxidation in toluene. In the ^1H and ^{13}C NMR spectra of compound **12** the signals for the epidioxyanthryl group appear, as expected, in regions very similar to the signals of **8** (**12**: ^1H NMR: methine proton: $\delta = 6.06$; ^{13}C NMR: anthryl C9,10: $\delta = 79.7$ and 80.2). IR, UV/Vis and mass spectra could also be obtained for ester **12**. The fullerene group and the anthryl group seem to be photosensitizers for singlet oxygen generation in the derivatives **3**, **7** and **10**, since the precursors 4-(9-anthryl)benzaldoxime (**2**) and 9-anthrylacetic acid are also photooxidized in the absence of fullerenes.

If the ester **10** is refluxed in toluene with the exclusion of oxygen, the new compound **11** is generated. The absence of any molecular symmetry could be recognized from the ^{13}C NMR analysis, according to the increased number of signals in the fullerene region. Obviously an intramolecular Diels–Alder reaction of the anthryl group with the fullerene sphere has occurred which leads to four new signals at the addition site (compared to the precursor **10**): for both sp^3-hybridized C atoms of the fullerene skeleton at $\delta = 70.5$ and 69.7 and for both sp^3-hybridized C-atoms of the 9,10-dihydroanthryl moiety at $\delta = 59.5$ and 50.9. This is in agreement with the NMR-spectroscopic data of the C_{60} monoadduct with anthracene ($\delta = 72.4$ and 58.4).[10] The ^1H NMR spectrum indicates that there is no anthryl group present in this molecule and that the protons of the methylene group are diastereotopic ($^2J_{H,H} = 18.5$ Hz). There are two possible regioisomers for this intramolecular three-atom-tether system, either *cis*-1 or *cis*-2, but only one product was isolated from the reaction mixture by chromatography. The spectroscopic data are in agreement with either of these two structures (Figure 1).

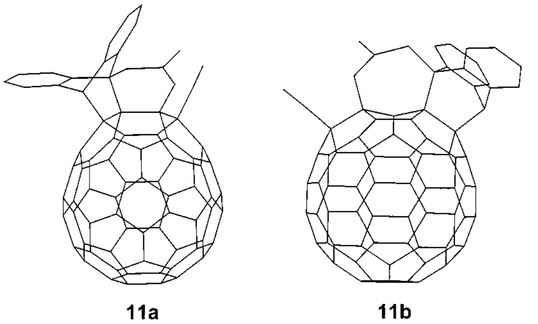


Figure 1. PM3 computational geometry optimized structures of the possible *cis*-1 (**11a**) and *cis*-2 (**11b**) intramolecular cycloadduct of fullerene derivative **10**

PM3 computational studies[11] indicate that isomer **11a** is more stable than isomer **11b** by 15.2 kJ/mol. Other three-tether intramolecular double adducts also showed rather small differences in the heats of formation.[12] On this basis no definite structural assignment of the product **11** can be made. Probably due to kinetic reasons one product is preferred.[13]

Conclusion

The anthryl group in anthracene-substituted fullerenes is converted easily to the stable 9,10-epidioxide by singlet oxygen. The photosensitizing moiety for the generation of this singlet oxygen could be either the anthryl or the fullerene group. In the case of compound **10** the anthryl substituent reacted intramolecularly with the fullerene core to form a chiral double adduct. For derivatives **3** and **7** no intramolecular adducts could be isolated, probably due to steric reasons.

Experimental Section

General Remarks: NMR: Bruker AC 300 (300 MHz and 75 MHz, for ^1H and ^{13}C, respectively); chemical shifts are given with respect to TMS. Calibration with solvent signal ($CDCl_3$: $\delta_H = 7.24$, $\delta_C = 77.0$). – FT-IR: Bruker IFS 66. – EI MS: VG ZAB-2F. – FAB MS: JOEL JMS-RSX 102A, positive ion mode (matrix: 3-nitrobenzyl alcohol/TFA 99/1) and JOEL JMS-700, positive ion mode (matrix: nitrobenzyl alcohol). – FD MS: JOEL JMS-700, positive ion mode. – MALDI-TOF MS: Bruker Biflex, negative ion mode (matrix 9-nitroanthracene). – UV: HP 8452 (diode array). – Elemental Analysis: Heraeus CHN-O-Rapid - HPLC: Preparative column Buckyclutcher® I (250 × 21.1 mm, 10 µm, 100 Å), mobile phase toluene.

4-(9-Anthryl)benzaldoxime (2): To a 100-mL round-bottom flask were added 4-(9-anthryl)benzaldehyde (**1**) (565 mg, 2×10^{-3} mol) and 40 mL of ethanol and the mixture was heated under reflux. To the boiling solution was added hydroxylamine hydrochloride (1.25 g, 1.8×10^{-2} mol, 9 equiv.), dissolved in 5 mL of water, and this mixture was then neutralized with Na_2CO_3. The reaction mixture was heated under reflux for 1 h. Iced water was added to the hot solution until the product started to precipitate. The oxime was allowed to crystallize overnight and was then washed several times with water and dried in the air. The solid was purified by sublimation yielding 522 mg (1.8×10^{-3} mol, 87.8%) of yellow crystals. – ^1H NMR (300 MHz, $CDCl_3$): δ = 7.32–7.48 (m, 6 H, arom.), 7.64 (d, ^3J = 8.7 Hz, 2 H, arom.), 7.79 (d, ^3J = 8.1 Hz, 2 H, arom.), 7.85 (s, 1 H, OH), 8.04 (d, ^3J = 8.5 Hz, 2 H, arom.), 8.31 (s, 1 H), 8.50 (s, 1 H, C=NOH). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 125.2, 125.6, 126.5, 126.9, 127.0, 128.4, 130.0, 131.3 (m), 131.8, 136.1 (m), 140.8 (m), 150.1 (C=NOH). – FT IR (KBr): $\tilde{\nu}$ = 3281 cm^{-1} (br. s, OH), 3052 (m), 3031 (m), 2923 (w), 972 (s), 961 (m), 945 (m), 934 (m), 886 (m), 874 (m), 820 (m), 742 (s), 734 (s), 612 (m). – UV/Vis (chloroform): $\lambda_{max.}$ (lg ε) = 258 nm (5.12), 350 (3.79), 368 (4.00), 386 (3.97). – MS (EI, 70 eV); *m/z* (%): 297 (100) [M^+], 280 (14) [M^+ – OH], 279 (50), 278 (19), 277 (16), 253 (43) [M^+ – CH_2NO], 252 (33), 250 (13), 126 (17), 125 (18), 113 (12). – HR EI-MS [$C_{21}H_{15}NO$]: calcd. 297.115; found. 297.114. – $C_{21}H_{15}NO$ (297.4): calcd. C 84.83, H 5.08, N 4.71; found C 84.53, H 5.11, N 4.39.

3′-[4-(9,10-Epidioxyanthryl-9)phenyl]isoxazolo[4′:5′:1,2][60]-fullerene (4): 4-(9-Anthryl)benzaldoxime (**2**) (82.5 mg, 2.8×10^{-4} mol) was dissolved in 40 mL of chloroform and cooled with an ice bath to 5 °C. To this solution was added *N*-chlorosuccinimide (74.2 mg, 5.6×10^{-4} mol, 2 equiv.) and 10 µl of pyridine. The reaction mixture was stirred for 3 h at 5 °C and then added to a suspension of C_{60} (200 mg, 2.8×10^{-4} mol), dissolved in 200 mL of toluene, and 23 mg of Na_2CO_3, dissolved in 5 mL of water. After stirring for 1 d exposed to sunlight and air, the mixture was washed five times with water. Purification by HPLC with toluene as eluent yielded 39 mg (3.7×10^{-5} mol, 13.4%) of black crystals. – ^1H NMR (300 MHz, $CDCl_3/CS_2$ 2:8): δ = 5.98 (s, 1 H, benzyl), 7.18 (d, ^3J = 7.0 Hz, 2 H, arom.), 7.19–7.25 (m, 2 H, arom.), 7.29–7.34 (m, 2 H, arom.), 7.47 (d, ^3J = 7.0 Hz, 2 H, arom.), 7.77 (d, ^3J = 8.5 Hz, 2 H, arom.), 8.49 (d, ^3J = 8.8 Hz, 2 H, arom.). – ^{13}C NMR (75 MHz, $CDCl_3/CS_2$ 2:8): δ = 74.2 (1 C), 80.1 (CH), 83.1 (q), 99.5 (1 C), 123.2, 123.6, 127.7, 128.0, 128.3, 128.7, 129.2, 135.7, 136.7 (2 C), 137.3 (2 C), 138.3, 139.8, 140.5 (2 C), 140.6 (2 C), 141.9 (2 C), 142.2 (2 C), 142.4 (2 C), 142.5 (2 C), 142.6 (2 C), 143.0 (2 C), 143.1 (2 C), 144.2 (2 C), 144.5 (2 C), 144.6 (2 C), 144.8 (2 C), 144.9 (2 C), 145.2 (2 C), 145.3 (2 C), 145.5 (2 C), 145.8 (2 C), 145.9 (4 C), 146.1 (2 C), 146.1 (2 C), 146.4 (2 C), 146.4 (4 C), 146.5 (2 C), 147.4 (1 C), 147.8 (1 C), 152.5 (CN). – FT-IR(KBr): $\tilde{\nu}$ = 1509 cm^{-1} (w), 1459 (w), 1303 (w), 1284 (w), 980 (w), 905 (m), 862 (m), 822 (m), 755 (s), 729 (s), 637 (w), 605 (w), 569 (w), 526 (s, fullerene), 463 (w). – UV/Vis (chloroform): $\lambda_{max.}$ (lg ε) = 230 (4.70), 254 (4.81), 316 (4.35), 346 (4.09), 392 (3.46), 412 (3.22), 422 (3.08). – MALDI-TOF MS; *m/z* (%): 1047 [M^-], 1015 [M^- – O_2], 720 [C_{60}^-]. – HR FAB-MS [$C_{81}H_{13}NO_3$]: calcd. 1047.090; found 1047.088.

2-Hydroxyethyl Isoxazolo[4′,5′:1,2][60]fullerene-3′-carboxylate (6): To a stirred solution of compound **5** (2.4 g, 8.3×10^{-3} mol) in 6 mL of water was added 0.7 mL of hydrochloric acid (*d* = 1.19 kg × dm^{-3}, 8.3×10^{-3} mol) at –5 °C. A solution of $NaNO_2$ (574 mg, 8.3×10^{-3} mol) in 1 mL of water was then added dropwise during a period of 10 min, and a second equivalent of HCl and $NaNO_2$ each was added in the same manner. The cooling was removed, and stirring was continued for 5 min. The reaction mixture was then extracted with diethyl ether (3 × 50 mL). The combined organic layers were dried (Na_2SO_4), and the volume of the solution was reduced to 10 mL in vacuo. A 1-mL portion of this slightly yellow solution was added in five portions to a stirred two-phase mixture of C_{60} (100 mg, 1.4×10^{-4} mol) in 250 mL of toluene and Na_2CO_3 (145 mg, 1.4×10^{-3} mol) in 20 mL of water during a period of 1 h. The brown organic layer was dried with Na_2SO_4, concentrated in vacuo, and the residue was chromatographed on a silica gel column with toluene/acetonitrile 9:1. The expected product **6** could be eluted with R_f = 0.51, yielding 30 mg (3.5×10^{-5} mol, 25% based on employed C_{60}) as a brown solid. – ^1H NMR (300 MHz, $CDCl_3$): δ = 4.61 (m, 2 H, CH_2), 4.05 (m, 2 H, CH_2), 2.12 (t, ^3J = 6.3 Hz, 1 H, OH). – FT-IR (KBr): $\tilde{\nu}$ = 3433 cm^{-1} (m, OH), 2921 (m, CH), 1725 (s, CO), 1587 (m), 1327 (m), 1146 (s), 527 (s, fullerene). – UV/Vis ($CHCl_3$): λ_{max} (lg ε) = 232 nm (4.77), 254 (4.90), 412 sh (3.33), 460 (3.31), 676 (2.71). – MALDI-TOF MS; *m/z* (%): 851.3 (100) [M^-], 720.2 (100) [C_{60}^-]. – HR FAB-MS [$C_{64}H_5NO_4$]: calcd. 851.0218; found 851.0229.

2-[2-(9-Anthryl)acetoxy]ethyl Isoxazolo[4′,5′:1,2][60]fullerene-3′-carboxylate (7): To a solution of alcohol **6** (15 mg, 1.8×10^{-5} mol) in 80 mL of toluene/acetonitrile 9:1, obtained directly from the column separation, were added 9-anthrylacetic acid (21 mg, 9×10^{-5} mol), DCC (19 mg, 9×10^{-5} mol) and DMAP (0.4 mg, 3.6×10^{-6} mol) under a nitrogen atmosphere and with the exclusion of light. The mixture was stirred at room temperature for 72 h, concentrated in vacuo and filtered through a silica gel column (toluene, R_f = 0.3) to produce 8.3 mg (7.8×10^{-6} mol, 43%) of a dark-brown powder. – ^1H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, arom.), 8.29 (d, ^3J = 7 Hz, 2 H, arom.), 7.01 (d, ^3J = 7 Hz, 2 H, arom.), 7.61–7.46 (m, 4 H, arom.), 4.66 (s, 2 H, CH_2), 4.65 (m, 2 H, CH_2), 4.45 (m, 2 H, CH_2). – MALDI-TOF MS; *m/z* (%): 1068.7 (53) [M^-], 891.5 (22) [M^- – anthryl], 719.6 (100) [C_{60}^-]. – HR FAB-MS [$C_{80}H_{15}NO_5$]: calcd. 1069.0950; found 1069.0973.

2-[2-(9,10-Epidioxyanthryl-9)acetoxy]ethyl Isoxazolo[4′,5′:1,2][60]-fullerene-3′-carboxylate (8): The fullerene derivative **7** (10 mg, 9.1 × 10^{-6} mol) was dissolved in 50 mL of toluene. The stirred solution was irradiated with a 100-W tungsten filament lamp (distance 0.5 m) at room temperature through pyrex glass while oxygen was bubbled in. After 20 h, no more precursor **7** could be detected (monitored by TLC, silica gel, toluene). The solution was concentrated in vacuo and purified by chromatography on a silica gel column with toluene/acetonitrile 9:1. The product **8** could be eluted with R_f = 0.46 as a dark-brown solid (7.6 mg, 6.9×10^{-6} mol, 76%). – ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.26 (m, 8 H, arom.), 5.97 (s, 1 H, CH), 4.71 (m, 2 H, CH_2), 4.60 (m, 2 H, CH_2), 3.67 (s, 2 H, CH_2). – ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.3 (CO), 159.7 (CO), 147.9 (1 C), 147.3 (2 C), 147.1 (2 C), 146.7 (2 C), 146.4 (2 C), 146.4 (4 C), 146.0, (4 C), 145.7 (2 C), 145.3 (2 C), 145.3 (2

C), 145.2 (2 C), 144.6 (2 C), 144.2 (4 C), 143.3 (2 C), 142.9 (2 C), 142.9 (4 C), 142.5 (4 C), 142.4 (2 C), 142.3 (2 C), 142.1 (2 C), 141.8 (4 C), 140.3 (2 C), 140.2 (2 C), 138.9, 138.3, 137.1 (2 C), 136.6 (2 C), 127.9, 127.8, 123.6, 121.9, 80.4, 79.8, 64.2 (CH_2), 62.3 (CH_2), 33.7 (CH_2), because of the long relaxation time the signals of the $C(sp^3)$ fullerene atoms could not be detected. – FT-IR (KBr): $\tilde{\nu}$ = 2923 cm^{-1} (m, CH), 2331 (w), 1745 (s, CO), 1729 (s, CO), 1145 (s), 759 (m), 527 (s, fullerene). – UV/Vis ($CHCl_3$): $\lambda_{max.}$ (lg ε) = 232 nm (4.56), 252 (4.63), 272 sh (4.45), 316 (4.17), 450 (2.90), 676 (2.22). – MALDI-TOF MS; *m/z* (%): 1101.6 (39) [M^-], 1070.2 (11) [$M^- - O_2$], 892.1 (40) [$M^- - 209$]. – HR FAB-MS [$C_{80}H_{15}NO_7$]: calcd. 1101.0848; found 1101.0841.

2-Cyano-1,2-dihydro[60]fullerenyl 2-(9-Anthryl)acetate (10): To a solution of alcohol **9** (10 mg, 1.3×10^{-5} mol) in 50 mL of toluene/acetonitrile 9:1, obtained directly from the column separation,[14] were added 9-anthrylacetic acid[15] (6 mg, 2.6×10^{-5} mol), DCC (5.4 mg, 2.6×10^{-5} mol) and DMAP (0.3 mg, 2.6×10^{-6} mol) under nitrogen and with the exclusion of light. The mixture was stirred at room temperature for 72 h, concentrated in vacuo and filtered through a silica gel column (toluene, $R_f = 0.74$) to produce 10.2 mg (10^{-5} mol, 80%) of a dark-brown powder. – ^1H NMR (300 MHz, $CDCl_3$): δ = 8.64–7.52 (m, 9 H, arom.), 5.41 (s, 2 H, CH_2). – ^{13}C NMR (75 MHz, $CDCl_3/CS_2$ 1:8): δ = 170.8 (CO), 148.1 (1 C), 147.5 (1 C), 146.3 (2 C), 146.3 (2 C), 146.3 (2 C), 146.0 (2 C), 145.9 (2 C), 145.89 (2 C), 145.7 (2 C), 145.2 (2 C), 145.2 (2 C), 145.1 (2 C), 145.0 (2 C), 144.2 (2 C), 144.2 (2 C), 143.8 (2 C), 143.6 (2 C), 142.7 (2 C), 142.5 (2 C), 142.4 (2 C), 142.0 (2 C), 141.99 (2 C), 141.5 (2 C), 141.2 (2 C), 141.17 (2 C), 140.7 (2 C), 139.8 (2 C), 139.4 (2 C), 137.6 (2 C), 136.3 (2 C), 131.3, 130.6, 129.0, 127.8, 126.4, 124.9, 124.3, 124.2, 115.5 (CN), 34.4 (CH_2), because of the long relaxation time the signals of the $C(sp^3)$ fullerene atoms could not be detected. – FT IR (KBr): $\tilde{\nu}$ = 2921 cm^{-1} (m, CH), 2330 (w), 2239 (w, CN), 1763 (m, CO), 1101 (s), 991 (s), 729 (s), 526 (s, fullerene). – UV/Vis ($CHCl_3$): $\lambda_{max.}$ (lg ε) = 226 nm (5.00), 258 (5.33), 316 (4.73), 368 sh (4.25), 388 sh (4.04), 416 sh (3.65), 684 (2.56). – FAB-MS; *m/z* (%): 981.1 (16), 746.0 (49) [$C_{61}N^+$], 720.0 (100) [C_{60}^{+}]. – HR FAB-MS [$C_{77}H_{11}NO_2$]: calcd. 981.0790; found 981.0814.

Intramolecular Diels–Alder Adduct of Compound 10 (11): A stirred solution of compound **10** (10 mg, 10^{-5} mol) in 100 mL of toluene was refluxed for 3 h in the dark under nitrogen. After this time, no remaining **10** could be detected (monitored by TLC, silica gel, toluene). The mixture was then concentrated in vacuo and chromatographed on a silica gel column with toluene. Compound **11** (R_f = 0.21) could be isolated as a dark-brown solid (8.7 mg, 8.7×10^{-6} mol, 87%). – ^1H NMR (300 MHz, $CDCl_3$): δ = 7.97–7.54 (m, 8 H, arom.), 5.77 (s, 1 H, CH), 4.36 (d, ^2J = 18.5 Hz, 1 H, CH_2), 3.95 (d, ^2J = 18.5 Hz, 1 H, CH_2). – ^{13}C NMR (75 MHz, $CDCl_3/CS_2$ 1:8): δ = 167.9 (CO), 153.7, 150.5, 149.4, 149.2, 148.8, 148.5, 147.4, 147.0, 146.8, 146.4, 146.1, 145.5, 145.4, 145.2, 145.1, 145.0, 144.8, 144.7, 144.6, 144.5, 144.4, 144.35, 144.3, 144.2, 144.1, 144.05, 144.0, 143.8, 143.7, 143.6, 143.57, 143.4, 143.1, 143.1, 143.0, 142.7, 142.4, 142.2, 142.1, 141.3, 141.2, 141.0, 140.8, 140.6, 140.5, 140.3, 139.6, 138.7, 138.4, 137.1, 135.2, 134.0, 133.6, 128.4 (arom.), 128.3 (arom.), 127.2 (arom.), 127.1 (arom.), 125.6 (arom.), 125.2 (arom.), 124.5 (arom.), 122.5 (arom.), 112.5 (CN), 90.4 (sp^3 fullerene), 70.5 (sp^3 fullerene), 69.7 (sp^3 fullerene), 59.5, 56.6 (sp^3 fullerene), 50.9, 34.2 (CH_2). – FT-IR (KBr): $\tilde{\nu}$ = 2921 cm^{-1} (w, CH), 1774 (s, CO), 1194 (m), 991 (m), 526 (m, fullerene). – UV/Vis ($CHCl_3$): $\lambda_{max.}$ (lg ε) = 232 nm (4.97), 258 (5.07), 300 sh (4.64), 324 sh (4.51), 426 (3.84), 636 (2.64), 698 (2.41). – FD-MS; *m/z* (%): 981.1 (38) [M^+], 720.1 (100) [C_{60}^{+}]. – HR FAB-MS [$C_{77}H_{11}NO_2$]: calcd. 981.0790; found 981.0801.

2-Cyano-1,2-dihydro[60]fullerenyl 2-(9,10-Epidioxyanthryl-9)acetate (12): The fullerene derivative **10** (10 mg, 10^{-5} mol) was dissolved in 50 mL of toluene. The stirred solution was irradiated with a 100-W tungsten filament lamp (distance 0.5 m) at room temperature through pyrex glass while oxygen was bubbled in. After 72 h, no precursor **10** could be detected (monitored by TLC, silica gel, toluene). The solution was then concentrated in vacuo and purified by chromatography on a silica gel column with toluene. The product **12** could be eluted ($R_f = 0.31$) and isolated as a dark-brown solid (8.2 mg, 8.1×10^{-6} mol, 81%). – ^1H NMR (300 MHz, $CDCl_3$): δ = 7.82–7.32 (m, 8 H, arom.), 6.09 (s, 1 H, CH), 4.43 (s, 2 H, CH_2). – ^{13}C NMR (75 MHz, $CDCl_3/CS_2$ 1:8): δ = 168.7 (CO), 148.3 (1 C), 147.8 (1 C), 146.6 (2 C), 146.5 (2 C), 146.3 (2 C), 146.2 (2 C), 146.2 (4 C), 146.0 (2 C), 145.4 (2 C), 145.3 (2 C), 145.3 (2 C), 145.1 (2 C), 144.5 (2 C), 144.4 (2 C), 144.0 (2 C), 143.9 (2 C), 142.9 (2 C), 142.7 (2 C), 142.68 (2 C), 142.3 (2 C), 142.2 (2 C), 141.9 (2 C), 141.5 (2 C), 141.4 (2 C), 140.9 (2 C), 140.0 (2 C), 139.8 (2 C), 138.7 (arom.), 138.3 (arom.), 137.8 (2 C), 136.6 (2 C), 127.7, 127.6, 123.3, 122.1, 116.5 (CN), 80.2, 79.7 (CH), 34.3 (CH_2), because of the long relaxation time the signals of the $C(sp^3)$ fullerene atoms could not be detected. – FT-IR (KBr): $\tilde{\nu}$ = 2922 cm^{-1} (m, CH), 2331 (w), 2239 (w, CN), 1765 (m, CO), 1106 (m), 993 (m), 758 (m), 527 (s, fullerene). – UV/Vis ($CHCl_3$): $\lambda_{max.}$ (lg ε) = 230 nm (4.68), 256 (4.83), 318 (4.45), 416 sh (3.38), 680 (2.48). – FD-MS; *m/z* (%): 1013.3 (29) [M^+], 720.2 (100) [C_{60}^{+}]. – HR FAB-MS [$C_{77}H_{11}NO_4$]: calcd. 1013.0688; found 1013.0725.

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Received October 20, 1999
[O99588]