[2 + 2] Cycloadditions of Fullerenes: Synthesis and Characterization of $C_{62}O_3$ and $C_{72}O_3$, the First Fullerene Anhydrides

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Abstract: [2 + 2] Cycloaddition of C_{60} with *N,N,N′,N′*-tetraethylethynediamine (**1a**) and *N,N*-diethyl-2-ethylthioethyneamine (**1b**) gave the stable, 1,2-dihydrofullerene[60]-1,2-cyclobutenediamine **2a** and thioenamine **2b**, respectively, in good yield. Self-sensitized photooxygenation of **2a** and **2b** produced 1,2-dihydrofullerene[60]-1,2-diamide **3a** and thioester amide **3b**, from which 1,2-dihydrofullerene[60]-1,2-dicarboxylic acid anhydride ($C_{62}O_3$) was readily prepared. Similarly, C_{70} reacted with **1a** (regiospecifically at the 1,9-bond) to give 1,9-dihydrofullerene[70]-1,9-cyclobutenediamine **5** or 1,9:61,62-biscyclobutenediamine **6** in good yields. In contrast to **2a**, self-sensitized photooxygenation of **5** regenerated C_{70} and the oxidized ynamine. 1,9-Dihydrofullerene[70]-1,9-dicarboxylic acid anhydride ($C_{72}O_3$) was prepared from a *tert*-butylthioester amide **10** in one pot by reaction of *N,N*-diethyl-2-*tert*-butylthioethyneamine (**1c**) with C_{70} and photooxygenation of the resultant cycloadduct.

Introduction

Preparative-scale isolation of C_{60} and C_{70} in 1990 has led to intensive investigations of these all-carbon, spherical molecules.[1–3] Representative reactions of C_{60} include cycloadditions and additions of nucleophiles, radicals, carbenes, and halogens.[4–6] The reactivities correlate well with the dieno- and dipolarophilicity and electron affinity of C_{60}. Some C_{60}-adducts (dihydrofullerenes, DHFs) with interesting structural, physical, and biological properties have been reported.[7–12] C_{70} shows similar reactivities to C_{60}. Complexes of C_{70} with iridium compounds have been characterized by X-ray crystallography, and the 1,9- and 7,8-bonds were shown to have the highest reactivity.[13,14] A few other C_{70}-adducts have also been prepared recently,[15–21] although purification and characterization of the products are still difficult, partially due to the increasing complexity of the isomers.

The preparation of synthetically useful monoadducts of C_{60} and C_{70} is currently one of the prime objectives in the rapidly growing area of fullerene chemistry. Considerable success has been achieved for C_{60}, much less for C_{70}. We demonstrated a high yield, one-pot photochemical addition of C_{60} with *N,N*-diethylpropynylamine followed by photochemical oxidation to give a ketoamidodihydrofullerene.[22] Here we report [2 + 2] cycloadditions of C_{60} and C_{70} with an yndiamine and thioynamines, self-sensitized photooxidation of the cycloadducts, and synthesis of $C_{62}O_3$ and $C_{72}O_3$, the first dihydrofullerene anhydrides.

Results

Additions to C_{60} and Synthesis of $C_{62}O_3$. At room temperature, C_{60} reacted readily with *N,NN′,N′*-tetraethylethynediamine[23] (**1a**) and *N,N*-diethyl-2-ethylthioethyneamine[24] (**1b**) to give a 1,2-dihydrofullerene[60]-1,2-cyclobutenediamine **2a** and thioenamine **2b** in 52 and 47% yields, respectively (Scheme 1). Self-sensitized photooxygenation of **2a** and **2b** in toluene cleanly afforded diamide **3a** and thioester **3b**. Treatment of **3a** or **3b** with *p*-toluenesulfonic acid (PTSA) produced 1,2-dihydrofullerene[60]-1,2-dicarboxylic acid anhydride (**4**) quan-

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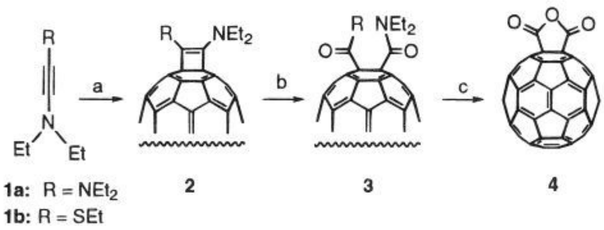
Scheme 1



1a: R = NEt$_2$ **2** **3** **4**
1b: R = SEt

titatively as shown by HPLC.[25] The overall yield of **4** is ca. 40%. More conveniently, the cycloaddition and photooxygenation were performed in one pot to give, in 40 min, comparable yields of **3a** and **3b**, which were even more easily separated from C_{60} by flash column chromatography due to the large difference in polarity.

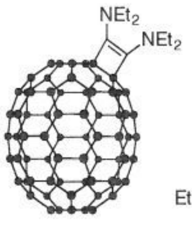
Although previous results indicated that a C_{60}-fused cyclobutenamine was extremely labile to oxygen/room light,[22] compounds **2a** and **2b** are sufficiently stable to allow isolation. The ^{1}H NMR (500 MHz) spectra of **2a** and **2b** resembled those of **1a** and **1b**, respectively, but with a downfield shift due to the ring current of the DHF and the double bond.[26] The ^{13}C NMR (125 MHz) spectrum of **2a** showed 16 signals between 157.1 and 136.9 ppm and a single sp^3 fullerene carbon at 74.9 ppm, indicating C_{2v} symmetry. The ^{13}C NMR (100 MHz) spectrum of **2b** shows a total of 31 signals between 158.56 and 101.50 ppm with two sp^3 fullerene carbons at 76.6 and 76.1 ppm, consistent with C_s symmetry. The cycloadditions of **1a** and **1b** occurred exclusively at the [6,6]-bond of C_{60}.

Diamide **3a** and thioester amide **3b** showed temperature-dependent dynamic behavior from the restricted rotations around the middle and thioester bonds. At room temperature, broad peaks were observed for the methylene hydrogens in both **3a** and **3b**; below −20 °C, all four NCH$_2$ in **3a** are nonequivalent and each shows an ABX$_3$ splitting pattern (J_{AB} = 15.75 Hz), while at 0 °C, **3b** showed well-split methylene hydrogens. The ^{13}C NMR spectrum of **3a** at −60 °C gave more and sharper lines than at room-temperature, apparently due to "freezing" rotational isomers on the NMR time scale at low temperature.

The ^{13}C NMR (126 MHz) of anhydride **4** displayed 17 signals for the C_{60} skeleton, of which four correspond to two carbons and 13 correspond to four: one at 72.1 and the remainder between 147.6 and 137.0 ppm. This is the correct number and intensity for an adduct of C_{2v} symmetry. A single carbonyl peak at 167.6 ppm, together with infrared stretches at 1850 (w) and 1786 (s) cm^{-1} unequivocally established the anhydride functionality. Unfortunately, FAB MS of **4** did not give the expected M + 1 ion at 794, instead an ion at 766 was detected, corresponding to loss of one CO molecule; the base peak is C_{60}. Fullerene derivatives commonly fragment under MS conditions, and this is the case here.

Additions to C_{70} and Synthesis of $C_{72}O_3$. C_{70} reacted with **1a** even faster (ca. four times by a competition experiment) than C_{60}, giving 1,9-dihydrofullerene[70]-1,9-cyclobutenediamine **5** in 60% yield after purification. The ^{1}H NMR spectrum of monoadduct **5** showed two sets of ethyls at 3.77 (q), 3.19 (q), 1.47 (t), and 1.30 (t) ppm. The ^{13}C NMR spectrum (125 MHz) revealed 37 sp^2 carbons between 156.8 and 129.2 ppm, four with intensity of one and 33 of two; two sp^3 fullerene carbons were located at 67.4 and 64.9 ppm. Both ^{1}H and ^{13}C NMR data suggest C_s symmetry, consistent with addition at the a=b site (1,9 bond) of C_{70}. That cycloaddition of **2a** to C_{70} occurred *regiospecifically* at the 1,9-bond was established by the clean ^{1}H NMR spectrum of the reaction mixture before chromatography, which showed no appreciable amount of other products.

Interestingly, a diadduct with C_2 symmetry, biscyclobutenediamine **6**, could also be prepared in 70% yield by addition of 2.2 equiv of **1a**. Compound **6** was more polar than **5** by TLC and was readily isolated by flash column chromatography. The ^{1}H NMR spectrum of the diadduct **6** was virtually identical to that of **5**, but its ^{13}C NMR spectrum was dramatically different. It showed 35 sp^2 carbons and two sp^3 fullerene carbons, all with double intensity, suggesting C_2 symmetry, with the second addition occurring from the bottom hemisphere at the a′=b′ bond. Two C_2 isomers, products of 1,9:61,62-additions and 1,9:67,68-additions, respectively, are possible.[27] ^{1}H NMR spectrum of the diadduct indicated two isomers are present in a 9:1 ratio. By comparison with a double addition adduct $C_{70}[Ir(CO)Cl(PPhMe_2)_2]_2$ which was characterized by X-ray crystallography,[14] we tentatively assign the major isomer as 1,9:61,62-biscyclobutenediamine (shown in **6** by solid line), and the minor one as 1,9:67,68-biscyclobutenediamine (shown in **6** by dashed line). The structure of the bisadduct was further secured by HR-FAB MS (M$^+$ 1176.3148, base peak!) and FT-IR (characteristic band at 1686 cm^{-1} for the cyclobutene C=C bond).



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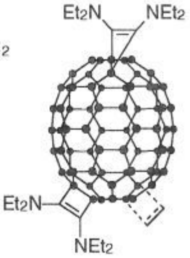

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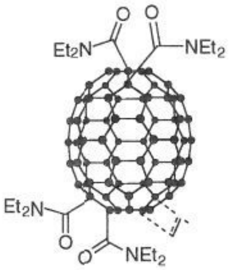

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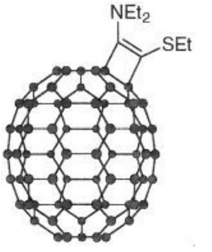
Surprisingly, photooxygenation of cyclobutenediamine **5** did not give the corresponding 1,9-dihydrofullerene[70]-1,9-diamide as did **2a**, instead, it produced C_{70} and tetraethyl oxamide. Singlet oxygen generated by thermal decomposition of 9,10-dimethylnaphthalene endoperoxide[28] gave no reaction with **5**. It is possible that **5** can undergo a photochemical cycloreversion via its triplet excited state. However, self-sensitized photooxygenation of a dilute solution of diadduct **6** gave a 20% yield of the corresponding 1,9:61,62-tetraamide (**7**); considerable C_{70} was recovered. Compound **7** also showed dynamic NMR as a result of restricted rotation of the amide bonds; at temperatures below −20 °C, well resolved split methylene hydrogens were observed.

Reaction of *N,N*-diethyl-2-ethylthioethyneamine (**1b**) with C_{70} at room temperature afforded a mixture of monoadduct **8** and diadduct **9**, which were separated by column chromatography in nearly equal amounts. **9** is a mixture of three isomers which could not be further separated, but one is predominant (>90%) from ^{1}H NMR (500 MHz).



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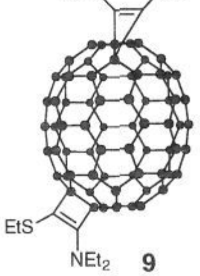

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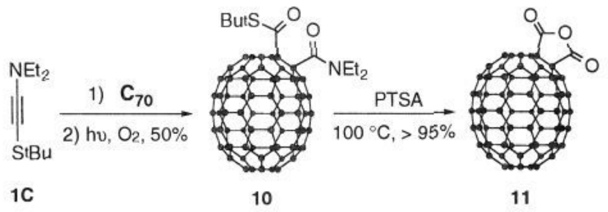
[25] Analytical HPLC were performed on the reversed-phase Hypersil column, with a mixture of toluene and acetonitrile (50:50, 1.0 mL/min) as mobile phase, and UV detection at 340 nm.

Scheme 2



Very importantly, both ^{1}H and ^{13}C NMR data (see Experimental Section) of **8** indicated a single isomer of C_s symmetry with addition occurring at the 1,9 bond.[29] This result, together with the equally regioselective reaction with *N,N*-diethyl-2-*tert*-butylthioethyneamine (**1c**) described below, implies that the 1,9-bond of C_{70} is highly polarized so that it can direct the regiochemistry of the addition.

The most predominant isomer (>90%) of the bisadducts has chemical shifts almost identical to those of the monoadduct **8**, suggesting C_2 symmetry. The C_2 symmetry is further proven by ^{13}C NMR: a total of 35 sp^2 carbon signals with equal intensity were detected between 157.90 and 99.15 ppm. As in the C_{70}-yndiamine bisadduct **5**, we tentatively assigned the major isomer to be 1,9-dihydrofullerene[70]-1,9-(ethylthio)cyclobutenamine **9**.

To prepare 1,9-dihydrofullerene[70]-1,9-dicarboxylic acid anhydride **11**, *tert*-butylthioester amide **10** was made in 50% yield in one pot (Scheme 2).[29] *N,N*-Diethyl-2-*tert*-butylthioethyneamine (**1c**) gave a better yield of cleaved thioesteramide than **1b**. Treatment of **10** with PTSA in toluene at 100 °C yielded anhydride **11** in quantitative yield. The ^{13}C NMR spectrum (125 MHz) showed a total of 35 signals for the fullerene skeleton, four of single intensity and 33 of double, two at 65.9 and 65.3 ppm, and the remainder between 156.2 and 129.4 ppm. Two carbonyl peaks at 166.8 and 166.6 ppm, together with infrared stretches at 1856 (w) and 1782 (s) cm^{-1}, unequivocally established the anhydride functionality.

Anhydrides **4** and **11** are thermally stable at 110 °C but slowly form C_{60} and C_{70} when treated with water at room temperature, probably through ring-opened intermediate dihydrofullerene diacids, which would easily decarboxylate to oxidizable dihydrofullerenes $C_{60}H_2$[30,31] and $C_{70}H_2$.[32]

Discussion

Although Diels−Alder reaction of C_{60} with a wide variety of dienes has been well documented,[33−39] examples of [2 + 2] cycloadditions are few but appear to give especially high yields of potentially useful DHFs.[22,40−42] Ynamines (**1a**−**c**) are especially electron-rich, and C_{60} and C_{70} are such good electron acceptors[43,44] that a ground state electron- or charge-transfer mechanism may account for the fast thermal [2 + 2] cycloaddition.

Like most reactions of C_{60}, addition of yndiamine and thioynamines occurred at the shorter [6,6] bonds with a higher double-bond character, rather than at the longer [6,5] bonds,[45] thus leading to formation of only a single monoadduct. Cycloadducts **2a** and **2b** have a photosensitizer (DHF[46]) and an easily photooxidizable group (enamine/or thioenol ether[47,48])-in the same molecule, making cleavage of the cyclobutene C=C bond in DHFs by $^1O_2$ highly efficient.

Some experimental work and theoretical calculations[49−51] have been undertaken to investigate the regioselectivity of addition reactions to C_{70}. Reactions of C_{70} give variable regiospecificity. Vaska's complex ($Ir(CO)Cl(PPh_3)_2$) bonds regiospecifically at the a=b site (1,9-bond).[13] Osmylation gave a mixture of 1,9- and 7,8-addition in a ratio of 2:1.[15] Hydroboration produced 7.8- and 1,9-$C_{70}H_2$ in a 2:1 ratio, with the former being equilibrated to the latter by a platinum catalyst.[16] Addition of 1,3-dipolar nitrile oxides gave both 1,9- and 7,8-additions in a ratio of ca. 2:1, and, for the 1,9-addition, two regioisomers were formed in nearly equal amount.[17] Our results indicate that ynamines add to the 1,9-bond of C_{70} regiospecifically, and, for the thioynamine, only one of two possible 1,9-isomers was formed. The preferential addition at 1,9-bond can be explained by the local curvature of the carbon sphere, with the strongest curvature corresponding to the most reactive bond. Production of the single 1,9-regioisomer in the thioynamine−C_{70} mono- and bisadducts strongly indicate a polarization of the 1,9-bond.

Conclusions

[2 + 2] Cycloadditions of an yndiamine and thioynamines to fullerene C_{60} and C_{70} give structurally interesting, isolable fullerenyl cyclobuteneamines in good yields. For the addition to C_{60}, bonding occurred exclusively at [6,6]-ring juncture; for C_{70}, the addition occurred specifically at the 1,9-bonds of the polar caps. More importantly, only one 1,9-isomer out of two possible was formed in the addition of unsymmetrical thioynamines, suggesting a strong directing effect of the 1,9-bond of C_{70}. Most of the initial fullerenyl cyclobuteneamines can

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be photooxygenated to dicarbonyl functionalized derivatives. The fullerene anhydrides prepared should be valuable intermediates for further chemical transformations. Since a variety of ynamines are easily accessible, this [2 + 2] cycloaddition method constitutes a versatile prototype for preparation of functionalized fullerene derivatives.

Experimental Section

General Methods. C_{70} (98% purity) was purchased from MER Corporation, Tucson, AZ 85706. C_{60} was purified from the extract (from MER Co.) according to a literature procedure.[52] Photooxygenation was done with a Cermax 300 W Xenon lamp filtered with 0.09 M $K_2Cr_2O_7$ solution, 3.5 cm pathlength. All reactions were performed under argon. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-400 or ARX-500 instrument equipped with a temperature control unit, and chemical shifts are in ppm (δ) relative to TMS in $CS_2/CDCl_3$. IR spectra were recorded as KBr pellets on a Nicolet FT-205 spectrophotometer. UV−vis spectra were recorded on a Varian Cary 2300 spectrophotometer in Optima solvents. HPLC were performed on a Waters instrument with a C_{18} *Hypersil* (250 × 4.6 mm) analytical column, and UV−vis detector (at 340 nm). FAB mass spectra were obtained on a VG-ZAB-SE mass spectrometer using *m*-nitrobenzyl alcohol as a matrix.

1,2-Dihydrofullerene[60]-1,2-cyclobutenediamine 2a. To a solution of C_{60} (200 mg, 0.28 mmol) in 100 mL of toluene was added **1a** (52 μL, 0.28 mol). The reaction mixture was stirred at room temperature for 30 min. The toluene was evaporated under reduced pressure. The crude product was chromatographed on SiO_2. Elution with hexane and toluene (4:1) gave C_{60} (43 mg) and **2a** (129 mg, 53%): ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 3.60 (q, 8 H, $J = 6.95$ Hz), 1.47 (t, 12 H, $J = 6.95$ Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 157.08 (4 C), 146.14 (4 C), 146.11 (2 C), 145.59 (8 C), 144.90 (4 C), 144.82 (2 C), 144.63 (4 C), 144.21 (4 C), 142.58 (2 C), 142.49 (4 C), 142.14 (4 C), 142.13 (4 C), 141.80 (4 C), 139.96 (4 C), 138.64 (4 C), 136.90 (2 C), 74.94 (2 C, sp^3 fullerene), 46.74 (4 C, CH_2N), 13.91 (4 C, CH_3CH_2N); FT-IR (KBr) cm^{-1} 2965 (w), 1684 (m), 1420 (m), 1374 (w), 1183 (w), 1034 (w), 527 (vs); FAB MS *m/z* 889 (M + H, 100), 720 (C_{60}, 50), FAB HRMS obsd 888.1627, calcd for $C_{70}H_{20}N_2$ 888.1626.

1,2-Dihydrofullerene[60]-1,2-diamide 3a. A solution of **2a** (100 mg, 0.11 mmol) in 50 mL toluene was photooxygenated for 40 min under a slow stream of oxygen at room temperature. TLC and HPLC indicated clean formation of a single product, determined to be **3a**. Analytically pure **3a** was obtained by column chromatography on SiO_2 eluting with toluene: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$, 25 °C) δ 5.12 (br s, 2 H), 3.65 (br s, 6 H), 1.42 (t, 6 H, $J = 6.55$ Hz), 1.31 (t, 6 H, $J = 6.65$ Hz); at −78 °C, δ 5.29 (ABX_3, 2 H, $J_{AB} = 15.75$ Hz, $J_{AX} = 7.45$ Hz), 3.69 (m, 2 H), 3.62 (m, 2 H), 3.58 (ABX_3, 2 H, $J_{AB} = 15.70$ Hz, $J_{AX} = 7.10$ Hz), 1.44 (t, 6 H, $J = 6.80$ Hz), 1.30 (t, 6 H, $J = 6.80$ Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$, 25 °C) δ 170.25 (2 C, NCO), 150.87 (br), 147.21, 146.07, 145.81, 145.35, 145.06, 143.04, 142.37, 141.91, 141.43 (br), 139.47 (br), 134.94 (br), 76.13 (2 C, sp^3 fullerene), 43.99 (2 C, CH_2N), 43.15 (2 C, CH_2N), 13.82 (2 C, CH_3CH_2N), 12.68 (2 C, CH_3CH_2N); FT-IR (KBr) cm^{-1} 1638 (s), 1420 (s), 1258 (s), 1144 (m), 527 (vs); FAB MS *m/z* 920 (M, 40), 760 (M − 154, 100), 720 (C_{60}, 65); UV−vis λ_{max} (CH_2Cl_2) 704, 432, 310, 252. **3a** could be more conveniently prepared in 61% yield (based on recovered C_{60}) by a one-pot procedure without purification of **2a**.

1,2-Dihydrofullerene[60]-1,2-(ethylthio)cyclobutenamine 2b and 1,2-dihydrofullerene[60]-1,2-thioester amide 3b were prepared in a procedure similar to that for **2a** and **2b**, respectively, and in similar yields. Physical data for **2b**: ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 4.01 (q, 4 H, $J = 7.06$ Hz, CH_2N), 3.06 (q, 2 H, $J = 7.34$ Hz, CH_2S), 1.60 (t, 3 H, $J = 7.34$ Hz, CH_3CH_2S), 1.49 (t, 6 H, $J = 7.06$ Hz, CH_3CH_2N); ^{13}C NMR (100 MHz, $CS_2/CDCl_3$) δ 158.56 (1 C, $=C-N$), 157.01 (2 C), 154.45 (2 C), 146.58 (2 C), 146.38 (1 C), 146.13 (1 C), 145.72 (2 C), 145.68 (2 C), 145.56 (2 C), 145.53 (2 C), 145.45 (2 C), 144.91 (2 C), 144.72 (2 C), 144.67 (2 C), 144.63 (2 C), 144.38 (2 C), 143.90 (2 C), 142.70 (4 C), 142.43 (2 C), 142.41 (2 C), 142.21 (2 C), 142.14 (2 C), 141.98 (2 C), 141.79 (2 C), 141.67 (2 C), 141.50 (2 C), 140.13 (2 C), 139.83 (2 C), 139.53 (2 C), 137.96 (2 C), 101.50 (1 C, $=C-S$), 76.55 (1 C), 76.13 (1 C), 43.64 (2 C, CH_2N), 31.46 (CH_2S), 15.31 (CH_3CH_2S), 13.97 (2 C, CH_3CH_2N); FT-IR (KBr) cm^{-1} 2971 (w), 1617 (s), 1457 (w), 576 (w), 527 (vs); FAB MS *m/z* 879 (M + 2, 88), 720 (C_{60}, 100), FAB HRMS obsd 877.0941, calcd for $C_{68}H_{15}NS$ 877.0925; UV−vis λ_{max} (ϵ) (CH_2Cl_2) 480 (1184), 431 (2307), 404 (sh, 3500), 32 (31 200), 306 (sh, 32 800), 253 (104 200). Physical data for **3b**: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$, 25 °C) δ 4.99 (br s, 1 H), 3.87 (br s, 1 H), 3.74 (br s, 1 H), 3.42 (br s, 1 H), 3.24 (br s, 2 H, CH_2S), 1.54 (t, 3 H, $J = 7.50$ Hz), 1.45 (t, 3 H, $J = 6.90$ Hz), 1.34 (t, 3 H, $J = 7.00$ Hz); at 0 °C, δ 5.02 (ABX_3, 1 H, $J_{AB} = 15.50$ Hz, $J_{AX} = 7.45$ Hz), 3.90 (ABX_3, 1 H, $J_{AB} = 13.20$ Hz, $J_{AX} = 6.75$ Hz), 3.70 (ABX_3, 1 H, $J_{AX} = 15.5$ Hz, $J_{AX} = 7.20$ Hz), 3.36 (ABX_3, 1 H, $J_{AX} = 13.20$ Hz, $J_{AB} = 6.65$ Hz), 3.24 (m, 2 H, CH_2S), 1.52 (t, 3 H, $J = 7.45$ Hz), 1.44 (t, 3 H, $J = 7.00$ Hz), 1.33 (t, 3 H, $J = 7.05$ Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$, 25 °C) δ 198.31 (COS), 169.43 (CON), 147.17, 146.08, 145.90, 145.20 (br), 142.88, 142.36, 141.95, 141.60 (br), 141.24 (br), 139.32 (br), 81.19, 75.41, 43.11 (CH_2N), 42.79 (CH_2N), 25.82 (CH_2S), 14.33 (CH_3CH_2S), 13.71 CH_3CH_2N), 11.99 (CH_3CH_2N); FT-IR (KBr) cm^{-1} 2950 (w), 1669 (s), 1636 (s), 1456 (w), 1348 (w), 1258 (s), 1144 (m), 576 (w), 527 (vs); FAB MS *m/z* 910 (M + H, 38), 848 (M − SCH_2CH_3, 53), 720 (C_{60}, 100), FAB HRMS obsd 910.0896, calcd for $C_{68}H_{16}NSO_2$ 910.0902; UV−vis λ_{max} (CH_2Cl_2) 704, 433, 312, 253.

1,2-Dihydrofullerene[60]-1,2-dicarboxylic Acid Anhydride (4) from 3a. Compound **3a** (24 mg, 0.026 mmol) and *p*-toluenesulfonic acid monohydrate (13 mg, 0.8 mmol) were heated in 15 mL of toluene at 60 °C for 10 h. HPLC indicated quantitative formation of anhydride **4**. After the reaction mixture had cooled to room temperature, phosphate buffer (20 mL) was added, and the organic layer was separated, dried (Na_2SO_4), and evaporated to give 18 mg (88%) of **4**. HPLC indicated that this sample contained ca. 10% of C_{60} (decomposition of the anhydride by water). Physical data for **4**: ^{13}C NMR (125 MHz, CS_2/acetone-d_6, $Cr(acac)_3$) δ 167.65 (2 C, CO), 147.63 (2 C), 146.87 (4 C), 146.82 (4 C), 146.73 (4 C), 146.44 (4 C), 146.31 (4 C), 145.77 (4 C), 145.69 (2 C), 144.66 (4 C), 143.45 (2 C), 143.20 (4 C), 142.72 (4 C), 142.46 (4 C), 141.75 (4 C), 141.09 (4 C), 136.98 (4 C), 72.07 (2 C, sp^3 fullerene); FT-IR (KBr) cm^{-1} 1850 (w), 1786 (s), 1420 (w), 1211 (s), 1186 (m), 1043 (m), 959 (s), 594 (m), 527 (s); FAB MS *m/z* 766 (M + 2 − CO, 50) 720 (C_{60}, 100); UV−vis λ_{max} (ϵ) (CH_2Cl_2) 426 (2030), 316 (32 300), 250 (96 900). An alternative procedure for workup of **4** is to filter the salt and excess of PTSA formed in the reaction, both of which precipitate after prolonged standing at room temperature. A sample prepared in this way contained significantly less C_{60}.

1,2-Dihydrofullerene[60]-1,2-dicarboxylic Acid Anhydride (4) from 3b. Compound **3b** (10 mg, 0.011 mmol) and *p*-toluenesulfonic acid monohydrate (20 mg, 0.11 mmol) in 15 mL of toluene were heated at 100 °C for 14 h. HPLC indicated quantitative formation of **4**. The reaction mixture was left at room temperature for 24 h under argon. A white precipitate was filtered, and the filtrate was condensed to give **4** (8 mg, 93%).

1,9-Dihydrofullerene[70]-1,9-cyclobutenediamine 5. To a solution of C_{70} (30 mg, 0.036 mmol) in 25 mL of toluene was added **1a** (6 μL, 0.035 mol). The reaction mixture was stirred at 0 °C for 15 min and at room temperature for 30 min, and the solvent was evaporated under reduced pressure. The crude product was chromatographed on SiO_2. Elution with hexane and toluene (4:1) gave **5** (19 mg, 60%): ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 3.77 (q, 4 H, $J = 7.10$ Hz), 3.19 (q, 4 H, $J = 7.15$ Hz), 1.47 (t, 6 H, $J = 7.10$ Hz), 1.30 (t, 6 H, $J = 7.15$ Hz). ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 156.79 (2 C), 156.40 (2 C), 151.99 (2 C), 151.50 (1 C), 151.24 (2 C), 150.61 (2 C), 150.48 (2 C), 149.86 (2 C), 149.74 (2 C), 149.61 (2 C), 149.51 (2 C), 149.25 (2 C), 149.09 (2 C), 148.77 (2 C), 148.67 (2 C), 147.36 (2 C), 147.32 (2 C), 146.73 (2 C), 146.70 (1 C), 146.58 (2 C), 146.06 (2 C), 145.69 (2 C), 145.28 (2 C), 143.52 (2 C), 143.28 (2 C), 143.12 (2 C), 142.59 (2 C), 142.55 (2 C), 141.50 (2 C), 139.50 (2 C), 138.47 (1 C), 134.33 (2 C), 133.28 (2 C), 131.13 (2 C), 131.04 (2 C), 131.01 (2 C), 129.22 (1 C), 67.38 (1 C, sp^3 fullerene), 64.87 (1 C, sp^3 fullerene), 47.54 (2 C, NCH_2), 46.03 (2 C, NCH_2), 14.09 (2 C, CH_3), 14.08 (2 C, CH_3); FT-IR (KBr) cm^{-1}

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[52] Scrivens, W. A.; Bedworth, P. V.; Tour, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 7917−7919.

2950 (w), 1684 (m), 1469 (m), 1427 (s), 1373 (m), 1235 (m), 1082 (w), 795 (m), 731 (m), 671 (m), 592 (w), 571 (w), 532 (s); FAB HRMS obsd 1008.1645, calcd for $C_{80}H_{20}N_2$ 1008.1626. UV−vis λ_{max} (cyclohexane) 536 (sh), 460, 396, 272 (sh), 234.

Tetrahydrofullerene[70]-1,9;61,62-biscyclobutenediamine 6. To a solution of C_{70} (15 mg, 0.018 mmol) in 25 mL of toluene was added **1a** (7 μL, 0.39 mol). The reaction mixture was stirred at room temperature for 40 min. The solvent was then evaporated under reduced pressure. The crude product was chromatographed on SiO_2. Elution with hexane/toluene (3:1) gave **6** (14 mg, 70%) as a mixture of two isomers in a ratio of 9:1. The major isomer is tentatively assigned as 1,9:61,62-biscyclobutenediamine **6**: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 3.76 (q, 4 H, J = 7.05 Hz), 3.20 (q, 4 H, J = 7.15 Hz), 1.47 (t, 6 H, J = 7.10 Hz), 1.30 (t, 6 H, J = 7.05 Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 159.27 (2 C), 157.30 (2 C), 156.09 (2 C), 154.99 (2 C), 154.77 (2 C), 152.37 (2 C), 151.53 (2 C), 151.24 (2 C), 150.75 (2 C), 150.13 (2 C), 149.61 (2 C), 148.45 (2 C), 148.41 (2 C), 147.03 (2 C), 147.01 (2 C), 146.95 (2 C), 146.57 (2 C), 145.94 (2 C), 144.89 (2 C), 143.84 (2 C), 143.30 (2 C), 143.07 (2 C), 141.68 (2 C), 141.15 (2 C), 140.77 (2 C), 140.53 (2 C), 139.87 (2 C), 139.22 (2 C), 137.95 (2 C), 136.91 (2 C), 133.52 (2 C), 133.33 (2 C), 131.79 (2 C), 131.33 (2 C), 128.45 (2 C), 67.73 (2 C, sp^3 fullerene), 65.50 (2 C, sp^3 fullerene), 47.29 (2 C, NCH_2), 45.64 (2 C, NCH_2), 13.90 (2 C, CH_3), 13.86 (2 C, CH_3); FT-IR (KBr) cm^{-1} 2967 (w), 1686 (s), 1472 (m), 1441 (s), 1412 (s), 1375 (s), 1267 (m), 1236 (m), 1061 (m), 794 (m), 669 (m), 527 (m); FAB MS m/z 1176 (M$^+$, 100), 1008 (M − 168, 30), 840 (C_{70}, 78); FAB HRMS obsd 1176.3184, calcd for $C_{90}H_{40}N_4$ 1176.3253; UV−vis λ_{max} (hexane) 660, 468, 406, 232.

Tetrahydrofullerene[70]-1,9;61,62-tetraamide 7. A solution of **6** (30 mg, 0.026 mmol) in 50 mL of CH_2Cl_2 was photooxygenated for 1.0 h under a slow stream of oxygen. TLC indicated disappearance of starting material **6**. The solvent was then evaporated, and the resulting crude product was chromatographed on SiO_2. Elution with toluene gave C_{70} (12 mg), then tetramide **7** (6 mg, 20%): ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) 25 °C, δ 4.92 (br s, 2 H, NCH_2), 4.58 (br s, 2 H, NCH_2), 3.59 (br s, 6 H, NCH_2), 3.36 (br q, 6 H, J = 6.80 Hz), 1.59 (br 5, 6 H, J = 6.80 Hz), 1.37 (br t, 6 H, J = 6.90 Hz), 1.20 (t, 12 H, J = 7.15 Hz), −20 °C d 4.91 (ABX_3, 2 H, J_{AB} = 15.8 Hz, J_{AX} = 8.30 Hz), 4.60 (ABX_3, 2 H, J_{AB} = 15.6 Hz, J_{AX} = 7.35 Hz), 3.60 (ABX_3, 2 H, J_{AX} = 15.6 Hz, J_{AX} = 7.30 Hz), 3.38 (m, 4H), 3.32 (m, 6 H), 1.57 (t, 6 HJ = 6.95 Hz), 1.34 (t, 6 H, J = 7.00 Hz), 1.17 (t, 12 H, J = 7.00 Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) 25 °C d 169.98 (CON), 168.89 (CON), 151.79, 151.59, 151.03, 150.62, 150.28, 150.19, 149.60, 149.53, 149.47, 149.13, 147.80, 147.48, 147.35, 146.22, 143.71, 143.65, 143.48, 133.72, 131.73, 131.51, 70.01, 68.16, 44.49, 43.63, 43.45, 14.84, 14.34, 13.34, 13.16; FT-IR (KBr) cm^{-1} 1638 (s), 1422 (s), 1258 (s), 1211 (m), 1142 (m), 795 (m), 729 (m), 671 (m), 598 (m), 569 (m), 542 (m), 534 (s); FABMS m/z 1240 (M, 32), 969 (M − 71, 100); UV−vis λ_{max} (hexane) 664, 532 (sh), 460, 396, 308 (sh), 230.

1,9-Dihydrofullerene[70]-1,9-(ethylthio)cyclobutenamine (8) and Dihydrofullerene[70]-1,9;61,62-bis(ethylthio)cyclobutenamine (9). To a stirred solution of C_{70} (20 mg, 0.024 mmol) in 20 mL of toluene was added **1b** (4.5 μL, 0.024 mmol). The reaction mixture was stirred at room temperature for 2.0 h. TLC indicated little C_{70} remained, and two products were formed in almost equal amounts. Toluene was evaporated under reduced pressure. The crude product was chromatographed on SiO_2. Elution with hexane:CS_2 (from 4:1 to 2:1) gave C_{70} (ca. 3 mg), **8** (9 mg, 38%), and **9** (6 mg, 27%). Physical data for **8**: ^{1}H NMR (400 MHz, $CS_2/CDCl_3$) δ 3.66 (q, 4 H, J = 7.09, NCH_2), 3.19 (q, 2 H, J = 7.34 Hz, SCH_2), 1.63 (t, 3 H, J = 7.34 Hz, $\mathbf{CH_3}CH_2S$), 1.32 (t, 6 H, J = 7.09 Hz, $\mathbf{CH_3}CH_2N$); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 156.94 (2 C), 155.18 (1 C), 153.41 (2 C), 152.16 (2 C), 151.30 (1 C), 151.07 (2 C), 150.44 (2 C), 150.16 (2 C), 149.78 (2 C), 149.74 (2 C), 149.49 (2 C), 149.47 (2 C), 149.05 (2 C), 148.78 (2 C), 148.64 (2 C), 148.35 (2 C), 147.18 (2 C), 146.79 (2 C), 146.56 (2 C), 146.48 (1 C), 146.37 (2 C), 146.21 (2 C), 145.61 (2 C), 145.47 (2 C), 143.12 (2 C), 143.08 (2 C), 143.03 (2 C), 142.25 (2 C), 141.70 (2 C), 141.18 (2 C), 140.53 (2 C), 133.69 (2 C), 132.96 (2 C), 131.09 (2 C), 130.78 (2 C), 130.70 (2 C), 99.55 (1 C), 69.90 (1 C, sp^3 fullerene), 67.18 (1 C, sp^3 fullerene), 43.35 (2 C, NCH_2), 31.19 (1 C, SCH_2), 15.35 ($\mathbf{CH_3}CH_2S$), 13.85 ($\mathbf{CH_3}CH_2N$); FT-IR (KBr) cm^{-1} 1624 (s), 1429 (s), 795 (m), 731 (m), 669 (m), 579 (m), 532 (s); FABMS m/z 998 (M + H, 50), 841 (C_{70} + H, 100), HRMS FAB calcd for $C_{78}H_{16}NS$ 998.1003, obsd 998.1041. Physical data for **9**: ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) δ 3.81 (q, 8 H, J = 7.15 Hz), 3.24 (q, 4 H, J = 7.30 Hz), 1.68 (t, 6 H, J = 7.30 Hz), 1.30 (t, 12 H, J = 7.15 Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) δ 157.90, 156.70, 156.55, 155.17, 155.02, 152.81, 152.08, 151.86, 151.40, 151.11, 150.07, 149.87, 148.60, 148.31, 148.07, 147.73, 147.38, 147.08, 146.24, 144.47, 143.52, 143.13, 142.68, 142.46, 141.30, 141.26, 141.17, 140.35, 139.05, 136.47, 133.50, 133.24, 132.03, 131.27, 99.15, 70.41, 68.01, 43.29, 31.22, 15.36, 13.78; FT-IR (KBr) cm^{-1} 2969 (w), 2923 (w), 1624 (s), 1443 (m), 1412 (m), 795 (m), 676 (m), 525 (m); FABMS m/z 1155 (M + H, 50), 841 (C_{70} + H, 100); HMRS FAB calcd for $C_{86}H_{31}N_2S_2$ 1155.1929, obsd 1155.1974; UV−vis λ_{max} (cyclohexane) 664, 528 (sh), 473 (sh), 412, 233.

1,9-Dihydrofullerene[70]-1,9-*tert*-butylthioester Amide 10. To a solution of C_{70} (50 mg, 0.060 mmol) in 40 mL of toluene was added **1c** (12 μL, 0.060 mol). The reaction mixture was stirred at room temperature overnight and then photooxygenated for 40 min. The solvent was evaporated under reduced pressure. The crude product was column chromatographed on SiO_2. Elution with toluene gave **10** (32 mg, 51%): ^{1}H NMR (500 MHz, $CS_2/CDCl_3$) 25 °C, δ 4.54 (br s, 1 H), 3.50 (br s, 2 H), 3.30 (br s, 1 H), 1.73 (s, 9 H), 1.26 (t, 3 H, J = 7.20 Hz), 1.23 (t, 3 H, J = 7.20 Hz); ^{13}C NMR (125 MHz, $CS_2/CDCl_3$) 25 °C δ 198.10 (COSO, 168.08 (CON), 160.64, 157.45, 153.75, 153.60, 151.09, 150.89, 150.39, 150.13, 149.90, 149.55, 149.04, 148.79, 148.58, 148.45, 147.24, 147.01, 146.87, 146.66, 146.19, 145.56, 143.75, 143.37, 143.07, 142.95, 142.85, 142.69, 141.72, 140.15, 139.86, 138.66, 134.55, 133.47, 133.05, 131.18, 130.79, 73.51, 68.73, 49.94, 43.22, 42.58, 29.44, 13.39, 12.22; FT-IR (KBr) cm^{-1} 2960 (w), 1663 (m), 1642 (s), 1454 (m), 1429 (s), 1416 (s), 1258 (m), 1036 (m), 850 (m), 797 (m), 673 (m), 534 (m); FAB MS m/z 1058 (M + H, 22), 841 (C_{70} + H, 50); FAB HRMS calcd for $C_{80}H_{20}NSO_2$ 1058.1215, obsd 1058.1206; UV−vis λ_{max} (hexane) 664, 532 (sh), 460, 396, 308 (sh), 232.

1,9-Dihydrofullerene[70]-1,9-dicarboxylic Acid Anhydride (11). Compound **10** (10 mg, 0.01 mmol) and p-toluenesulfonic acid monohydrate (34 mg, 0.18 mmol) in 35 mL of toluene were heated at 100 °C overnight. HPLC indicated quantitative formation of **11**. The reaction mixture was slowly cooled to room temperature. A white precipitate that formed upon cooling was filtered, and the filtrate was condensed to give a solid. The solid was redissolved in a small amount of CS_2. Upon adding petroleum ether, 9 mg (100%) of pure anhydride **11** precipitated: ^{13}C NMR (125 MHz, CS_2/CD_2Cl_2, Cr(acac)$_3$) δ 166.77 (1 C, CO), 166.59 (1 C, CO), 156.21 (2 C), 151.59 (2 C), 151.46 (2 C), 151.37 (2 C), 151.14 (2 C), 150.97 (2 C), 150.66 (2 C), 150.17 (2 C), 150.10 (2 C), 149.87 (2 C), 149.26 (2 C), 149.07 (2 C), 148.49 (2 C), 148.32 (2 C), 147.63 (2 C), 147.45 (1 C), 147.28 (2 C), 147.25 (2 C), 146.76 (2 C), 146.34 (2 C), 144.05 (2 C), 143.81 (2 C), 143.65 (2 C), 143.55 (2 C), 141.54 (1 C), 140.52 (2 C), 139.91 (2 C), 138.83 (2 C), 137.87 (2 C), 134.16 (2 C), 134.02 (2 C), 132.12 (2 C), 131.74 (2 C), 131.50 (2 C), 129.36 (2 C), 65.86 (1 C), 65.33 (1 C); FT-IR (KBr) cm^{-1} 1856 (w), 1782 (s), 1509 (m), 1428 (s), 1210 (s), 1019 (m), 957 (m), 797 (m), 671 (m), 596 (m); UV−vis λ_{max} (cyclohexane) (ϵ) 660 (1080), 460 (8890), 392 (9730, 233 (62 500); FABMS for m/z 841 (C_{70} + 1, 100), 738 (M − 174, 40).

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Supplementary Material Available: ^{1}H NMR and ^{13}C NMR spectra of compounds **2−11** (24 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm versino of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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