Functionalization of [60]Fullerene and of [60]Fullerene Monoadducts by Photochemical Cycloaddition of 4-Methyl-1,2,4-triazoline-3,5-dione

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The photoreactions of 4-methyl-1,2,4-triazoline-3,5-dione (NMTAD) with C_{60} and with several fullerene derivatives have been studied. In general, NMTAD cycloadds to C_{60} and to its monoadducts with closed structures in a highly regioselective [2+2] fashion at a *cis*-1 [6,6] double bond. Cycloadditions to azafulleroids occur by a slightly different pathway and result in partially cluster-opened bis(adducts). 1,6-Methano[60]fulleroid, however, also undergoes a [2+2+2] cycloaddition in the absence of light.

Introduction

Investigations into the regioselectivity of multiple functionalizations of fullerenes have revealed three aspects to be responsible for the observed regioselectivity of twofold additions to fullerenes.[1−4] These are enhanced frontier orbital coefficients, more reactive, compressed [6,6] double bonds and the possibility of forming thermodynamically more stable addition products and they can be related to the characteristic cage distortion present in monoadducts.[2b,3] The addition reactions to [6,6] double bonds of 1,2-monoadducts of C_{60} proceed with a preference for attack at the *e*- and *trans*-3 bonds for sterically demanding addends such as $C(COOEt)_2$, and at *e*-, *trans*-3 and *cis*-1 for sterically less demanding addends such as imino groups. Second functionalizations of azafulleroids proceed highly regioselectively at the [6,6] double bond next to the imino bridge.[5−10]

The most versatile and straightforward reactions in fullerene chemistry are cycloadditions to the [6,6] double bonds, and it is known from previous investigations that fullerenes react as dienophiles in [4+2] cycloadditions.[3] Rubin et al., however, reported a reaction sequence, opening the fullerene cage, in which a [60]fullerene derivative acts as diene.[11] One of the most reactive dienophiles for Diels−Alder reactions is 4-methyl-1,2,4-triazoline-3,5-dione (NMTAD),[12] and Sheridan et al. have reported photoinduced [4+2] cycloadditions of NMTAD to arenes.[13] On the other hand, NMTAD reacts with alkenes through photoinduced [2+2] cycloadditions to yield diazetidines.[12a] In this report we focus on photoinduced reactions of NMTAD with [60]fullerene and with several fullerene derivatives.

Results and Discussion

Our initial idea was to carry out [4+2] cycloaddition reactions with fullerene derivatives and NMTAD, in which the fullerenes would react as dienes. Since the *cis*-1 [6,6] double bond in sterically less demanding monoadducts is the preferred bond to be attacked, we chose as the first fullerene compound the Diels−Alder adduct **1** of C_{60} and cyclopentadiene. The advantage of this fullerene derivative is the reversibility of the cyclopentadiene addition on heating, so it should be possible to remove the cyclopentadiene addend after addition of NMTAD. Furthermore, we also investigated additions of NMTAD to the 1-functionalized 1,2-dihydro[60]fullerenes **2** and **3**, since the *cis*-1 bond near the hydrogen atom is not subject to any steric demand.[14]

For the preparation of the addition products **4**, **5** and **6**, solutions of NMTAD and fullerene monoadducts **1**, **2** and **3** in 1,1,2,2-tetrachloroethane were irradiated at 419 nm for 3−4 h (Scheme 1). Chromatography on silica gel afforded bis(functionalized) fullerene derivatives **4**, **5** and **6** in 30, 24 and 43% yields, respectively. Their compositions were confirmed by mass spectrometry.

The ^{13}C NMR spectra of all three products each display 60 resonances for the fullerene carbon atoms: 56 sp^2 resonances in the region of $\delta = 120-150$ ppm and four single-intensity resonances assigned to sp^3-hybridized fullerene carbon atoms. Additionally, the spectra also each show two signals for the carbonyl groups at $\delta \approx 162$ ppm and one signal for the methyl group linked to the nitrogen atom. The remaining signals are attributable to the carbon atoms of the cyclopentadiene addend and the alkyl groups, respectively.

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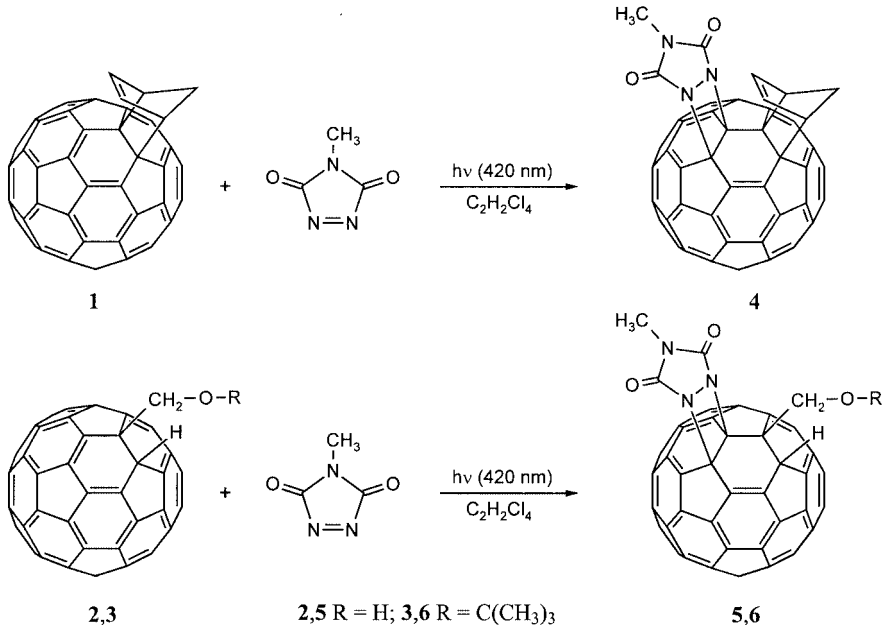


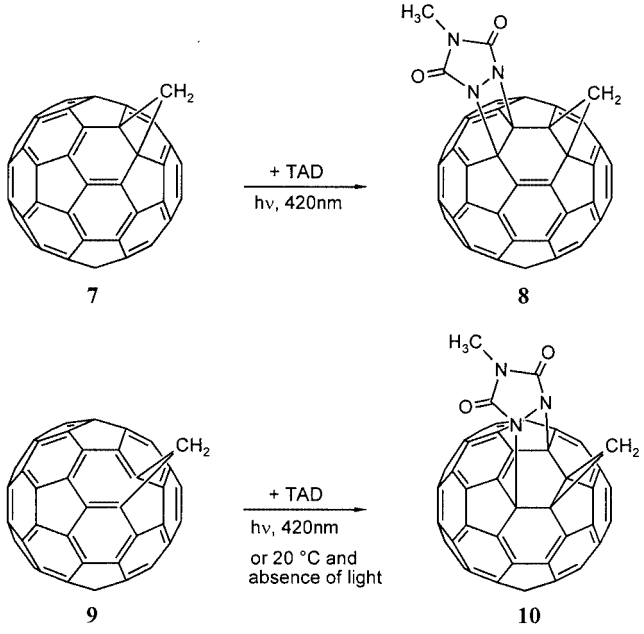
Scheme 1. Photochemical addition of NMTAD to 1,2-dihydro[60]fullerene derivatives

The ^{1}H NMR spectrum of **4** contains seven signals: one singlet for the *N*-methyl group, two double doublets at δ = 7.01 and 6.87 ppm for the olefinic hydrogen atom, two multiplets at δ = 4.51 and 4.48 ppm for the bridgehead hydrogen atom and a broad doublet for the methylene hydrogen atom. Because of the stronger shift of the olefinic hydrogen signal in relation to the bridgehead hydrogen signal we regard the olefinic hydrogen atom as closer to the second addend than the bridgehead hydrogen atom. The ^{1}H NMR spectra of **5** and **6** show, besides the signals for the addend, hydrogen singlets at δ = 6.62 and 6.33 ppm, respectively, attributable to the fullerenyl hydrogen atom. These patterns are indicative of C_1-symmetrical tetrahydro[60]fullerene derivatives. Further evidence is provided by the UV/Vis spectra, which each exhibit the characteristic absorption for [6,6] closed fullerene derivatives at λ ≈ 425 nm, typically, however, slightly shifted to longer wavelength than in the monoadducts.[15]

The connectivity of **6** is confirmed by a two-dimensional NMR spectrum (heteronuclear multiple bond correlation). The spectrum clearly shows *cis*-1 stereochemistry. Furthermore, the spectra indicate that the addition of NMTAD has occurred at the *cis*-1 [6,6] double bond next to the alkyl group. From this structure determination we assume the same stereochemistry for **4** and **5**.

The 1,2-methano[60]fullerene **7** behaves similarly, addition of NMTAD having been accomplished through a photoinduced reaction in a [2+2] fashion, also giving rise to a tetrahydro[60]fullerene derivative **8** (Scheme 2). The structure is inferred from ^{13}C NMR spectra and comparison to the structure determination of **6**, revealing C_1 symmetry with *cis*-1 regiochemistry.

The 1,6-methano[60]fulleroid **9** behaves quite differently though. The photoinduced reaction with NMTAD proceeds through a [2+2+2] cycloaddition, giving rise to a



Scheme 2. Products of NMTAD addition to the isomeric monoadducts 1,2- and 1,6-$C_{61}H_2$

bis(functionalized) [60]fullerene adduct **10** with a [5,6] closed structure and a plane of symmetry (Scheme 2). In accord with this result, 1,6-methano[60]fulleroid **9** also reacts with NMTAD without irradiation; that is, in a thermal process even at room temperature, yielding the identical addition product **10**. Alternatively, one might consider an equilibrium between **9** and its ring-closed valence isomer, which could undergo a Diels−Alder reaction with NMTAD to yield **10**. No such equilibrium has yet been reported, however, especially at room temperature.

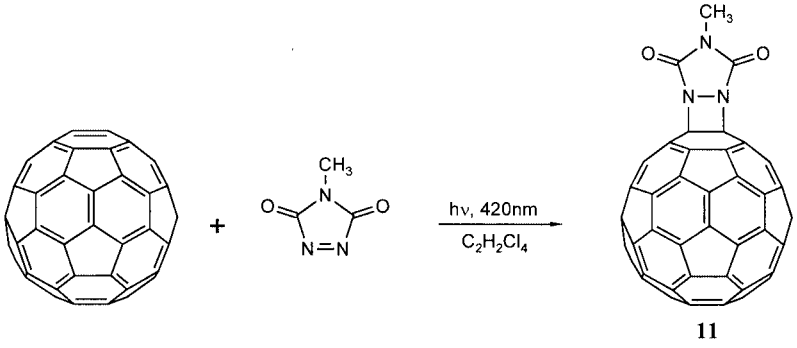
The structure of **10** was elucidated by ^{13}C and ^{1}H NMR spectroscopy. Its ^{13}C NMR spectrum consists of 35 reson-

ances. Of these, 32 can be attributed to the fullerene carbon atoms: 30 in the sp^2 region and two at δ = 93.04 and 70.53 ppm for the sp^3 carbon atoms in the fullerene framework. The remaining three resonances are attributable to the carbonyl carbon atoms (δ = 162.60 ppm), the methano bridge (δ = 30.17 ppm) and the *N*-methyl group (δ = 26.36 ppm). The appearance of the signals at δ = 93.04 and 70.53 ppm, with intensities of two, indicate two types of sp^3-hybridized fullerene carbon atoms. Together with the number of sp^2 resonances, the structure is assignable as C_s-symmetrical with four sp^3 fullerene carbon atoms (i.e., both the triazolanedione addend and the methano bridge are connected to sp^3 carbon atoms of the fullerene core). A [2+2+2] cycloaddition of NMTAD at both [6,6] double bonds next to the methano bridge in **9** is the only possible means by which to achieve a structure showing such a ^{13}C NMR spectrum. The ^1H NMR spectrum displays a singlet at δ = 3.18 ppm for the methyl hydrogen atom and a broad singlet at δ = 1.30 ppm for the methano hydrogen atom. Furthermore, the strong upfield shift of the methano hydrogen resonances in relation to 1,6-methano[60]fulleroid[16] indicates the triazolanedione addend to be close to the methano bridge.

In the photoinduced reaction with NMTAD, C_{60} shows similar behaviour, forming the [2+2] cycloadduct **11** (Scheme 3). However, the reactivity of C_{60} in relation to the monoadducts seems to be strongly decreased. Whereas **11** was obtained only in 5% yield, addition of NMTAD to the investigated dihydrofullererenes yielded 23−43%. The ^{13}C NMR spectrum verifies the structure of **11**. The spectrum displays 19 resonances: 16 fullerene sp^2 signals and one sp^3 signal, indicating the expected C_{2v} symmetry. Further evidence is provided by the UV/Vis spectrum, which shows the characteristic absorption for 1,2-functionalized [60]fullerene derivatives at λ = 418 nm.[15]

To verify the differences in the reactions of NMTAD with the two isomers 1,2-$C_{61}H_2$ (**7**) and 1,6-$C_{61}H_2$ (**9**), we investigated the photochemical additions of NMTAD to two pairs of isomeric imino[60]fullerenes: 1,2-[(4′-methylphenylsulfonyl)aziridino][60]fullerene (**12**)/1,6-[(4′-methylphenylsulfonyl)aza][60]fulleroid (**13**) and 1,2-(phenylaziridino)[60]fullerene (**14**)/1,6-(phenylaza)[60]fulleroid (**15**). Solutions of the monoadducts and NMTAD in 1,1,2,2-tetrachloroethane were therefore irradiated at 419 nm for 1−2 h. In both cases − addition of NMTAD to **12** and **13** as well as to **14** and **15** − the formation of the same cycloadducts **16** and **17**, respectively, was observed (Scheme 4).

The structures of **16** and **17** were confirmed by mass spectrometry and by spectroscopic methods. MALDI-TOF mass spectra show the molecular ion peaks at *m*/*z* = 1002



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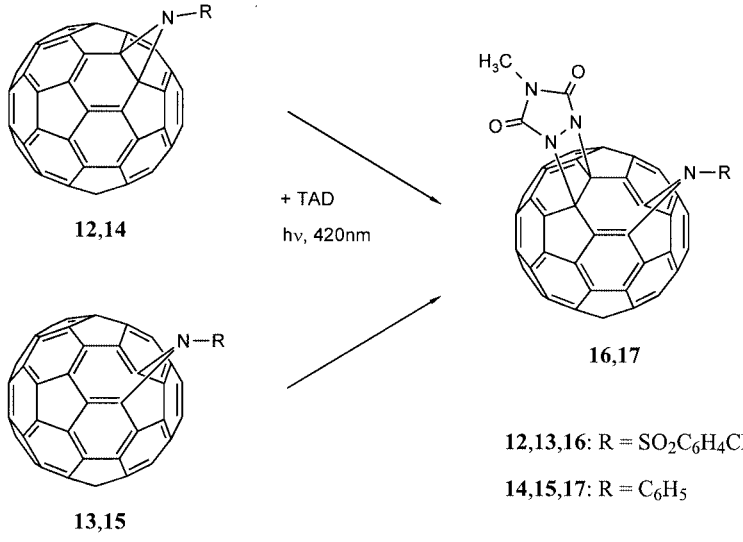
Scheme 3. Photochemical addition of NMTAD to C_{60}



12,13,16: R = $SO_2C_6H_4CH_3$

14,15,17: R = C_6H_5

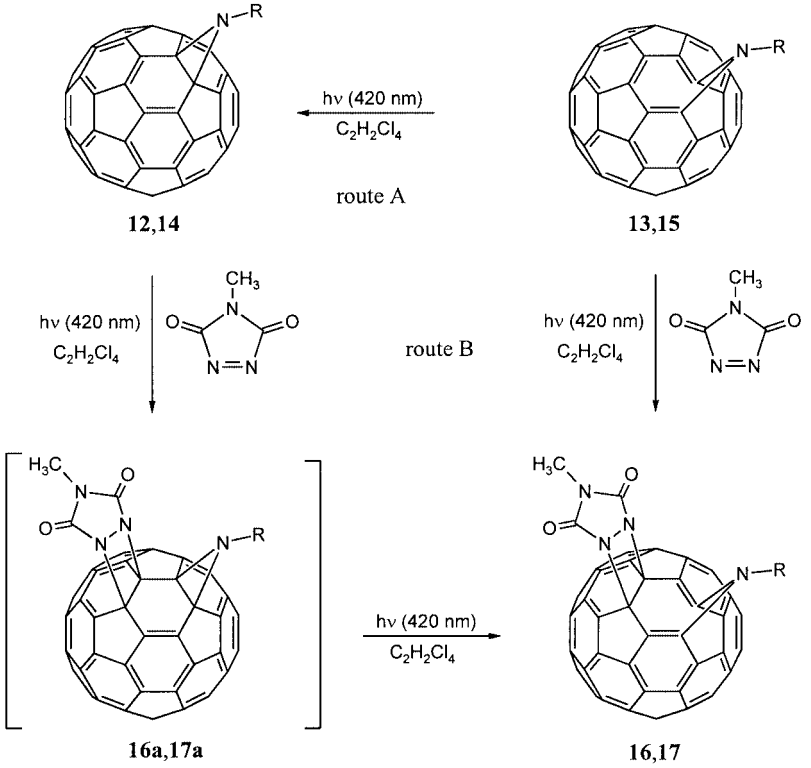
Scheme 4. Addition of NMTAD to the aziridinofullerene/azafulleroid pairs **12/13** and **14/15**

(**16**) and 924 (**17**). The ^{13}C NMR spectra each show 31 signals in the sp^2 region for the fullerene carbon atoms and only one resonance for sp^3-hybridized fullerene carbon atoms, but with an intensity of two. Furthermore each spectrum displays one signal for the two carbonyl carbon atoms and four signals each for the aromatic carbon atoms. These results indicate C_s-symmetrical structures for both adducts, in which the two addends are perpendicular to the plane of symmetry. In addition, one addend must be connected to sp^3-hybridized fullerene carbon atoms and the other one to sp^2-hybridized fullerene carbon atoms, indicating a combination of cluster-opened and cluster-closed functionalization. These results are only consistent with the proposed structures of **16**/**17** in Scheme 3. We suggest, at least for the addition of NMTAD to the 1,2-closed isomers, that rearrangement must be involved at a certain stage (Scheme 4).

Two routes for the formation of **16** and **17** through photochemically induced cycloaddition of NMTAD to **12** and **14** might be possible. The first possibility is addition of NMTAD to a *cis*-1 [6,6] double bond, as in the case of 1,2-dihydrofullerenes to the intermediates **16a** and **17a**, followed by a rearrangement of the imino bridge from the 1,2 to the 1,6 position (route A, Scheme 5). The second possibility is initial rearrangement of the imino bridge into the 1,6 position, followed by [2+2] cycloaddition of NMTAD to the [3,4] double bond. However, the second pathway seems to be impossible since irradiation of **12** and **14** at λ = 419 nm in tetrachloroethane in the absence of NMTAD does not produce the cluster-opened isomers **13** and **15**.

Two reaction pathways might also be possible for the formation of **16** and **17** by photoinduced cycloaddition of NMTAD to **13** and **15**: either direct addition of NMTAD to the [6,6] double bond in position 3,4 (route B) or a pathway containing three reaction steps (route A). In the latter case, a rearrangement of the azafulleroid to the corresponding aziridinofullerene occurs first, followed by [2+2] cycloaddition of NMTAD with formation of the intermediates **16a** and **17a** and final rearrangement of the imino bridge into the opened form. Two factors are consistent with the second pathway: (i) irradiation of azafulleroids **13** and **15** in the presence of NMTAD yielded traces of the corresponding aziridinofullerenes **12** and **14** together with the bis(functionalized) main products **14** and **17**, and (ii) irradiation of **13** and **15** in the absence of NMTAD exclusively yielded the corresponding aziridinofullerenes **12** and **14**.

In consideration of these observations, we assume a [2+2] cycloaddition to a *cis*-1 double bond followed by a rearrangement of the 1,2-connected imino bridge to a 1,6-connected bridge with azafulleroid structure for the mecha-



Scheme 5. Possible reaction pathways for addition of NMTAD to **12**, **13**, **14**, and **15** with formation of **16** and **17**

nism of photoinduced addition of NMTAD to the corresponding isomers **12/13** and **14/15**. For the azafulleroids this means that a previous rearrangement to the corresponding aziridinofullerenes must occur.

Conclusions

In agreement with previous investigations into bis(functionalizations) of fullerenes,[1−4] photoinduced addition of NMTAD to 1,2-dihydro[60]fullerenes proceeds at a *cis*-1 [6,6] double bond with formation of 1,2,3,4-tetrahydro[60]fullerene derivatives. NMTAD addition to 1-substituted 1,2-dihydrofullerenes takes place at the *cis*-1 double bond next to the substituent, indicating its higher reactivity in relation to the *cis*-1 double bond next to the fullerenyl hydrogen atom. In accord with previous investigations,[3] this double bond might have more enhanced frontier orbital coefficients or be the more compressed *cis*-1 double bond. NMTAD undergoes a [2+2+2] cycloaddition with the 1,6-opened methano[60]fulleroid, achievable either by irradiation or in a thermal process even at room temperature.

Surprisingly, photoinduced additions of NMTAD to isomeric iminofullerenes yield identical 1,3,4,6-functionalized bis(adducts) with partially opened cluster structure. Presumably, these reactions occur through [2+2] cycloaddition and one or two rearrangements, depending on the choice of isomer used.

Experimental Section

General Remarks: The C_{60} used was gold grade (Hoechst, ≥ 99.4%). All reactions were performed under argon. *o*-Dichlorobenzene was of purum grade (≥ 98%), toluene, carbon disulfide, acetonitrile and 1,1,2,2-tetrachloroethane were used in per analysis quality. Cyclohexane was used freshly distilled. Removal of all solvents was carried out under reduced pressure. The solutions were irradiated in Pyrex tubes (10 mL) in an RPR 100 Rayonet Photochemical Chamber Reactor with RPR 4190 Å lamps. Analytical high performance liquid chromatography (HPLC) was performed on a C_{18}-reversed-phase column (Macherey ET 250/4 Nucleosil 100-5) with toluene/acetonitrile (1:1.1) as liquid phase (UV/Vis detection at 300 nm Kontron HPLC detector 432), flow 1.1 mL min^{-1} (Merck L-6000 pump). For preparative HPLC, a Bucky Clutcher column (Regis, precolumn 50 × 10.0 mm, column 250 × 21.1 mm, Bucky Clutcher I, 10 μm, 100 Å), an Abimed-Gilson Spectrochrom detector (UV/Vis detection at 300 nm) and a Kontron HPLC pump 420 (flow: 10 mL min^{-1}) were used. Column chromatography was performed on silica gel (Macherey−Nagel, 63−200 μm and 40−60 μm). After isolation, products were purified by dissolving in CS_2, precipitating with *n*-pentane, centrifugation and decantation to remove the pentane-soluble components. They were finally dried under vacuum. Matrix laser desorption time-of-flight mass spectra (MALDI-TOF) were recorded with a Voyager™ DE instrument {PE Biosystems, nitrogen laser, λ = 337 nm, matrix: 2-[(2*E*)-3-(4-*tert*-butylphenyl)-2-methylprop-2-enylidene]malonodinitrile (DCTB), linear mode}. Relative intensities are given in percentages. NMR spectra were recorded with Bruker AM 300 and DRX 500 spectrometers. Chemical shift data are reported relative to the solvent peak as reference. Fourier transform IR spectra were recorded with a Perkin−Elmer 1600-FTIR spectrometer. UV/Vis spectra were measured with a Perkin−Elmer Lambda 40 spectrophotometer.

Photochemical Addition of NMTAD to 1,2-Dihydrofullerenes

Synthesis of 4′-Methyl-3′,5′-dioxo-1′,2′,4′-triazabicyclo[3.2.0]-heptano-[6′,7′:1,2]-endonorboneno-[6′′,7′′:3,4]-1,2,3,4-tetrahydro-[60]fullerene (4): A solution of cyclopentadiene−C_{60} adduct **1** (50 mg, 0.06 mmol) and NMTAD (14 mg, 0.12 mmol) in 1,1,2,2-tetrachlorethane (30 mL) was deoxygenated by purging with argon and irradiated at λ = 419 nm for 4 h in Pyrex tubes. The solvent was evaporated under reduced pressure. Chromatography on silica gel 60 first gave C_{60} (12 mg, 26%, eluent: toluene/cyclohexane, 1:1) and then **4** (17 mg, 30%, 2nd fraction, eluent: chloroform). ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 4:1): δ = 7.01 (dd, $^3J_{H,H}$ = 3.0, 5.7 Hz; 1 H, 2′′-H or 3′′-H), 6.87 (dd, $^3J_{H,H}$ = 3.2, 5.7 Hz; 1 H, 2′′-H or 3′′-H), 4.52−4.50 (m, 1 H, 1′′-H or 4′′-H), 4.49−4.47 (m, 1 H, 1′′-H or 4′′-H), 3.76 (d, $^2J_{H,H}$ = 9.9 Hz; 1 H, 5′′-H), 3.34 (s, 3 H, 8′-H), 2.57 (dt, $^2J_{H,H}$ = 9.9, $^3J_{H,H}$ = 1.7 Hz, 1 H, 5′′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 4:1): δ = 161.19 and 160.06 (3′-C, 5′-C), 157.26, 150.94, 149.10, 148.77, 148.29, 148.17, 147.49, 147.41, 146.99, 146.61, 146.57, 146.54, 146.31, 146.29, 146.14, 146.10, 145.57, 144.97, 144.78, 144.76, 144.71, 144.67, 144.40, 144.32, 144.27, 144.17, 144.05, 143.99, 143.95, 143.87, 143.78, 143.63, 143.48, 143.45, 143.32, 142.88, 142.43, 142.39, 142.30, 142.26, 141.79, 141.56, 140.56, 140.45, 140.34, 140.27, 138.19, 138.08, 137.49, 137.46, 136.56, 136.35, 136.04, 134.92, 127.84, 127.39, 125.48, 125.39 (56 C_{60} sp^2 signals, 2′′-C, 3′′-C), 83.74 and 82.95 (1-C, 2-C), 73.49 and 68.71 (3-C, 4-C), 55.48 and 55.19 (1′′-C, 4′′-C), 46.00 (5′′-C), 26.13 (8′-C). FT-IR (KBr): $\tilde{\nu}$ = 2921 m (CH_2), 1721 s (C=O), 1636 m, 1508 w, 1430 m, 1379 m, 1261 m, 1097 m, 1017 m, 804 m, 696 m, 524 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [> 220 nm] (ε) = 228 (44870), 257 (55120), 301 sh (17560), 323 sh (14530), 428 (1150) nm. MS (MALDI-TOF, pos. ion mode, DCTB, 15 kV): *m*/*z* (%) = 899 (20) $[M]^+$ {calcd. 899.32}, 721 (100) $[M - C_8H_9N_3O_2]$.

Synthesis of 4′-Methyl-3′,5′-dioxo-1,2,3,4-tetrahydro-1′,2′,4′-triazabicyclo[3.2.0]heptano-[6′,7′:1,2]-3-hydroxymethyl-[60]fullerene (5): A solution of 1-hydroxy-1,2-dihydro[60]fullerene (**2**) (114 mg, 0.152 mmol) and NMTAD (108 mg, 0.900 mmol) in 1,1,2,2-tetrachlorethane (80 mL) was deoxygenated by purging with argon and irradiated at 419 nm for 3 h in Pyrex tubes. The solvent was evaporated under reduced pressure. Chromatography on silica gel 60 first gave traces of C_{60} and remaining starting material (toluene). A change in the eluent to chloroform gave **5** (32 mg, 24%).^{1}H NMR (500.13 MHz, *o*-$C_6D_4Cl_2$): δ = 6.24 (s, 1 H, 4-H), 5.33−5.25 (m, 1 H, 1′′-H), 5.15−5.06 (m, 1 H, 1′′-H), 3.99−3.90 (m, 1 H, 1′′-OH), 3.25 (s, 3 H, 8′-H) ppm. ^{13}C NMR (125.76 MHz, *o*-$C_6D_4Cl_2$): δ = 161.59 and 161.39 (3′-C, 5′-C), 153.83, 149.15, 148.87, 148.31, 148.26, 148.24, 148.10, 147.25, 146.63, 146.54, 146.48, 146.19, 146.08, 146.03, 145.90, 145.82, 145.15, 144.83, 144.75, 144.54, 144.36, 144.34, 144.26, 144.19, 144.10, 144.03, 143.81, 143.73, 143.68, 143.46, 143.28, 143.08, 142.87, 142.64, 142.63, 142.30, 142.17, 141.99, 141.49, 141.10, 140.73, 140.35, 139.82, 139.28, 138.46, 137.52, 137.28, 136.80, 135.58, 135.30 (50 C_{60} sp^2 signals), 83.29 (ts, $^3J_{C,H}$ = 4.36 Hz, 2-C), 82.08 (s, 1-C), 71.63 (dt, $^1J_{C,H}$ = 149.06, $^3J_{C,H}$ = 9.42 Hz, 1′′-C), 61.70 (ds, $^2J_{C,H}$ = 4.94 Hz, 3-C), 53.69 (td, $^1J_{C,H}$ = 138.23, $^3J_{C,H}$ = 3.18 Hz, 4-C), 26.56 (q, $^1J_{C,H}$ = 142.45 Hz, 8′-C). FT-IR (KBr): $\tilde{\nu}$ = 3447 bm (OH), 2918 w, 1792 w, 1718 s (C=O), 1438 m, 1386 m, 1184 w, 1066 w, 525 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [> 220 nm] (ε) = 255 (106500), 322 sh (31300), 425 (4600) nm. MS (ESI): *m*/*z* (%) = 864 (95) $[M - H]^-$ {calcd. 865.08}, 752 (100) $[M - C_3H_3N_3O_2]^-$.

Synthesis of 4′-Methyl-3′,5′-dioxo-1′,2′,4′-triazabicyclo[3.2.0]heptano-[6′,7′:1,2]-3-*tert*-butoxymethyl-1,2,3,4-tetrahydro[60]fullerene (6): A solution of 1-(*tert*-butoxymethyl)-1,2-dihydro[60]fullerene **3** (175 mg, 0.217 mmol) and NMTAD (300 mg, 2.65 mmol) in 1,1,2,2-tetrachlorethane (120 mL) was deoxygenated by purging with argon and irradiated at 419 nm for 4 h in Pyrex tubes. The solvent was evaporated under reduced pressure. Chromatography on silica gel 60 first gave traces of C_{60} and remaining starting material (toluene). A change in the eluent to chloroform gave **6** (85 mg, 43%). ^{1}H NMR (500.13 MHz, *o*-$C_6D_4Cl_2$): δ = 6.33 (s, 1 H, 4-H), 5.14 (d, $^2J_{H,H}$ = 8.2 Hz, 1 H, 1′′-H), 4.82 (d, $^2J_{H,H}$ = 8.2 Hz, 1 H, 1′′-H), 3.26 (s, 3 H, 8′-H), 1.51 (s, 9 H, 4′′,5′′,6′′-H), ppm. ^{13}C NMR (125.76 MHz, *o*-$C_6D_4Cl_2$): δ = 161.97 and 160.61 (3′-C, 5′-C), 153.19, 149.15, 149.09, 148.82, 148.57, 148.34, 148.29, 148.27, 147.55, 147.28, 146.74, 146.63, 146.61, 146.52, 146.21, 146.07, 146.06, 145.97, 145.78, 145.14, 144.80, 144.75, 144.73, 144.36, 144.33, 144.19, 144.14, 144.04, 143.88, 143.79, 143.73, 143.54, 143.29, 143.23, 142.83, 142.77, 142.66, 142.36, 142.26, 142.16, 141.49, 140.93, 140.66, 140.42, 139.95, 138.90, 138.54, 138.06, 137.91, 137.57, 136.78, 136.64, 136.62 (53 C_{60} sp^2 signals), 81.97 (2-C), 81.61 (1-C), 73.95 (3′′-C), 70.85 (1′′-C), 59.02 (3-C), 55.65 (4-C), 27.18 (4′′,5′′,6′′-C), 26.56 (8′-C). FT-IR (KBr): $\tilde{\nu}$ = 1727 s (C=O), 1511 m, 1431 m, 1381 m, 1186 m, 524 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [> 220 nm] (ε) = 255 (97200), 322 sh (27200), 427 (4000) nm. MS (ESI): *m*/*z* (%) = 920 (100) $[M - H]^-$ {calcd. 921.11}, 807 (10) $[M - C_3H_4N_3O_2]^-$.

Synthesis of 4′-Methyl-3′,5′-dioxo-1′,2′,4′-triazabicyclo[3.2.0]heptano-[6′,7′:1,2]-cyclopropano-[2′′,3′′:3,4]-1,2,3,4-tetrahydro[60]-fullerene (8): 1,2-Cyclopropano[60]fullerene **7** (730 mg, 0.04 mmol) was dissolved in 1,1,2,2-tetrachlorethane (20 mL). After deoxygenation by purging with argon, NMTAD (14 mg, 0.12 mmol) was added and the solution was irradiated at 419 nm for 30 min in Pyrex tubes. The solvent was evaporated under reduced pressure. Chromatography on silica gel 60 with toluene/cyclohexane (1:1) first gave C_{60} (1.5 mg, 5%) and then 8 (17 mg, 30%, 2nd fraction). ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 4:1): δ = 4.74 (d, $^2J_{H,H}$ = 6.7 Hz; 1 H, 1′′-H), 3.37 (s, 3 H, 8′-H), 3.22 (d, $^2J_{H,H}$ = 6.7 Hz; 1 H, 1′′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 4:1): δ = 161.35 and 160.69 (3′-C, 5′-C), 155.56, 149.43, 149.29, 148.50, 148.42, 147.98, 147.62, 147.23, 146.87, 146.52, 146.46, 146.18, 146.13, 145.93, 145.80, 145.70, 145.66, 145.60, 145.36, 145.23, 145.04, 144.93, 144.71, 144.60, 144.53, 144.46, 144.45, 144.11, 144.06, 144.02, 143.98, 143.96, 143.79, 143.76, 143.71, 143.48, 143.46, 143.44, 143.23, 143.21, 142.92, 142.65, 142.54, 142.51, 142.27, 141.87, 141.58, 140.63, 140.60, 140.16, 140.00, 138.42, 138.09, 137.59, 137.45, 136.01 (56 C_{60} sp^2 signals), 85.17 and 80.81 (1-C, 2-C), 58.76 and 57.87 (3-C, 4-C), 29.20 (1′′-C), 26.58 (8′-C). FT-IR (KBr): $\tilde{\nu}$ = 2923 m (CH_3), 1792 w, 1720 s (C=O), 1510 m, 1430 m, 1382 m, 1261 m, 1180 m, 1097 m, 1021 m, 960 w, 798 m, 526 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [> 220 nm] (ε) = 230 (38470), 257 (49200), 316 (14890), 422 (860) nm. MS (MALDI-TOF, pos. ion-mode, DCTB, 15 kV): *m*/*z* (%) = 849 (77) $[M]^-$ {calcd. 847.24}, 735 (100) $[M^- - C_3H_3N_3O_2]$.

Synthesis of Addition Product 10 of 1,6-Methano[60]fulleroid and NMTAD. a) 1,6-Cyclopropano[60]fulleroid **9** (20 mg, 0.03 mmol) was dissolved in 1,1,2,2-tetrachlorethane (20 mL). After deoxygenation by purging with argon, NMTAD (11 mg, 0.10 mmol) was added and the solution was irradiated at 419 nm for 5 min in Pyrex tubes. The solvent was evaporated under reduced pressure. Chromatography on silica gel 60 with toluene first gave C_{60} (1 mg, 5%) and then **10** (9 mg, 39%, 2nd fraction). **b)** 1,6-Cyclopropano[60]fulleroid **9** (20 mg, 0.03 mmol) was dissolved in 1,1,2,2-tetrachlorethane (20 mL). After deoxygenation by purging with argon, NMTAD (11 mg, 0.10 mmol) was added and the solution was stirred at room temperature for 60 min. The solvent was evaporated under reduced pressure. Chromatography on silica gel 60 with toluene first gave C_{60} (1 mg, 5%) and then **10** (10 mg, 41%, 2nd fraction). ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 3:1): δ = 3.18 (s, 3 H, 3′-H), 1.30 (br. s, 2 H, 1′′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 3:1): δ = 162.60 (3′-C, 5′-C), 158.10, 149.11, 148.73, 147.89, 147.57, 147.38, 146.94, 146.78, 146.07, 145.64, 145.63, 144.59, 144.58, 144.54, 144.34, 144.24, 144.20, 144.08, 143.62, 143.05, 141.76, 141.32, 141.11, 140.98, 140.77, 139.77, 138.38, 138.26, 135.95, 129.13 (30 C_{60} sp^2 signals), 93.04 (1-C, 4-C), 70.53 (2-C, 3-C), 30.17 (t, $^1J_{C,H}$ = 126.0 Hz; 1′′-C), 26.36 (q, $^1J_{C,H}$ = 142.2 Hz; 6′-C). FT-IR (KBr): $\tilde{\nu}$ = 2922 s (CH_2), 1722 s (C=O), 1430 m, 1377 m, 1261 m, 1106 m, 1019 m, 800 m, 536 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [> 220 nm] (ε) = 229 (42590), 259 (48070), 323 (16150), 421 sh (1470) nm. MS (MALDI-TOF, pos. ion-mode, DCTB, 15 kV): *m*/*z* (%) = no $[M]^-$ {calcd. 847.24}, 735 (65) $[M^- - C_3H_3N_3O_2]$, 721 (100) $[M^- - C_4H_5N_3O_2]$.

Synthesis of 4′-Methyl-3′,5′-dioxo-1′,2′,4′-triazabicyclo[3.2.0]heptano-[6′,7′:1,2]-[60]fullerene (11): C_{60} (216 mg, 0.300 mmol) and NMTAD (113 mg, 0.993 mmol) were dissolved in 1,1,2,2-tetrachlorethane (100 mL). After deoxygenation by purging with argon, the solution was irradiated at 419 nm for 5 h in Pyrex tubes. The solvent was evaporated under reduced pressure and the residue was dissolved in toluene (15 mL) and filtered. Chromatography of the filtrate on silica gel 60 with toluene gave C_{60} (145 mg, 67%, 1st fraction). A change in the eluent to toluene/chloroform (4:1) gave **11** (12 mg, 5%, 2nd fraction). ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 3.47 (s, 3 H, 8′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 161.29 (3′-C, 5′-C), 147.80, 146.67, 146.45, 146.32, 145.31, 144.99, 144.65, 144.50, 143.24, 143.18, 143.07, 142.78, 142.49, 141.76, 140.57, 139.84 (16 C_{60} sp^2 signals), 86.27 (1-C, 2-C), 26.70 (8′-C). FT-IR (KBr): $\tilde{\nu}$ = 2923 m (CH_3), 1797 m, 1728 s (C=O), 1510 m, 1432 m, 1384 m, 1183 m, 1015 m, 968 w, 951 w, 942 w cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [> 220 nm] (ε) = 254 (97900), 318 (34200), 418 sh (2300), 456 sh (1400), 537 sh (800), 598 sh (400), 677 (150) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m*/*z* (%) = 833 (100) $[M]^-$ {calcd. 833.02}, 720 (65) $[M - C_3H_3N_3O_2]^-$.

Synthesis of 4′-Methyl-3′,5′-dioxo-1′,2′,4′-triazabicyclo[3.2.0]heptano-[6′,7′:3,4]-1,6-[*N*-(6′′-methylphenylsulfonyl)]aza[60]fulleroid (16). a) A solution of 1,2-[(4′-methylphenylsulfonyl)aziridino][60]-fullerene **12** (10 mg, 0.01 mmol) in 1,1,2,2-tetrachlorethane (10 mL) was deoxygenated by purging with argon, and NMTAD (3.5 mg, 0.03 mmol) was added. The solution was irradiated at 419 nm for 1 h in Pyrex tubes. The solvent was evaporated under reduced pressure and the residue was dissolved in toluene (10 mL) and filtered. Chromatography of the filtrate on silica gel 60 with toluene/cyclohexane (1:1) gave 1,2-[(4′-methylphenylsulfonyl)aziridino][60]-fullerene (0.5 mg, 5%, 1st fraction). A change in the eluent to chloroform gave **16** (3 mg, 30%, 2nd fraction). **b)** A solution of 1,6-[(4′-methylphenylsulfonyl)aza][60]fulleroid **13** (120 mg, 0.14 mmol) in 1,1,2,2-tetrachlorethane (50 mL) was deoxygenated by purging with argon, and NMTAD (52 mg, 0.45 mmol) was added. The solution was irradiated at 419 nm for 2 h in Pyrex tubes. The solvent was evaporated under reduced pressure and the residue was dissolved in toluene (20 mL) and filtered. Chromatography of the filtrate on silica gel 60 with toluene/cyclohexane (1:1) gave C_{60} (4.7 mg, 5%, 1st fraction) and 1,2-[(4′-methylphenylsulfonyl)aziridino][60]fullerene (3 mg, 2.5%, 2nd fraction). A change in the eluent to chloroform gave **16** (34 mg, 25%, 3rd fraction). 2nd fraction of

experiment a) and 3rd fraction of experiment b) are identical. ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 7.95 (d, $^3J_{H,H}$ = 8.2 Hz; 2 H, 4′′-H, 8′′-H), 7.30 (d, $^3J_{H,H}$ = 8.2 Hz; 2 H, 5′′-H, 7′′-H), 3.62 (s, 3 H, 8′-H), 2.46 (s, 3 H, 9′′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 160.11 (3′′-C, 5′′-C), 152.17, 150.43, 149.52, 148.14, 146.69, 146.50, 146.19, 146.11, 145.40, 145.31, 145.18, 144.89, 144.41, 144.14, 144.12, 143.93, 143.82, 143.64, 143.23, 142.56, 142.37, 142.05, 141.75, 141.50, 141.16, 140.57, 138.03, 137.81, 133.19, 132.03 (29 C_{60} sp^2 signals, 3′′-C), 135.07 (6′′-C), 130.35 (5′′-C, 7′′-C), 129.57 (4′′-C, 8′′-C), 91.94 (3-C, 4-C), 26.99 (8′-C), 21.73 (9′′-C). FT-IR (KBr): $\tilde{\nu}$ = 2817 m (CH_3), 1734 s (C=O), 1654 m, 1560 m, 1508 m, 1437 m, 1360 m, 1186 m, 1168 m (SO_2N), 1086 m (SO_2), 705 w, 526 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [> 220 nm] (ε) = 228 (40000), 253 (44000), 317 (15000) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m/z* (%) = 1003 (100) $[M]^-$ {calcd. 1002.93}, 889 (40) $[M - C_3H_3N_3O_2]^-$.

Synthesis of 4′-Methyl-3′,5′-dioxo-1′,2′,4′-triazabicyclo[3.2.0]heptano-[6′,7′:3,4]-1,6-(phenylaza)[60]fulleroid (17). a) A solution of 1,2-(phenylaziridino)[60]fullerene **14** (45.0 mg, 0.055 mmol) in 1,1,2,2-tetrachlorethane (50 mL) was deoxygenated by purging with argon, and NMTAD (20 mg, 0.21 mmol) was added. The solution was irradiated at 419 nm for 1 h in Pyrex tubes. The solvent was evaporated under reduced pressure and the residue was dissolved in toluene (10 mL) and filtered. Chromatography of the filtrate on silica gel 60 with toluene/chloroform (3:1) gave 1,2-(phenylaziridino)[60]fullerene (8 mg, 18%, 1st fraction) and a mixture of **17** and traces of by-products (35 mg, 2nd fraction). Repeated chromatography by HPLC (Bucky Clutcher I, eluent toluene) gave **17** (26 mg, 51%). **b)** A solution of 1,6-(phenylaza)[60]fulleroid **15** (40 mg, 0.05 mmol) in 1,1,2,2-tetrachlorethane (40 mL) was deoxygenated by purging with argon, and NMTAD (20 mg, 0.21 mmol) was added. The solution was irradiated at 419 nm for 1 h in Pyrex tubes. The solvent was evaporated under reduced pressure and the residue was dissolved in toluene (20 mL) and filtered. Chromatography of the filtrate on silica gel 60 with toluene/chloroform (3:1) gave a mixture of C_{60}, 1,6-(phenylaza)[60]fulleroid and 1,2-(phenylaziridino)[60]fullerene (9 mg, 1st fraction) and a mixture of **17** and traces of by-products (28 mg, 2nd fraction). Second chromatography with HPLC (Bucky Clutcher I, eluent toluene) gave **17** (23 mg, 50%). The products **17** of experiment a) and b) are identical. ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 7.39 (dd, $^3J_{H,H}$ = 7.4, $^3J_{H,H}$ = 8.6 Hz, 2 H, 4′′-H, 6′′-H), 7.25 (dd, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 8.6 Hz, 2 H, 3′′-H, 7′′-H), 7.13 (tt, $^4J_{H,H}$ = 1.1, $^3J_{H,H}$ = 7.4 Hz, 1 H, 5′′-H), 2.68 (s, 3 H, 8′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 161.46 (3′-C, 5′-C), 158.93, 149.33, 147.45, 146.93, 146.62, 146.48, 146.23, 146.15, 145.59, 145.24, 144.79, 144.45, 144.14, 144.12, 144.07, 143.88, 143.81, 143.79, 143.64, 143.23, 143.09, 142.58, 142.39, 142.31, 141.59, 141.37, 141.31, 138.85, 138.03, 135.90, 134.76, 133.33 (31 C_{60} sp^2 signals, 2′′-C), 129.39 (4′′-C, 6′′-C), 122.79 (5′′-C), 116.30 (3′′-C, 7′′-C), 91.90 (3-C, 4-C), 25.99 (8′-C). FT-IR (KBr): $\tilde{\nu}$ = 2928 m (CH_3), 1729 s (C=O), 1600 m, 1582 m,1512 s, 1490 m, 1434 m, 1383 m, 1179 m, 1017 m, 753 m, 691 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} [> 220 nm] (ε) = 254 (60200), 319 (17200), 413 sh (4800), 423 sh (3900), 453 (1200) nm. MS (MALDI-TOF, pos. ion-mode, DCTB, 15 kV): *m/z* (%) = 924 (100) $[M]^+$ {calcd. 924.06}, 811 (39) $[M - C_3H_3N_3O_2]^+$.

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