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Exohedral Functionalization of [60]Fullerene by [3+2] Cycloadditions: Syntheses and Chemical Properties of Triazolino-[60]fullerenes and 1,2-(3,4-Dihydro-2*H*-pyrrolo)-[60]fullerenes

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Key words: *[60]fullerene, cycloaddition, triazoline, aziridine, azafulleroid, nitrene, azide, nitrile ylide, azirine.*

Abstract: *The reaction of C_{60} with aryl azides 5 in dichlorobenzene at room temperature leads to isolable triazolinofullerene derivatives **6a** and **6b**. Photolysis of 6 selectively yields the aziridinofullerenes 7. In contrast to the photolysis the thermolysis affords the azafulleroids 8 as main product next to C_{60}. In addition the first photochemically induced rearrangement of azafulleroids (1,6-aza-bridged isomers) to aziridinofullerenes (1,2-aza-bridged isomers) is described. Beside aziridines 7 the photochemical reactions of azides 5 with C_{60} predominantly yield one novel C_s symmetrical bisadduct, respectively. Furthermore the syntheses of symmetrical 1,2-(3,4-dihydro-2H-pyrrolo)-[60]fullerenes **12a-c** by [3+2] cycloaddition of nitrile ylides 11 are reported.*

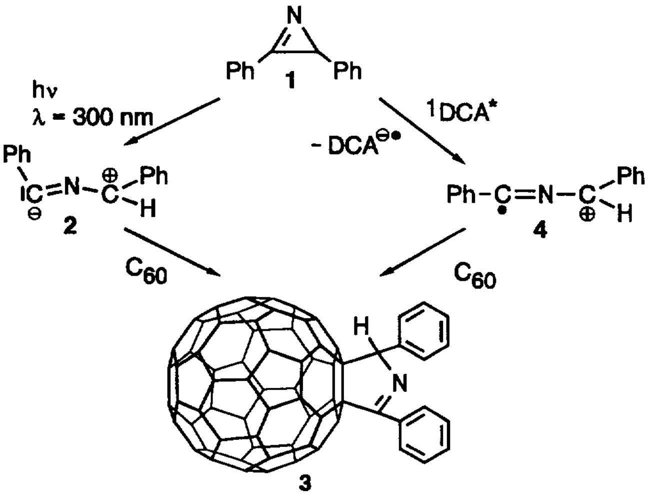
INTRODUCTION

Functionalization by cycloaddition reactions represents a useful strategy to modify fullerenes.[1] Stable cycloadducts, which are interesting with regard to the development of new materials with unique physical properties or biological activities[2] are available by [2+1], [2+2] and [4+2] as well as [3+2] cycloadditions.[1] Some typical examples of reactions of the latter type are the addition of diazo compounds[1,3,4,5], azomethine ylides[6,7], nitrile oxides[8,9] and disiliranes[10].

We recently reported the first [3+2] photocycloaddition of a nitrile ylide to C_{60} (Scheme 1).[11] The nitrile ylide **2**, which was generated by direct irradiation of 2,3-diphenyl-2*H*-azirine (**1**), added to C_{60} acting as 1,3-dipolarophile under formation of C_1 symmetrical 1,2-(3,4-dihydro-2,5-diphenyl-2*H*-pyrrolo)-[60]fullerene (**3**). Mechanistic studies revealed a second reaction pathway, i. e. the addition of azirine **1** under photoinduced electron transfer (PET) conditions using 9,10-dicyanoanthracene (DCA) as a PET sensitizer and light above 400 nm wavelength. In this case the addition obviously occurs via an 2-azaallenyl radical cation **4**.[11]

Other interesting 1,3-dipolar compounds are azides, which were generally used to prepare azafulleroids[12] and aziridinofullerenes[13-16], respectively. The open 1,6-aza-bridged azafulleroids were predominantly formed by thermal addition of alkyl azides[12] whereas closed 1,2-aza-bridged aziridinofullerenes are available by addition of azidoformates[13,14,16] and aroyl azides[15]. The divergent formation of azafulleroids and aziridinofullerenes was explained either by 1,3-dipolar addition of alkyl azides followed by N_2-elimination from the intermediately formed triazoline adduct[1,13] or by [2+1] cycloaddition of nitrene intermediates[1,13,15,17]. Unrelated to our investigations of addition reactions of aryl azides[18] Hirsch et al.

recently reported the syntheses of stable triazolinofullerenes by [3+2] cycloadditions of alkyl azides and confirmed the formation of azafulleroids via triazoline intermediates[19,20].



Scheme 1. Addition of 2,3-diphenyl-2*H*-azirine (**1**) to C_{60} under direct irradiation and PET-conditions.

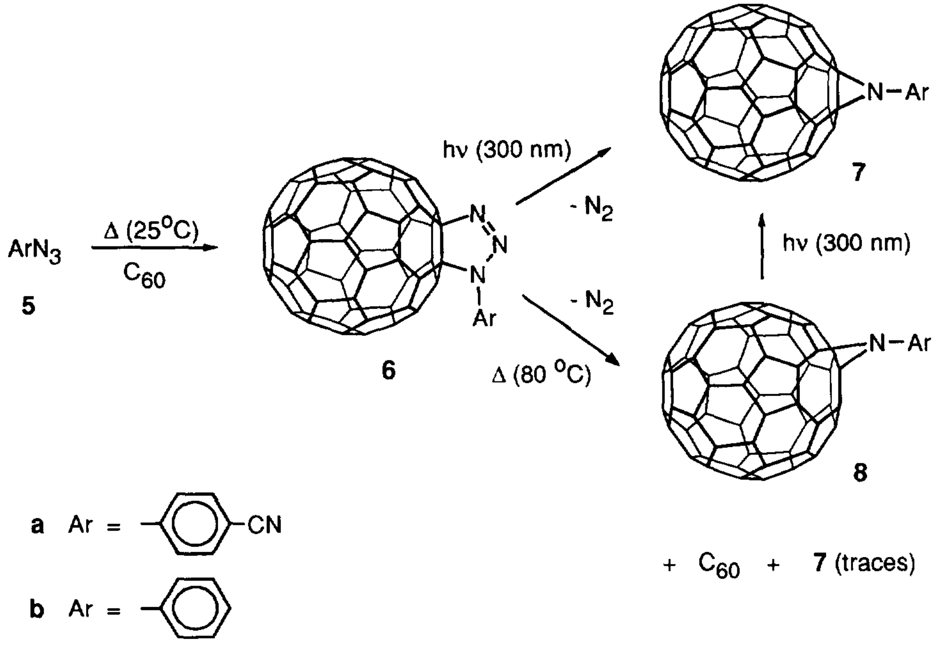
We now report our results of the formation of aryltriazolinofullerenes by [3+2] cycloaddition and discuss the differences between thermal and photochemical conversion of these compounds to arylazafulleroids and arylaziridinofullerenes, respectively. In addition we describe the syntheses of C_s symmetrical 1,2-(3,4-dihydro-2*H*-pyrrolo)-[60]fullerenes by [3+2] cycloaddition of nitrile ylides.

RESULTS AND DISCUSSION

1,2-(4,5-Dihydro-1*H*-1,2,3-triazolo)-[60]fullerenes 6a, 6b by [3+2] cycloaddition of aryl azides to C_{60}

In a typical experiment to synthesize triazolinofullerenes (Scheme 2) we stirred solutions of 0.3 mmol of C_{60} and an excess (20-40 times) of aryl azides **5a**[21] and **5b**[22] in 1,2-dichlorobenzene protected from light and oxygen for several days at room temperature. The fullerenes were separated by column chromatography on alumina N to give residual C_{60} and the triazoline derivatives **6a** and **6b** in $\geq 23\%$ yield ($\geq 50\%$ based on consumed C_{60}). 1,1,2,2-tetrachloroethane may also be used as solvent. However, longer reaction times are required due to the lower solubility of C_{60}.

In both cases the structural assignment of the 1,2-dihydrofullerenes **6a** and **6b** is based on spectroscopic arguments. The ^{13}C NMR spectra show 30 resonances of the fullerene carbons in the area between 148 - 136 ppm in both cases together with two resonances of sp^3 bridgehead fullerene carbons at 108 and 80 ppm. The number and chemical shifts of the fullerene signals reveal 6-6-ring fused C_s symmetrical structures of **6a** and **6b**. The only resonances in the ^{1}H NMR spectra result from the phenyl protons. The UV/Vis spectra of the triazolines displaying an absorption at 427 nm (**6a**, toluene) and 424 nm (**6b**, hexane), respectively, which is characteristic for the 1,2-dihydrofullerene structure, give additional information.[23] The triazolines easily lose nitrogen and therefore we were not able to detect the molecular ion peaks. On the other hand the desorptive chemical ionization mass spectra (DCI MS) with ammonia as reagent gas show fragment ion peaks at m/e 837 ($MH^+ - N_2$) (**6a**) and 812 ($MH^+ - N_2$) (**6b**), respectively. The N elemental analyses of **6a** and **6b** were considered consistent with the triazolino structures.



Scheme 2. Syntheses of triazolinofullerenes **6** and conversion to aziridinofullerenes **7**.

Conversion of triazolines 6 by photochemical and thermal extrusion of nitrogen

1,2,3-Triazolino derivatives from phenyl azide (**5b**) can also be synthesized by [3+2] cycloaddition of olefins with strained double bonds.[24] These triazolines are known as precursors for *N*-phenylaziridines, which are available by photochemically or thermally induced nitrogen extrusion.[24] Similar conditions were chosen to transform the triazolines **6a** and **6b** to aziridinofullerenes (Scheme 2).

Solutions of **6a** and **6b** ($c = 1 \times 10^{-3}$ mol l^{-1}) in deoxygenated toluene were irradiated (λ_{max} = 300 nm) for one day. In both cases analyses with HPLC (reversed phase) indicated the transformation of the triazolines **6** into a new less polar adduct. Chromatography on silica gel gave wine-red solutions of the closed 1,2-aza-bridged aziridinofullerenes **7a** and **7b** in 49% and 63% yield, respectively.

The DCI mass spectra of compound **7a** and **7b** present molecular ion peaks (MH^+) at m/e 837 and 812. Due to the relatively high intensity of the molecule ion peak at electron impact mass spectroscopy (EI MS) conditions high resolution mass determination of **7a** was possible. The mass value of 836.0404 (calc. 836.0374) confirms the formation of **7a**. The number and chemical shifts of the ^{13}C NMR resonances of compound **7a** and **7b** (Fig. 1) are characteristic for C_{2v} symmetrical aziridinofullerenes.[13-16] Both times 16 fullerene resonances (13 signals with relative intensity of 4 and three with relative intensity of 2) are displayed in the sp^2 region between 146 and 141 ppm. The resonances at 83.48 and 84.18 ppm, respectively, are attributed to the two bridgehead fullerene carbons of **7a** and **7b**. The signals of the phenyl substituents of **7a** and **7b** show nearly the same chemical shifts as **6a** and **6b**. Contrary to the triazoline **6a** the aziridine **7a** does not show an AA'MM' splitting of the aromatic protons in two doublets of multiplets (^3J = 8.7 Hz) in the ^1H NMR spectrum but one multiplet due to an AA'BB' system. The UV/Vis spectra of the aziridines **7** indicate closed 1,2-bridged structures just as those from the triazoline **6**. The spectral data are crucial for the photochemical conversions of the triazolines **6** to the aziridines **7**. It is remarkable that the HPLC analyses do not indicate the formation of azafulleroids during and after the irradiation of the solutions.

In contrast to the photolysis thermally induced conversions of the triazolines **6a** and **6b** predominantly yielded opened 1,6-aza-bridged azafulleroids beside C_{60}. The reactions were performed as follows. Solutions of the triazolinofullerenes **6a** and **6b** in toluene were purged with argon and stirred at 80 °C for 40 and 20 min, respectively, while protected from light. In both cases HPLC analyses indicated the formation of a new compound next to C_{60} and small amounts of the aziridinofullerenes **7a** and **7b**. The products of the conversion of **6a** were purified by chromatography on silica gel to give first C_{60} (in 55% yield) and then **8a** as a black brown solid in 39% yield. Further elution gave a wine-red solution containing aziridine **7a** in 4 % yield. Similar results were obtained for the thermal reaction of **6b**: C_{60} and **8b** were isolated in 55% and 41% yield, respectively. Probably C_{60} is formed from **6** by cycloreversion.

The spectroscopic data of **8a** and **8b** are significantly different to those of compounds **6** and **7**. Both ^{13}C NMR spectra do not show any resonances in the sp^3 region. The proton decoupled ^{13}C NMR spectrum of **8a** displays signals, 31 of those between 148 and 135 ppm are attributed to the fullerene carbons (the signal at 144.55 ppm is not resolved) and the remaining 5 signals are characteristic of the 4-cyanophenyl group. The spectrum of **8b** presents 36 resolved resonances. Next to the expected 4 signals of the phenyl group, we found 32 resonances of fullerene carbons in the sp^2 region. The absence of sp^3 hybridized carbons clearly indicates that compounds **8** must possess an open 1,6-aza-bridged structure.[12] Further evidence for an open annulene structure of **8a** and **8b** is given by their UV/Vis spectra. Contrary to the 1,2-dihydrofullerenes **6a**, **6b**, **7a** and **7b** they do not have a weak absorption at about 424 nm (in *n*-hexane). The absence of this absorption is typical of fulleroids as well.[23] In comparison with **7a** and **7b** the azafulleroids **8** show small highfield shifts of the phenyl protons in the ^1H NMR spectra. The masses of the molecular ion peaks (DCI MS) of **8a** (m/e 837 (MH^+)) and **8b** (812 (MH^+)) are identical with those of the aziridines **7**.

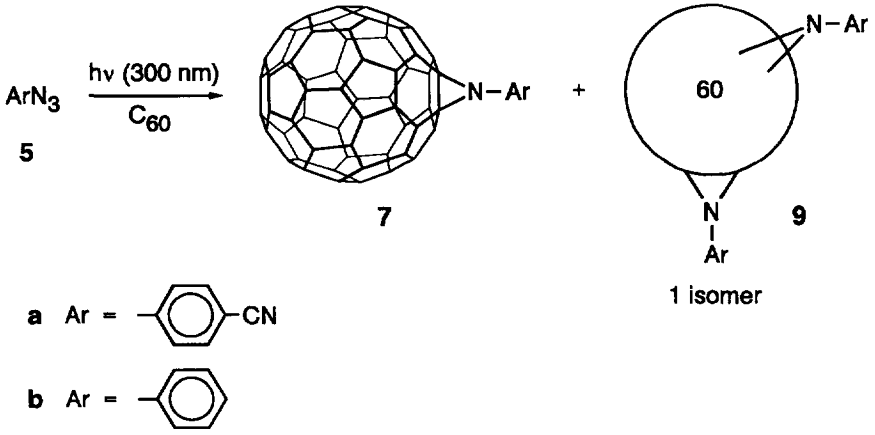
These results clearly show that aryltriazolinofullerenes can be precursors of aziridinofullerenes and azafulleroids.

Photochemical conversion of 1,6 isomers 8 to 1,2-isomers 7

Recently Wudl et al. reported the first photochemical conversion of a fulleroid to a methanofullerene by the di-π-methane rearrangement.[25] We expected a similar reactivity of the azafulleroids **8** and irradiated solutions of **8a** and **8b** in deoxygenated toluene (c = 6 x 10^{-4} mol l^{-1}) with light of 300 nm wavelength. HPLC analysis showed a complete transformation of the azafulleroids **8** exclusively to the 1,2-isomers **7** (Scheme 2). The efficient conversion to **7** is confirmed by the ^1H, ^{13}C NMR and UV/Vis spectra of the isolated products (in

≥ 74 % yield) which are consistent with the known spectra of the aziridinofullerenes **7**. Attempts to transform **8b** in boiling toluene failed.

To some extent our results differ from the report about the synthesis of a ring-opened fullero ketolactam by photooxygenation of a *N*-methoxyethoxymethyl-substituted azafulleroid.[26]



Scheme 3. Photochemical reaction of aryl azides **5** to C_{60}.

Photoaddition of aryl azides 5a and 5b to C_{60}

In an earlier work we described the syntheses of aroylaziridinofullerenes by the addition of photochemically generated acylnitrenes.[15] We chose this method to synthesize the aziridinofullerenes **7** in one step (Scheme 3). Solutions of 0.3 mmol of C_{60} and an excess of 1.8 mmol of aryl azides **5** in deoxygenated 1,1,2,2-tetrachloroethane were irradiated (λ_{max} = 300 nm) for a few hours. Purification of the reaction mixtures offered next to residual C_{60} **7a** and **7b** in 11 and 8% yield (not optimized), respectively, and in addition one predominantly formed bisadduct isomer **9** was selectively available by simple column chromatography in either case.

DCI MS analyses of **9a** and **9b** revealed molecule ion peaks of bisadducts at m/e 970 (MNH_4^+) and 904 (MH^+). The proton spectra of **9a** and **9b** show similar multiplets with a small highfield shift in comparison to the monoadducts **7**. **9a** shows 32 fullerene resonances in the ^{13}C NMR spectrum and, in addition, 5 resonances of the 4-cyanophenyl group. Two of the 32 fullerene resonances which are attributed to the bridgehead fullerene carbons appear at 75.63 and 69.75 ppm. Similar to **9a** 31 fullerene resonances of **9b** are resolved in the ^{13}C NMR spectrum, 29 in the 'aromatic' fullerene region (the signal at 145.63 ppm is not resolved) and two sp^3 hybridized fullerene resonances at 76.49 and 70.90 ppm. The relative intensities of the signals of the phenyl carbons at 129.55, 124.22 and 121.88 ppm are clearly increased in comparison with the corresponding signals of **7b** (Fig. 1). Due to the second phenyl group of **9b** the phenylic infrared absorptions at 1595, 1512 and 1488 cm^{-1} are increased in intensity in comparison with the absorptions of the fullerene core and the corresponding absorptions of **7b** as well. The UV/Vis spectra of **9a** and **9b** exhibit absoptions at 424 nm and 423 nm, respectively, which are very characteristic of 1,2-bridged cycloadducts.[1,23] Altogether the spectral data support our assumption of the formation of C_s symmetrical bisadduct isomers **9** with symmetrical additions to 6-6 bonds.[27,29] According to Hirsch et al. these C_s symmetrical structures may have cis-1, cis-2 or trans-4 structure.[27] **9a** and **9b** possess only two sp^3 resonances, this excludes the structure of regioisomer e.[27] Due to the number and intensity of the fullerene resonances we exclude C_2 symmetry of **9a** and **9b**.[27]

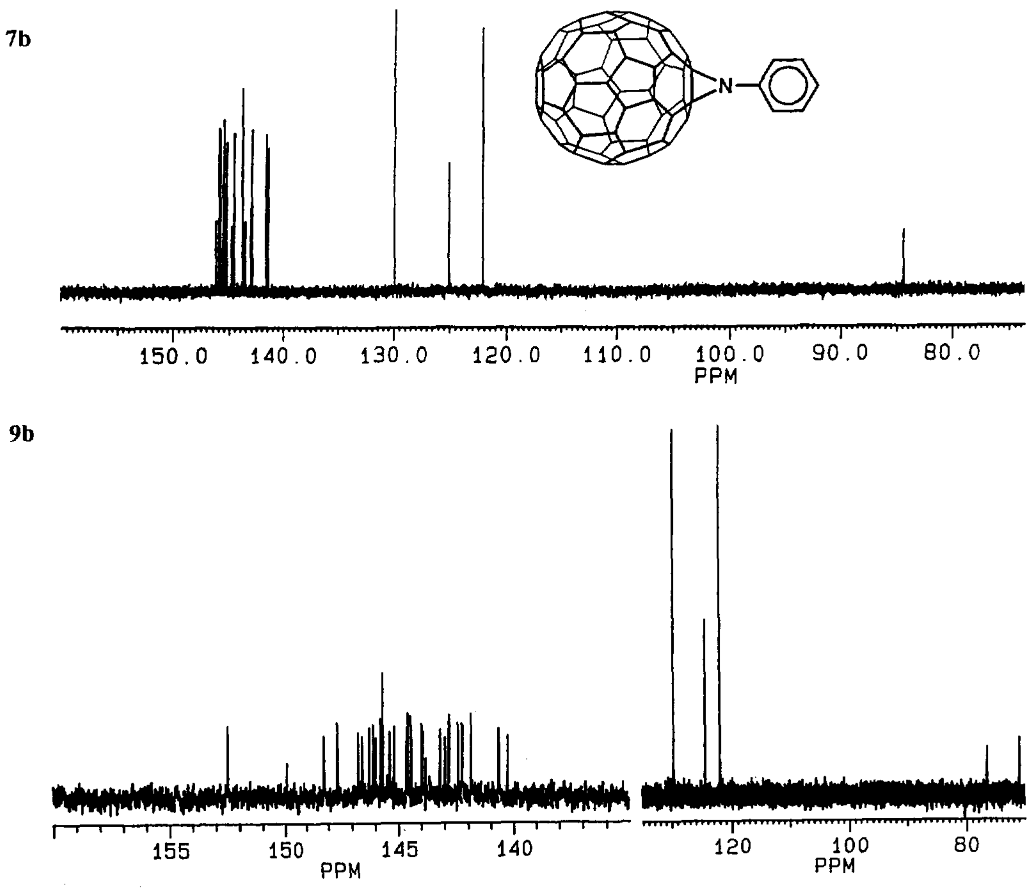
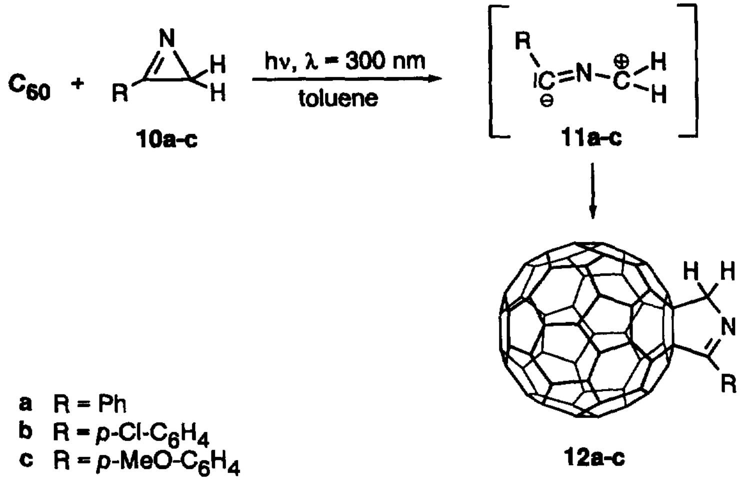


Fig. 1. ^{13}C NMR spectra of aziridinofullerene **7b** and of bisadduct **9b** (90.5 MHz, $CS_2/(D_6)$acetone 10:1).

Isolable amounts of **7b** and **9b** were also available by addition of 4-cyanophenyl azide (**5b**) to C_{60} in boiling 1,1,2,2-tetrachloroethane (146 °C). In accordance with the direct photochemical addition of azides **5** we did not observe the formation of the open 1,6-aza-bridged isomers **8** under these conditions. The exclusive formation of **7** supports a reaction mechanism via nitrene intermediates.

Synthesis of 1,2-(3,4-dihydro-2*H*-pyrrolo)-[60]fullerenes

Symmetrical 1,2-(3,4-dihydro-2*H*-pyrrolo)-[60]fullerenes are not accessible via [3+2] cycloaddition of nitrile ylides, which were generated by photolysis of 2,3-disubstituted 2*H*-azirines.[11] To prepare C_s symmetrical cycloadducts we chose the monophenyl-2*H*-azirines **10a**, **10b** and **10c**[28] as precursors of the corresponding nitrile ylides. Aliphatic 2*H*-azirines are not suitable because they have shorter excitation wavelength than the phenylic substituted 2*H*-azirines with forbidden $\pi \rightarrow \pi^*$ transitions of the phenyl group.



Scheme 4. Addition of 2*H*-azirines **10a-c** to C_{60}.

In a typical experiment (Scheme 4) a solution of 0.2 mmol of C_{60} and 0.2 mmol of 2*H*-azirines **10a**, **10b** and **10c** respectively, in oxygen free toluene was irradiated for several hours (λ_{max} = 300 nm). Column chromatography on alumina N followed by preparative reversed phase HPLC gave unreacted C_{60} and the 1,2-pyrrolidinofullerenes **12a** and **12b** in 22% and 26% yield, respectively, based on consumed C_{60}. Compound **12c** was easily obtained in 56% yield by chromatography on silica gel. In addition in each case we isolated a fraction of regioisomeric bisadducts, which were not separated.

The spectroscopic data of the closed 6-6 ring fused 1,2-isomers **12** are similar to those of the triazolino compounds **6**. They all display 32 fullerene resonances (28 with intensity of 2 and 4 with intensity of 1) in their ^{13}C NMR spectra, including two resonances of sp^3 hybridized bridgehead carbons. Next to the multiplets of the phenylic protons in all cases the ^1H NMR spectra of **12a-c** exhibit one singlet of the methylene groups at about 6.0 ppm. The electronic absorption spectra of **12a-c** present a sharp band near 430 nm and an additional band about 696 nm in the visible region together with the dominant fullerene absorptions in the UV region. Both absorptions are diagnostic for [3+2][6,11] and [4+2][30,31] cycloadducts of fullerenes. At last the structures of **12a-c** are confirmed by mass spectra analysis. The laser desorption time of flight mass spectra (LDTOF MS) show molecular ion peaks at m/e 837 ± 0.1% (**12a**) and 873 ± 0.1% (**12b**). The molecular ion peak of **12c** was determined at m/e 867 under field desorption conditions (FD MS). In summary the spectral data are only compatible with the C_s symmetrical structure of the 1,2-pyrrolidinofullerenes **12a-c**.

The pyrrolidinofullerenes **12** are stable on air and in solution. Due to its methoxy group **12c** possesses a higher solubility in usual solvents for fullerenes than **12a** and **12b**.

SUMMARY

The presented [3+2] cycloadditions of aryl azides **5** and nitrile ylides **11** to C_{60} represent a versatile route to prepare 1,2-dihydrofullerene adducts with annexed 5-membered heterocyclic rings. The differences between the photolysis and thermolysis of the aryltriazolinofullerenes **6** were studied in detail.[18] The thermolysis of the triazolines **6** yielded the open 1,6-aza-bridged azafulleroids **8** as main product next to C_{60}. This is in accordance to the predominant formation of azafulleroids via thermolysis of triazolinofullerenes, which are available from alkyl azides.[19,20] In addition small amounts of aziridinofullerenes **7** were formed, while the formation of bisazafulleroids[20] were not observed. Moreover, for the first time we demonstrated the conversion of triazolinofullerenes to aziridinofullerenes by photolysis. The irradiation of the triazolines **6** led to the aziridinofullerenes **8**, which are exclusively formed. No indication of a reaction pathway via azafulleroids as intermediates were found. The reactivity of the triazolines **6** differs from that of the pyrazoline $C_{61}N_2$, of which the photolysis gives the 1,2-isomer of the parent methanofullerene $C_{61}H_2$ as major and the 1,6-isomer as minor product.[32,33] In the latter case the thermolysis of the pyrazoline leads to only one compound, the 1,6-isomer. Furthermore we have shown the first photochemical rearrangement of azafulleroids into aziridinofullerenes. Good yields and easy chromatographic isolations using colum chromatography or standard HPLC-conditions make these reactions to a promising method of functionalization of the fullerene surface.

In addition to the syntheses of fulleroaziridines **7** via triazolines **6** or azafulleroids **8** as precursors a direct synthesis of **7a** and **7b** is provided. The irradiation of azides **5** in C_{60} solution afforded the aziridines **7** probably by [2+1] cycloaddition of nitrene intermediates. This finding is in accordance with the report about the addition of *N*-succinimidyl-4-azido-2,3,5,6-tetrafluorobenzoate to C_{60}.[34] In difference to that report we also observed the formation of novel bisadducts with a preference for either cis-1, cis-2 or trans-4 structure, respectively. The present reactions and methods offer powerful tools for specific syntheses of aza-bridged fullerenes and related fullerene derivatives.

EXPERIMENTAL

General remarks and materials

Azirines **1a-d**[28] were prepared according to literature procedures. C_{60} was used in *gold grade* quality (Hoechst, ≥ 99.4%). All reactions were performed under an argon atmosphere. Toluene and carbon disulfide were used in *per analysis* quality. 1,1,2,2-Tetrachloroethane and 1,2-dichlorobenzene were of *purum* grade ≥ 98%), and *n*-hexane and acetonitrile were freshly distilled. Removal of all solvents was carried out under reduced pressure. The solutions were irradiated in pyrex tubes (of 10 ml) in a RPR 100 Rayonet Photochemical Chamber Reactor with RPR-3000 Å lamps. Analytical high performance liquid chromatography (HPLC) was performed by using a C_{18}-reversed phase column (Bischoff 250 x 4 mm, Merck LiChrosorb RP18, 7 μm) and toluene/acetonitrile mixtures (1:1 or 1:1.25) as liquid phase (UV/Vis detection at 300 nm (Kontron HPLC detector 432), flow: 1.25 ml min^{-1} (Merck L-6000 pump). For preparative reversed phase HPLC a C_{18}-reversed phase column (250 x 20 mm, Merck LiChrosorb RP18, 7 μm), an Abimed-Gilson Spectrochrom detector (UV/Vis detection at 300 nm) and a Kontron HPLC pump 420 (flow: 9.5 ml min^{-1}) were used. Column chromatography was performed on silica gel 60 (Merck, 63-200 μm) or neutral alumina (ICN Alumina

N, Akt. I). Direct chemical ionization mass spectra (DCI MS) were recorded on a Finnigan MAT 8200 instrument with ammonia as carrier gas. The electron impact mass spectra (EI MS) and also the field desorption mass spectra (FD MS) were obtained on a Finnigan MAT 312. Relative intensities are given in percentages. NMR spectra were recorded on a Bruker AM 360 spectrometer at 360 MHz for ^{1}H NMR spectra and 90.5 MHz for ^{13}C NMR spectra. Chemical shift data are reported in parts per million (δ in ppm relative to (D_6)acetone ($\delta = 2.04$ for proton and 29.80 ppm for carbon) and (D_2)-1,1,2,2-tetrachloroethane ($\delta = 5.98$ for proton and 73.76 for carbon) as internal standard) where s, dm and m designate singlet, doublet of multiplet and multiplet, respectively. Fourier transform infrared spectra (FT IR) were recorded on a Nicolet 5DXC FT-IR spectrometer and the absorptions are given in cm^{-1}. UV/Vis spectra were performed on a Shimadzu UV-2100 spectrophotometer.

1,2-[1-(4-Cyanophenyl)-4,5-dihydro-1*H*-1,2,3-triazolo]-[60]fullerene (6a)

A solution of 283 mg (0.39 mmol) of C_{60} and 1115 mg (7.74 mmol) of 4-cyanophenyl azide (**5a**) in 20 ml of 1,2-dichlorobenzene was stirred protected from light at room temperature for 10 d. The fullerenes were separated by precipitation with 150 ml of acetonitrile. The resulting precipitate was collected and washed thoroughly with acetonitrile. Chromatography on alumina N (100 g) with toluene followed by toluene/ acetonitrile 99: 1 gave 153 mg (54%) of unconverted C_{60} (1st fraction) and 77 mg (23%, 49% based on consumed C_{60}) of **6a** (2nd fraction) as a brown black powder. **6a** undergoes a slow thermal conversion at room temperature under formation of **8a** and C_{60}.

6a. DCI MS (NH_3, m/e (%)): 856 (35), 855 (70), 854 ($MNH_4^+ - N_2$; 98), 838 (56) 837 (100; $MH^+ - N_2$), 721 (26), 720 (30). Anal. Calcd. for $C_{67}H_4N_4$: C, 93.06; H, 0.47; N, 6.48. Found: C, 88.94; H, 0.98; N, 5.94.[35] ^{1}H NMR (360 MHz; $CS_2/(D_6)$acetone 10:1, 286 K): $\delta = 8.30$ (dm, 2 H, $^3J = 8.7$ Hz, Ph), 7.86 (dm, 2 H, $^3J = 8.7$ Hz, Ph) ppm. ^{13}C NMR (90.5 MHz; $CS_2/(D_6)$acetone 10:1, 268 K): $\delta = 148.05$, 147.80, 146.77, 146.74, 146.61, 146.45, 146.33, 146.20, 145.98, 145.75, 145.66, 145.58, 145.06, 144.83, 144.48, 144.24, 143.82, 143.41, 143.36, 143.23, 142.95, 142.82, 142.68, 142.62, 142.24, 142.22, 141.35, 140.57, 140.16, 137.38, 136.51, 134.19, 120.98, 117.97, 109.71, 108.64, 80.30 ppm. FT IR (KBr): 2223w, 1601s, 1501ss, 1428m, 1325m 1282w, 1178w, 1038s, 978m, 861w, 829m, 610w, 563w, 550w, 526ss. UV/Vis λ_{max} (ε) in toluene: 321 (53000), 427 (3100) nm.

1,2-(1-Phenyl-4,5-dihydro-1*H*-1,2,3-triazolo)-[60]fullerene (6b)

216 mg (0.30 mmol) of C_{60} and 1440 mg (12.1 mmol) of phenyl azide (**5b**) were dissolved in 20 ml of 1,2-dichlorobenzene and stirred protected from light at room temperature for 3 d. After precipitation of the fullerenes with 300 ml of acetonitrile, the mixture was filtered, the residue thoroughly washed with acetonitrile and finally extracted with toluene. The extract was chromatographed on alumina N (100g). Elution with toluene gave 150 mg (66%) of unconverted C_{60} and elution with toluene/acetonitrile 99: 1 gave 62 mg (25%, 80% based on consumed C_{60}) of **6b** as a brown black powder. **6b** undergoes a slow thermal conversion at room temperature under formation of **8b** and C_{60}.

6b. DCI MS (NH_3, m/e (%)): 814 (36), 813 (66), 812 (100; $MH^+ - N_2$), 721 (26), 720 (30). Anal. Calcd. for $C_{66}H_5N_3$: C, 94.40; H, 0.60; N, 5.00. Found: C, 90.00; H, 1.15; N, 4.70.[35] ^{1}H NMR (360 MHz; $CS_2/(D_6)$acetone 10:1, 286 K): $\delta = 7.94$ (m, 2 H), 7.54 (m, 2 H), 7.37 (m, 1H) ppm. ^{13}C NMR (90.5 MHz; $CS_2/(D_6)$acetone 10:1, 268 K): $\delta = 147.92$, 147.70, 146.61, 146.59, 146.38, 146.30, 146.21, 146.14, 146.07, 145.81, 145.51, 145.47, 145.38, 144.76, 144.74, 144.23, 143.31, 143.22, 143.09, 142.87, 142.86, 142.59, 142.51, 142.36, 142.17, 141.63, 141.17, 140.25, 140.23, 136.94, 136.43, 130.23, 127.38, 123.43, 107.67, 81.53 ppm. FT IR (KBr): 1549m, 1509s, 1493s, 1478s, 1427m, 1313m, 1183m, 1145w, 1114m, 1088m, 1047s, 1032sh, 1014w, 979m, 861w, 745s, 689m, 575m, 543w, 526ss. UV/Vis $\lambda_{max} \geq 240$ (ε) in *n*-hexane: 257 (106000), 314 (33000), 424 (1100), 460br (1000) nm.

1,2-[*N*-(4-Cyanophenyl)aziridino]-[60]fullerene (7a)

Method 1: A solution of 38 mg (0.044 mmol) of **6a** in 44 ml toluene was irradiated for 19 h. During irradiation the yellow brownish colour of the solution changed to a reddish colour. After the irradiation the toluene solution was filtered and then concentrated *in vacuo*. 50 ml of acetonitrile were added to the residual solution (10 ml) and the resulting precipitate was separated by filtration. Column filtration with silica gel (toluene/n-hexane, 1 : 1) afforded 18 mg (49% yield) of the fulleroaziridine **7a** as a brown black solid.

7a. DCI MS (NH_3, m/e (%)): 856 (32), 855 (66), 854 (100, MNH_4^+), 838 (10), 837, (7; MH^+), 720 (5). Exact mass (HR EI MS) calc. for $C_{67}H_4N_2^+$: 836.0374, found 836.0404. ^1H NMR (360 MHz; CS_2/(D_6)acetone 10:1) δ = 7.80 (m, 4 H, Ph) ppm. ^{13}C NMR (90.5 MHz; CS_2/(D_6)acetone 10:1): δ = 149.41, 145.79, 145.69, 145.45, 145.31, 145.08, 145.00, 144.46, 144.34, 144.20, 143.67, 143.63, 143.37, 142.68, 142.58, 141.58, 141.19, 133.68, 122.38, 118.00, 109.04, 83.48. FT IR (KBr): 2222w, 1600s, 1501ss, 1426m, 1393m, 1263w, 1178w, 1162w, 833m, 574m, 553m, 525ss. UV/Vis $\lambda_{max} \geq 240$ (ε) in *n*-hexane: 256 (50000), 326 (14000), 422 (1900) nm.

Method 2: A solution of 216 mg (0.30 mmol) of C_{60} in 1,1,2,2-tetrachloroethane (90 ml) containing 275 mg (1.91 mmol) 4-cyanophenyl azide (**5a**) was irradiated in quartz tubes for 6 h. Then 300 ml acetonitrile were added to the brownish solution and the resulting residue was collected by filtration of the mixture. Column chromatography on alumina N with toluene gave 143 mg (65%) of C_{60} and elution with toluene/acetonitrile 98 : 2 afforded 27 mg (11%, 31% based on consumed C_{60}) of fulleroaziridine **7a** as a brown black solid.

Further elution of the column with toluene/acetonitrile 1: 1 afforded a yellow brown solution of 13 mg (5%, 13% based on consumed C_{60}) of bisadduct **9a** which was purified by a second column chromatography (silica gel, toluene/acetonitrile 99 : 1).

Bisadduct **9a**. DCI MS (NH_3, m/e (%)): 972 (26), 971 (56), 970 (100, MNH_4^+), 954 (14), 953 (18; MH^+), 837 (6; $MH^+ - C_7H_4N_2$), 720 (4; $M^{\bullet +} - C_{14}H_8N_4$). ^1H-NMR (300 MHz; (D_2)-1,1,2,2-tetrachloroethane): δ = 7.91 (m, 4 H, Ph), 7.76 (m, 4 H, Ph) ppm. ^{13}C-NMR (75 MHz; (D_2)-1,1,2,2-tetrachloroethane): δ = 150.16, 148.61, 148.53, 147.01, 146.94, 146.20, 145.87, 145.66, 145.45, 145.23, 145.20, 144.62, 144.50, 144.08, 143.86, 143.81, 143.34, 143.27, 143.13, 142.59, 142.51, 141.98, 141.95, 141.74, 141.48, 141.47, 141.17, 141.05, 140.36, 137.80, 137.71, 133.24, 121.69, 118.74, 107.19, 75.63, 69.75 ppm. FT IR (KBr): 2220m, 1600ss, 1500s, 1460w, 1379w, 1258w, 122w, 1161w, 1107w, 834m, 740w, 547w, 525s. UV/Vis λ_{max} (ε) in dichloromethane: 258 (109000), 320 (33000), 424 (2500), 463 (1750, br) nm.

1,2-(*N*-Phenylaziridino)-[60]fullerene (7b)

Method 1: 54 mg (0.064 mmol) of **6b** were dissolved in 60 ml of toluene and then irradiated for 24 h. During irradiation the colour of the solution changed from yellow brownish to reddish. The solvent was subsequently evaporated *in vacuo* and purification of the residue by column chromatography on silica gel with toluene/*n*-hexane 1 : 2, followed by chromatography on alumina N (to remove residual traces of C_{60}) with toluene gave 33 mg (63%) of aziridine **7b** as a black brown powder. No reaction was observed in the dark.

7b. DCI MS (NH_3, m/e (%)): 813 (40), 812 (100; MH^+), 721 (5), 720 (10). ^1H NMR (360 MHz; CS_2/(D_6)acetone 10:1): δ = 7.65 (m, 2 H, Ph), 7.48 (m, 2 H, Ph), 7.22 (m, 1 H, Ph) ppm. ^{13}C NMR (90.5 MHz; CS_2/(D_6)acetone 10:1): δ = 146.05, 145.74, 145.65, 145.39, 145.33, 145.28, 145.23, 145.08, 144.62, 144.39, 143.63, 143.61, 143.36, 142.76, 142.72, 141.46, 141.23, 129.77, 124.85, 121.98, 84.18. FT IR (KBr): 1595m, 1510m, 1488s, 1427w, 1385w, 1263w, 1223w, 1182m, 1165w, 1022w, 759w, 753m, 735w, 712w, 703w, 579w, 573w, 568w, 564w, 542w, 526ss. UV/Vis λ_{max} (ε) in dichloromethane: 253 (113000), 322 (39000), 423 (2300), 490 (1460, br), in toluene: 328 (50000), 426 (2700) nm.

Method 2: A solution of 218 mg (0.30 mmol) of C_{60} and 220 mg (1.85 mmol) of phenyl azide (**5b**) in 100 ml of 1,1,2,2-tetrachloroethane was irradiated for 5 h. Then the fullerenes were separated by precipitation with 500 ml of acetonitrile. The resulting mixture was filtered and the residue was washed thoroughly with acetonitrile. Column chromatography on alumina N with toluene followed by toluene/acetonitrile 99: 1 gave 75 mg (34%) of unconverted C_{60} (1st fraction) and a mixture of monoadduct **7a** (2nd fraction) and a bisadduct. Column chromatography of this mixture on silica gel (toluene/*n*-hexane 2:1) afforded a wine-red solution of 19 mg (8%, 12% based on consumed C_{60}) of aziridine **7a** (as solid a black brown powder). Further elution of the column gave a yellow brown solution of 3.3 mg (1.2%) of bisadduct **9b**.

Bisadduct **9b**. DCI MS (NH_3, m/e (%)): 906 (19), 905 (32), 904 (100), 903 (79; MH^+), 812 (33; MH^+ - C_6H_5N). ^1H NMR (360 MHz; CS_2/(D_6)acetone 10:1): δ = 7.48 (m, 4 H, Ph), 7.39 (m, 4 H, Ph), 7.12 (m, 2 H, Ph) ppm. ^{13}C NMR (90.5 MHz; CS_2/(D_6)acetone 10:1): δ = 152.49, 149.90, 148.17, 147.58, 146.71, 146.53, 146.24, 146.07, 145.95, 145.75, 145.63 (2x), 145.35, 145.16, 144.61, 144.55, 144.42, 143.96, 143.92, 143.79, 143.17, 142.95, 142.80, 142.76, 142.39, 142.22, 142.19, 141.84, 140.65, 140.63, 140.26, 129.55, 124.33, 121.88, 76.49, 70.90 ppm. FT IR (KBr): 1595s, 1512s, 1488ss, 1388w, 1263w, 1220w, 1190w, 1074w, 1025w, 756m, 741s, 708w, 687m, 572w, 568w, 526s cm^{-1}. UV/Vis λ_{max} (ε) in dichloromethane: 259 (102000), 323 (31000), 423 (2800) nm.

1,6-[*N*-(4-Cyanophenyl)]aza-[60]fulleroid (8a)

A solution of 87 mg (0.10 mmol) of triazoline **6a** in 100 ml of toluene was added to 200 ml of stirred toluene at 80 °C. After stirring in darkness for 40 min the solution was cooled with an ice-water cooling bath and the solvent was then evaporated *in vacuo*. Column chromatography on 500 g silica gel with toluene/*n*-hexane 1:1 gave 34 mg (55%) C_{60} (1st fraction), a dark blackish solution of azafulleroid **8a** (2nd fraction), and a wine-red fraction of aziridinofullerene **7a**. **8a** and **7a** were purified separately by a second column chromatography (silica gel, toluene/*n*-hexane 1:1) and isolated as brown black solids in 33 mg (39%) (**8a**) and 3.2 mg (4%) (**7a**), respectively.

8a. DCI MS (NH_3, m/e ≥ 400 (%)): 856 (30), 855 (79), 854 (100; MNH_4^+), 838 (30), 837 (67; MH^+), 836 (32), 720 (33). ^1H NMR (360 MHz; CS_2/(D_6)acetone 10:1): δ = 7.66 (m, 4 H) ppm. ^{13}C NMR (90.5 MHz; CS_2/(D_6)acetone 10:1): δ = 151.27, 147.96, 145.30, 145.15, 145.08, 145.05, 144.92, 144.87, 144.79, 144.72, 144.55, 144.29, 144.24, 144.12, 144.10, 143.90, 143.81, 143.68, 143.57, 143.38, 142.29, 142.02, 141.62, 140.55, 140.47, 139.70, 139.28, 138.92, 138.27, 137.90, 136.96, 135.35, 134.01, 118.47, 116.80, 106.82 ppm. FT IR (KBr): 2221m, 1604, 1557w, 1506s, 1427w, 1395w, 1346w, 1262w, 1175w, 1109m, 1087m, 1026m, 828m, 809sh, 543m, 525s. UV/Vis λ_{max} (ε) in *n*-hexane: 207 (105000), 259 (65000), 314 (21000) nm.

1,6-(*N*-Phenyl)aza-[60]fulleroid (8b)

32.4 mg (0.039 mmol) of triazoline **6b** was dissolved in 20 ml of toluene and stirred at 80 °C in darkness for 20 min. The solvent was then evaporated *in vacuo* and the main part of C_{60} was separated by column chromatography on 250g alumina N with toluene (1st fraction). Further elution gave a black purple solution of azafulleroid **8b** contaminated with traces of C_{60} (2nd fraction). Both compounds were then separated by preparative reversed phase HPLC with toluene/acetonitrile 1.5:1. Finally 15.4 mg (55%) C_{60} and 12.8 mg (41%) azafulleroid **8b** were obtained as a brown black powder. Next to the formation of the isolated compounds HPLC analysis indicated the formation of traces of aziridine **7b**.

8b. DCI MS (NH_3, m/e (%)): 813 (74), 812 (100; MH^+). ^1H NMR (360 MHz; CS_2/(D_6)acetone 10:1): δ = 7.54 (m, 2 H), 7.37 (m, 2 H), 7.08 (m, 1H) ppm. ^{13}C NMR (90.5 MHz; CS_2/(D_6)acetone 10:1): δ = 148.24, 148.14, 145.20, 145.11, 145.09, 144.82, 144.79, 144.68, 144.67, 144.50, 144.47, 144.40, 144.21, 144.00, 143.99, 143.94, 143.89, 143.83, 143.59, 143.56, 143.36, 142.40, 142.31, 141.91, 140.88, 140.36, 140.27, 139.22, 138.50, 138.34, 138.09, 137.48, 135.57, 129.90, 123.60, 116.97 ppm. FT IR (KBr): 1595m, 1551w, 1531w, 1508s, 1493s, 1427w, 1344w, 1261m, 1178w, 1098w, 1023w, 803m, 743m, 684m, 571w, 523s. UV/Vis λ_{max} (ε) ≥ 240 in *n*-hexane: 260 (35000), 326 (9000).

Photochemical conversion of azafulleroid 8a to aziridinofullerene 7a

A deoxygenated toluene solution (25 ml) of 13 mg (0.015 mmol) of azafulleroid **8a** was irradiated for 16 h at 25 - 30 °C (ambient temperature). The colour of the solution changed during irradiation from brown blackish to wine-red. The toluene solution was concentrated *in vacuo* and filtrated through 50 g of silica gel. The solvent was evaporated and the residue was dissolved in carbon disulfide. Evaporation to dryness *in vacuo* gave 9.5 mg (74%) aziridinofullerene **7a**. No reaction was observed in the dark.

Photochemical conversion of azafulleroid 8b to aziridinofullerene 7b

4.6 mg (5.7 μmol) of azafulleroid **8b** dissolved in 10 ml deoxygenated toluene was irradiated for 27 h. The reddish solution was then concentrated and purified by column filtration with toluene/acetonitrile 99:1. Finally evaporation of the solvent to dryness *in vacuo* yielded 4.2 mg (91%) of fulleroaziridine **7b**.

1,2-(3,4-Dihydro-2-phenyl-2*H*-pyrrolo)-[60]fullerene (12a)

Irradiation of a purple solution of 141 mg (0.19 mmol) C_{60} and 26 mg (0.22 mmol) 2-phenyl-2*H*-azirine (**10a**) in 70 ml of toluene in quartz tubes for 2 h gave a dark brown product solution. 62 mg (43%) residual C_{60} was separated by column chromatography on alumina N with toluene. Further elution gave a mixture of monoadduct **12a** and bisadducts as 2nd fraction. Finally preparative reversed phase HPLC of the 2nd fraction with toluene/acetonitrile 3:2 gave a reddish brown solution of 21 mg (13%, 22% based on converted C_{60}) monoadduct **12a**, next to a fraction of 8 mg (8%) regioisomeric bisadducts (FD+ MS: m/e: 954 (M^+).

12a. LDTOF MS 16 kV, 337 nm (m/e): 837 ± 0.1% (M^+, calc.: 837.8), FD+ MS: (m/e (%): 838 (16), 837 (100, M^+), 836 (9, M^+ - H). ^1H NMR (360 MHz; $CS_2/(D_6)$acetone 10:1): δ = 8.31 (m, 2 H, Ph), 7.50 (m, 3 H, Ph), 6.01 (s, 2 H, CH_2) ppm. ^{13}C NMR (90.5 MHz; $CS_2/(D_6)$acetone 10:1): δ = 169.12, 155.34, 148.54, 147.77, 147.56, 146.92, 146.66, 146.57, 146.50, 146.45, 146.04, 146.01, 145.97, 145.79, 145.77, 145.06, 144.69, 143.84, 143.73, 143.39, 143.31, 143.17, 142.93, 142.83, 142.72, 142.64, 142.30, 141.07, 140.67, 136.78, 135.45, 134.94, 130.99, 129.73, 129.22, 85.41, 76.00, 72.97 ppm. FT IR (KBr): 1616m, 1491w, 1462w, 1458sh, 1442w, 1430w, 1301m, 1260, 1183w, 1034m, 997m, 868w, 832w, 766m, 726m, 693w, 683m, 669w, 650w, 576w, 567w, 562w, 554w, 527s. UV/Vis λ_{max} ≥ 220 (ε) in *n*-hexane: 255 (36000), 310 (11100), 321 (10800), 427 (1000), 692 (≈ 100), in toluene (≥ 400): 431 (3000), 696 (300) nm.

1,2-[3,4-Dihydro-2-(4-chlorophenyl)-2*H*-pyrrolo]-[60]fullerene (12b)

142 mg (0.19 mmol) of C_{60} and 32 mg (0.21 mmol) of 2-(4-chlorophenyl)-2*H*-azirine (**10b**) were dissolved in 80 ml of toluene and irradiated in pyrex tubes for 11.5 h. Column chromatography on alumina N with toluene yielded 60 mg (42%) residual C_{60}. Further elution with toluene/acetonitrile 1:1 gave a mixture of monoadduct **12b** and bisadducts, which were separated by preparative reversed phase HPLC (toluene/acetonitrile 5:4). **12b** was obtained as a dark brown solid in 27 mg (16%, 27% based on consumed C_{60}) yield next to a fraction of 30 mg (15%, 26% based on consumed C_{60}) regioisomeric bisadducts (FD+ MS: m/e (%): 1022 (78, M^+), 1024 (100).

12b. LDTOF MS 16 kV, 337 nm (m/e): 873 ± 0.1% (M^+, calc.: 872.3), FD+ MS: m/e: 871 (M^+). ^1H NMR (360 MHz; $CS_2/(D_6)$acetone 10:1): δ = 8.17 (dm, 2 H, ^3J = 8.4 Hz, Ph), 7.49 (dm, 2 H, ^3J = 8.4 Hz, Ph), 6.01 (s, 2 H, CH_2) ppm. ^{13}C NMR (90.5 MHz; $CS_2/(D_6)$acetone 10:1): δ = 168.09, 155.03, 148.07, 147.52, 147.49, 147.47, 146.89, 146.61, 146.53, 146.45, 146.34, 146.01, 145.94, 145.86, 145.74, 145.73, 145.01, 144.60, 143.80, 143.66, 143.36, 143.27, 143.07, 142.87, 142.76, 142.66, 142.53, 142.25, 141.06, 140.67, 136.87, 134.83, 133.78, 131.20, 129.431, 86.44, 75.85, 72.92 ppm. FT IR (KBr): 1616m, 1594w, 1486m, 1425w, 1395w, 1302m, 1254w, 1179w, 1092m, 1040m, 996m, 838w, 824m, 748m, 669w, 606w, 575w, 562m, 556w, 543w, 531sh, 527s, 439w. UV/Vis λ_{max} (ε) in dichloromethane: 255 (96000), 308 (32000), 325sh (31000), 428 (3100); in toluene: 431 (3200), 696 (200) nm.

1,2-[3,4-Dihydro-2-(4-methoxyphenyl)-2*H*-pyrrolo)-[60]fullerene (12c)

A solution of 219 mg (0.30 mmol) C_{60} and 33 mg (0.22 mmol) of 2-(4-methoxyphenyl)-2*H*-azirine (**10c**) in 120 ml toluene was irradiated in quartz tubes for 60 min. The colour of the solution changed from purple to reddish brown. The solution was filtered, concentrated *in vacuo* and then chromatographed on 150 g silica gel with toluene. **12c** was obtained as dark brown solid in 92 mg (35%, 56% based on consumed C_{60} next to 85 mg (39%) C_{60}.

12c. FD+ MS (m/e (%)): 867 (100; M^+), 866 (38, M^+ - H). ^{1}H NMR (360 MHz; $CS_2/(D_6)$acetone 10:1): δ = 8.17 (dm, 2 H, ^3J = 9.0 Hz, Ph), 6.98 (dm, 2 H ^3J = 9.0 Hz, Ph), 5.96 (s, 2 H, CH_2), 3.87 (s, 3H, OCH_3) ppm. ^{13}C NMR (90.5 MHz; $CS_2/(D_6)$acetone 10:1): δ = 167.93, 161.89, 155.34, 148.71, 147.78, 147.46, 147.43, 146.83, 146.57, 146.47, 146.39, 146.37, 145.94, 145.91, 145.87, 145.70, 145.66, 145.00, 144.60, 143.76, 143.31, 143.24, 143.06, 142.84, 142.77, 142.63, 142.60, 142.18, 141.04, 140.49, 136.70, 134.81, 131.52, 127.68, 114.55, 85.01, 75.65, 73.08, 55.54 ppm. FT IR (KBr): 1604m, 1570w, 1507s, 1457w, 1432w, 1300m, 1251s, 1174s, 1033m, 995m, 827m, 765w, 618w, 565w, 526s. UV/Vis λ_{max} (ε) in dichloromethane: 256 (150000), 309 (48000), 323sh (44000), 428 (3500), 694 (200) nm.

Further elution with toluene/acetonitrile 99:1 gave 38 mg (12%) regioisomeric bisadducts.
FD+ MS (m/e (%)): 1014 (100, M^+), 1015 (72), 1016 (55).

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