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Addition of Photochemically Generated Acylnitrenes to C_{60}. Synthesis of Fulleroaziridines and Thermal Rearrangement to Fullerooxazoles.[1]

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Abstract: *The reaction of C_{60} to acylnitrenes **2**, generated by photolysis of aroylazides **1** in dichloromethane, creates the stable fulleroaziridine derivatives **3a**, **3b**, **3c**, and **3d**. The rearrangement of the fulleroaziridines **3** by boiling in tetrachloroethane leads to the formation of the corresponding fullerooxazoles **4a**, **4b**, **4c**, and **4d**. The formation of a fullerooxazole **4b** was also observed by irradiation of C_{60} and **1b** in benzene.*

INTRODUCTION

The functionalization of C_{60} by means of photochemical reactions is now emerging as an useful method for exohedral derivatizations.[2] Some of the first examples of photochemical derivatizations were the epoxidation of C_{60}[3] as well as the [2 + 2] photocycloadditon of enones[4] and *N,N*-diethylpropynylamine to C_{60}.[5] We have recently reported about the photochemical [3 + 2] photocycloaddition of 2,3-diphenyl-2*H*-azirine to C_{60}.[6] Further [3 + 2] photocycloadditions with fullerenes have been published by Ando et al.[7,8] We are now reporting the results of our investigations of the addition of photochemically generated acylnitrenes to C_{60}, which are part of our general studies of the photoreactions of acylazides.[9]

The first examples of reactions of azides with C_{60} were the formation of azafulleroids by thermally induced reactions of alkyl azides with C_{60} reported by Wudl et al.[10] In contrast to these results the thermally reaction of an azidoformate leading to the formation of a fulleroaziridine have been published during our work by Banks et al.[11] The divergent formation of fulleroids and fulleroaziridines can probably be explained either via 1,3-dipolar addition of alkyl azides followed by N_2-elimination from the intermediately formed triazoline adduct or via nitrene addition.[11] Further evidence is reported by Nogami et al. who observed the selective formation of a fulleroaziridine by addition of singlet pthalimidonitrene to C_{60}.[12,13]

In general the formation of three- or five-membered heterocyclic rings by the reaction of acylnitrenes to olefins depends on the electron density at the double bond. In presence of 2,5-dihydrofuran the addition of acylnitrenes **2** which are exclusively available by photolysis of aroylazides beside the corresponding arylisocyanate leads to the formation of aziridines by a cheletropic reaction.[9] But with enolethers, such as 3,4-dihydro-2-methoxy-2*H*-pyrane, singlet acylnitrenes yield oxazolines in a [3 + 2] cycloaddition.[9] Our initial interest was to investigate the reaction pattern of photochemically generated acylnitrenes **2** and C_{60} leading either to fulleroaziridine or fullerene oxazole derivatives.

RESULTS

*Synthesis of fulleroaziridines **3a-d***

In a typical experiment (fig. 1) a solution of 0.2 mmol of C_{60} and 1.0 mmol of azide **1**[14] in 600 mL of oxygen free dichloromethane was irradiated for 60 min in pyrex tubes (of 10 mL) using a RPR 100 Rayonet Photochemical Chamber Reactor fitted with RPR-3000 Å lamps (fig. 1.) The colour of the solution changed from purple to red brown. Chromatography on silica gel with *n*-hexane followed by *n*-hexane / toluene mixtures yielded unconverted C_{60} (1st fraction) and the fulleroaziridine derivatives **3a**, **3b**, **3c**, and **3d** (2nd fraction) in > 11 % yield (> 22 % based on consumed C_{60}).

Higher yields of the fulleroaziridines **3a-d** (at about 40 % based on consumed C_{60}) are obtained by reaction of C_{60} with the acylazides **1** in 1,1,2,2-tetrachloroethane (TCE) probably because of the higher concentration of C_{60} (5 x 10^{-3} M) compared with dichloromethane.

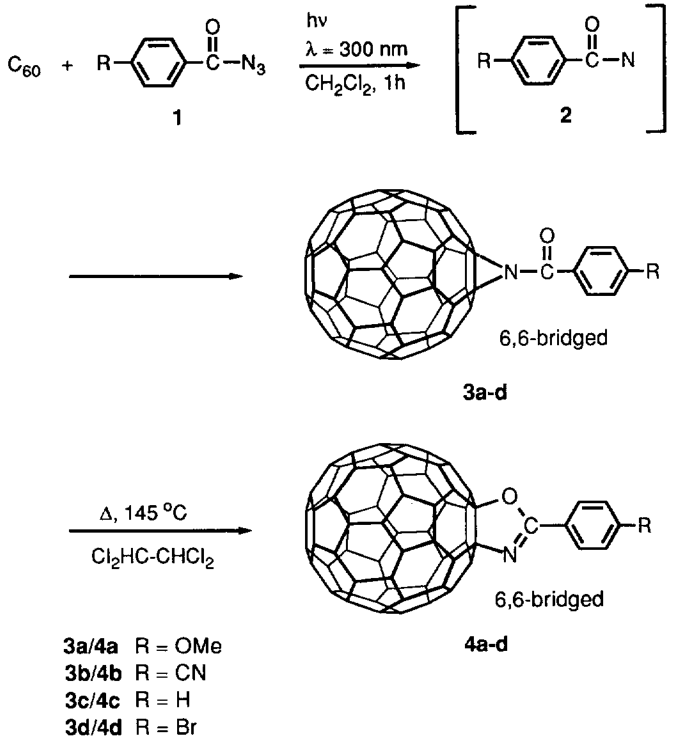


Fig. 1. Formation of fulleroaziridines **3** and thermal rearrangement to fullerooxazoles **4**.

The structures of the closed 6-6-ring fused 1,2-dihydrofullerenes **3a**, **3b**, **3c**, and **3d** have been identified by standard spectroscopic methods. The DEI mass spectra show the molecular ion peaks at m/e 869 (**3a**), 864 (**3b**), 839 (**3c**) and 917/919 (**3d**) together with peaks at m/e 720 owing to the fragment C_{60}. The proton decoupled ^{13}C-NMR spectrum of **3a** displays only 23 signals indicating C_{2v} symmetry of the molecule. The 17 signals of the C_{60} skeleton (16 between 146 und 140 ppm and one for the two sp^3 hybridized carbons appearing at 81.82 ppm), consist of 13 signals with a relative intensity of 2, and four signals with a relative intensity of 1. The remaining 6 signals are attributed to a carbonyl carbon atom at 169.34 ppm, to the six aromatic carbon atoms and to a aliphatic carbon at 55.89 ppm, respectively. The ^{1}H-NMR spectrum of **3a** shows three signals with a relative intensity of 2, 2 and 3 at 8.44, 7.13 and 3.96 ppm, respectively. The ^{13}C-NMR and ^{1}H-NMR spectra of **3b**, **3c**, **3d** exhibit signals, which have nearly the same chemical shift as the signals of **3a**. The UV/Vis absorption spectra (*n*-hexane) of the fullerene adducts are virtually identical to that of C_{60}, apart from the fact that the spectra show an additional absorption at about 420 nm (in toluene: 425 nm), which is characteristic of the dihydrofullerene structure. [15] The IR-spectra of **3a** exhibits characteristic broadened or splitted bands at 527, 576, 1182 and 1427 cm^{-1} of the fullerene moiety[16] and, in addition, an absorption of C=O at 1700 cm^{-1}. These results are only compatible with the C_{2v} symmetrical structure of the closed nitrogen-bridged fullerenes **3a-d**, and incompatible with iminoannulene or oxazole structures. [10,15,17]

By irradiation at wavelengths ≥ 380 nm (RPR-4190 Å lamps) no reaction was observed. Therefore, the formation of the acylnitrenes does not occur via excited C_{60}. In this case the formation of fullerene oxazole derivatives was not observed. This confirms that the reactivity of C_{60} is similar to the reactivity of electron deficient olefins. [18]

*Thermal rearrangement of the fulleroaziridines **3a-d** to fullerooxazoles **4a-d***

To investigate the thermodynamic stability solutions of **3a-d** in 1,1,2,2-tetrachloroethane were refluxed several hours. The colour of the solutions changed from wine-red to brown-red. The analysis with high performance liquid chromatography (HPLC)[19] shows the formation of new less polar products. These products were separated by precipitation with acetonitrile and yielded 90-97 % of fullerooxazoles **4a-d**.

The DCI mass spectra of compound **4a-d** show molecule ion peaks (MH^+) at m/e 870, 865, 840 and 918-921. Therefore the mass of the molecules **4a-d** are identical with the mass of the fulleroaziridines **3a-3d**. Surprisingly, the ^{13}C-NMR spectrum of **4a** does not show the expected 17 fullerene resonances as **3a,** but it exhibits, similar to the spectra of the fullerooxazole reported by Banks et al.[11], 32 signals (28 signals with relative intensity of 2, and 4 with intensity of 1) for the C_{60} skeleton including the signals of the bridgehead fullerene carbons[20] in the sp^3 region at 97.76 and 92.95 ppm (fig. 2.). The signal at 165,41 ppm is attributed to a C=N carbon and the signals of the aromatic and aliphatic carbons show similar highfield shifts as **3a** . The ^{13}C-NMR chemical shift of the bridgehead C-atoms and the number of ^{13}C-NMR resonances are the criteria for an 6,6-oxazole **4a** with a closed 6-6-ring fused 1,2-dihydrofullerene structure with C_s symmetry.[15,11] The fullerene adducts **4b-d** show about 30 fullerene resonances (partly unresolved) in the aromatic region and two resonances for the sp^3 fullerene carbons[20] between 100 and 90 ppm as well.

In difference to the FT-IR specta of **3a-3d** the spectra of **4a-d** do not show absorptions of C=O, but they display C=N absorption bands at about 1640 cm^{-1}. The UV/Vis spectra (*n*-hexane) of **4a-d** are similar to that

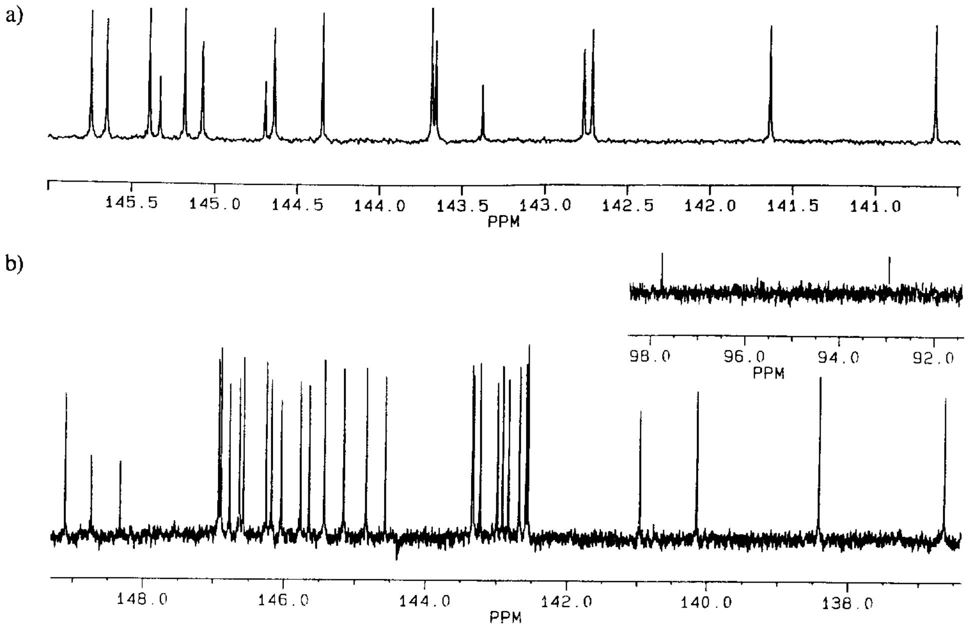


Fig. 2. Fulleroid ("aromatic") region of the ^{13}C-NMR spectra (90.5 MHz, $CS_2/(D_6)$acetone 10:1) of a) **3a** and b) **4a** (included the fulleroid sp^3 carbons at 97.76 (C-O) and 92.95 (C-N) ppm).

of C_{60}. The ^1H-NMR resonances of **4a-d** show nearly the same chemical shifts as those of the fulleroaziridines **3a-d**.

The transformation of **3a** to **4a** also occurs by heating of the fulleroaziridine **3a** in the solid state at 170 °C for a few hours.

Addition of acylnitrene 2b to C_{60} in benzene

The irradiation of a solution of 0.3 mmol of C_{60} and 1.7 mmol of 4-cyanobenzoylazide **1b** in 150 mL of benzene at $\lambda = 300$ nm did not lead to the expected formation of the fulleroaziridine **3b** (fig. 3.). However, the chromatographic analysis on a RP_{18} column (HPLC)[19] indicated the formation of a main fullerene adduct **A** (2nd fraction), beside a minor fullerene adduct (3rd fraction) and unconverted C_{60} (4th fraction). The mass spectrometrical analysis of the first fraction denotes a reaction of 4-benzoylnitrene **2b** with benzene (DCI-MS, m/e (MH^+) 223). The main product **A** was isolated in 20 mg yield by semipreparative HPLC[21]. FD+ mass spectral analysis shows a molecular ion peak at m/e 943 together with fragment ions at m/e 720, 360 and 224. This indicates an asymmetrical fullerene structure formed by reaction of the nitrene **2b** to C_{60} with incorporation of benzene, similar to the incorporation of benzene in the reaction of 1,8-dehydronaphthalene with C_{60}.[22] Additional support is given by the proton decoupled ^{13}C NMR showing more than 67 signals (some are unresolved). The UV/Vis spectrum exhibits the typical bands of 6,6-bridged dihydrofullerenes, including the bands at 433 and 701 nm (in toluene).[23] Further efforts to elucidate the structure of **A** are in progress.

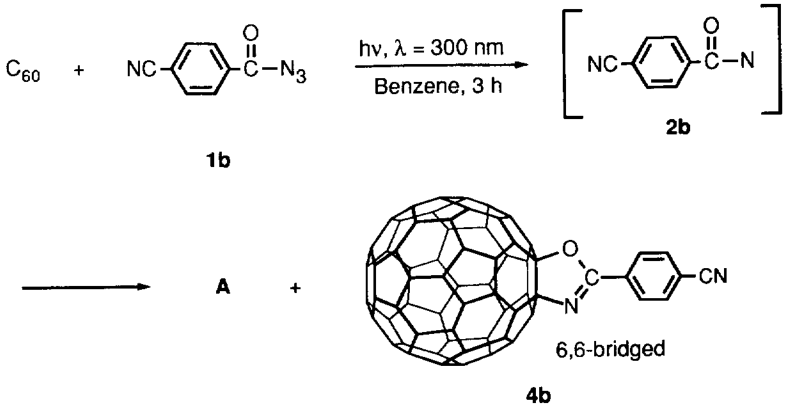


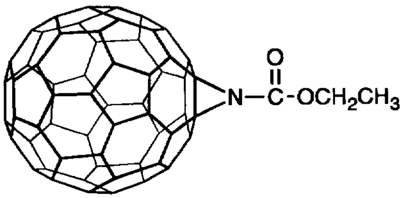
Fig. 3. Reaction of acylnitrene **2b** with C_{60} in benzene.

The minor fullerene adduct was separated in 4% yield by semipreparative HPLC and identified spectroscopically as the fullerooxazole **4b**. Similar results are observed in the photoaddition of benzoylnitrene **2c** to C_{60} in toluene.

DISCUSSION AND SUMMARY

The formation of **3** in dichloromethane seems to be surprising. We have found that the irradiation of **1b** in the absence of reaction partners exclusively leads to the corresponding isocyanate. But, by adding 2-methoxy-3,4-dihydro-2*H*-pyrane the cycloadduct of the acylnitrene to the olefin[9] has been obtained in 50% yield beside 40% of the corresponding isocyanate. This clearly demonstrates the formation of the acylnitrene in dichloromethane. The isocyanate is formed via an intermediate generated by the reaction of the nitrene with the solvent. Obviously, the reaction to the adduct **3b** can already compete with the solvent reaction of the acylnitrene at the very low concentration of C_{60} (3×10^{-4} M).

In summary the reaction of acylnitrenes **2** generated by photolysis of acylazides **1** with C_{60} in dichloromethane or in 1,1,2,2-tetrachloroethane gives the fullerene adducts with the closed 6-6-ring fused fulleroaziridine structures **3a-d**. They are similar to the fulleroaziridine derivatives, which were recently reported.[11-13] Our results confirm the nitrene addition to be the key step for the formation of fulleroaziridine derivatives. In addition we have shown that the fulleroaziridines **3a-d** can be rearranged to the fullerooxazoles **4a-b** at higher temperatures. Furthermore we observed that the addition of 4-cyanobenzoylnitrene **2b** in benzene also leads to the fullerooxazoles **4b**.



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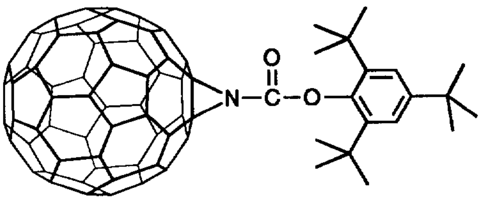

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Our results differ from the report about the synthesis of the fulleroaziridine **5** by a one-pot reaction from C_{60}, NaN_3, $ClCO_2C_2H_5$ and 15-crown-5 ether in refluxing toluene.[13] The authors did not observe any conversion of **5** after refluxing in o-dichlorobenzene for 8 h. On the other hand Banks et al.[11] described the thermal rearrangement of the fulleroaziridine **6** to a fullerene 4,5-substituted oxazole.

The present reactions demonstrate a versatile route to synthesize a variety of stable and soluble fullerene derivatives by photochemical functionalization of C_{60}.

EXPERIMENTAL

General remarks and materials

Azides **1a-d** were prepared according to literature procedures.[14] C_{60} was used in *gold grade* quality (Hoechst, ≥ 99.4 %). All reactions were performed under an argon atmosphere. Toluene, dichloromethane and trichloromethane were used in *per analysis* quality. 1,1,2,2-Tetrachloroethane was of *purum* grade (> 98 %), and *n*-hexane and acetonitrile were freshly distilled. Removal of all solvents was carried out at 40 °C 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. Column chromatography was perfomed on silica gel 60 (Merck, 63-200 µm) or neutral alumina (ICN Alumina N, Akt. I). Direct chemical ionization mass spectrometry (DCI-MS) was performed on a Finnigan MAT 8200 instrument, and the electron impact mass spectra (EI-MS) were obtained on a Finnigan MAT 312. Relative intensities are given in percentages. NMR spectra were obtained from a Bruker AM 360 spectrometer at 360 MHz for ^{1}H-NMR spectra and 90.5 MHz for ^{13}C-NMR spectra. Chemical shifts are given in ppm downfiled of tetramethylsilane (TMS). Fourier transform infrared specta (FT-IR) were recorded on a Nicolet 5DXC FT-IR spectrometer and the absorptions are given in cm^{-1}. UV/Vis spectra were obtained on a Shimadzu UV-2100 spectrophotometer.

1,2-[N-(4-methoxybenzoyl)aziridino]-[60]fullerene (**3a**).

A solution of 434 mg (0.60 mmol) of C_{60} and 428 mg (2.42 mmol) of 4-methoxybenzoylazide **1a** in 120 mL of 1,1,2,2-tetrachloroethane was irradiated for 5 h. The fullerenes were separated by precipitation with 600 mL of acetonitrile. The resulting precipitate was collected and washed thoroughly with acetonitrile. Chromatography on silica gel (300 g) with *n*-hexane followed by *n*-hexane / toluene 1 : 1 gave 202 mg (47 %) of unconverted C_{60} (1st fraction) and 96 mg (18 %, 34 % based on consumed C_{60}) of **3a** (2nd fraction) as a black grey powder.

EI-MS 70 kV (m/e (%)): 869 (24; $MH^{\bullet+}$), 722 (57), 721 (88), 720 (100; $M^{\bullet+}$ - $C_8H_7NO_2$). Exact mass calc. for $C_{68}H_7NO_2{}^{\bullet+}$: 869.047679, found: 869.04531. +^{1}H-NMR (360 MHz; $CS_2/(D_6)$acetone 10 : 1): δ = 8.44 (m, 2 H), 7.13 (m, 2 H), 3.96 (s, 3 H) ppm. ^{13}C-NMR (90,5 MHz; $CS_2/(D_6)$acetone 10 : 1): δ = 169.34, 164.85, 145.77, 145.68, 145.42, 145.36, 145.21, 145.11, 144.72, 144.67, 144.37, 143.71, 143.69, 143.41, 142.80, 142.75, 141.67, 140.66, 132.02, 123.76, 115.39, 81.82, 55.89 ppm. FT-IR (KBr): 1693s, 1602s, 508m, 1459w, 1428m, 1396m, 1316w, 1265m, 1254s, 1182m, 1164s, 1092w, 1043m, 1026m, 950w, 843m, 793m, 727m, 694m, 576m, 527ss. UV/Vis λ_{max} (ε) in *n*-hexane: 211 (64000), 257 (54000), 318 (15000), 421 (1200).

1,2-[N-(4-cyanobenzoyl)aziridino]-[60]fullerene (**3b**).

143 mg (0.20 mmol) of C_{60} and 137 mg (0.77 mmol) of 4-cyanobenzolazide **1b** were dissolved in 40 mL of 1,1,2,2-tetrachloroethane and irradiated for 4.5 h. After precipitation of the fullerenes with 200 mL of acetonitrile, the mixture was filtered and the residue was thoroughly washed with acetonitrile and finally extracted with toluene. The extract was chromatographed on silica gel. Elution with *n*-hexane/toluene 2:1 gave 52 mg (36%) of unconverted C_{60} and elution with toluene/*n*-hexane 1:1 gave 47 mg (27%, 42% based on consumed C_{60}) of **3b** as a dark grey powder.

EI-MS 70 kV (m/e (%)): 865 (27; $MH^{\bullet+}$), 864 (19), 720 (100; $M^{\bullet+}$ - $C_8H_4N_2O$). Exact mass calc. for $C_{68}H_4NO_2^{\bullet+}$: 864.032362, found: 864.03483. ^{1}H-NMR (360 MHz; CS_2/(D_6)acetone 10:1): δ = 8.65 (m, 2 H), 8.03 (m, 2 H) ppm. ^{13}C-NMR (90,5 MHz; CS_2/(D_6)acetone 10:1): δ = 168.91, 145.84, 145.75, 145.57, 145.45, 145.13, 144.99, 144.59, 144.36, 143.76 (2x), 143.75, 143.43, 142.78, 142.60, 141.76, 140.69, 134.89, 133.59, 130.31, 118.36, 117.54, 81.32 ppm. FT-IR (KBr): 2228w, 1700s, 1696s, 1428m, 1400s, 1317w, 1296w, 1263ss, 1183w, 1093s, 1042s, 1016s, 950w, 862w, 802sh, 798ss, 727w, 691m, 578w, 573w, 565w, 555w, 544w, 526ss, 525sh. UV/Vis λ_{max} (ε) in *n*-hexane: 213 (64000), 255 (64000), 319 (24000), 420 (3400).

1,2-(N-benzoylaziridino)-[60]fullerene (**3c**).

A solution of 288 mg (0.40 mmol) of C_{60} and 252 mg (1.71 mmol) of benzoylazide **1c** in 80 mL 1,1,2,2-tetrachloroethane was irradiated for 7.5 h. After precipitation of the fullerenes with acetonitrile the 1,1,2,2-tetrachloroethane was removed by filtration. The residue was washed twice with acetonitrile, then eluted with toluene and after evaporation of the solvent chromatographed on silica gel. Elution with *n*-hexane gave 63 mg (22%) of unconverted C_{60} and elution with *n*-hexane/toluene 3:2 created 133 mg (40%, 51% based on consumed C_{60}) of **3c**. With *n*-hexane/toluene 1:1 a 3rd fraction of 55 mg of dark brown powder was eluted. Mass-spectrometrical analysis (DCI) indicates the formation of higher fullerene adducts up to a ratio of 1:4.

EI-MS 70 kV (m/e (%)): 839 (6; $MH^{\bullet+}$), 838 (10; $M^{\bullet+}$ - H), 721 (46), 720 (100; $M^{\bullet+}$ - C_7H_5NO). ^{1}H-NMR (360 MHz; CS_2/(D_6)acetone 10:1): δ = 8.48 (m, 2 H), 7.73 (m, 1 H), 7.64 (m, 2H) ppm. ^{13}C-NMR (90,5 MHz; CS_2/(D_6)acetone 10:1): δ = 169.77, 145.71, 145.61, 145.39, 145.30, 145.08, 145.04, 144.61, 144.32, 144.29, 143.66, 143.63, 143.33, 142.72, 142.64, 141.63, 140.60, 134.40, 131.51, 129.832, 129.72, 81.62 ppm. FT-IR (KBr): 1700s, 1448w, 1427m, 1395m, 1316w, 1264s, 1254s, 1182m, 1043m, 1021m, 953w, 692s, 590w, 576w, 565w, 527ss. UV/Vis λ_{max} (ε) in *n*-hexane: 208 (61000), 255 (43000), 322 (11000), 420 (400-500).

1,2-[N-(4-bromobenzoyl)aziridino]-[60]fullerene (**3d**).

A solution of 293 mg (0.41 mmol) of C_{60} and 368 mg (1.63 mmol) of 4-bromobenzoylazide **1d** in 80 mL of 1,1,2,2-tetrachloroethane was irradiated for 5 h. The fullerenes were separated by precipitation with 600 mL of acetonitrile. The resulting mixture was filtered and the residue was washed thoroughly with acetonitrile. Chromatography on silica gel with *n*-hexane followed by *n*-hexane/toluene 3:2 gave 154 mg (52%) of unconverted C_{60} (1st fraction) and 78 mg (21%, 44% based on consumed C_{60}) of **3d** (2nd fraction) as a black grey powder. A 3rd fraction a orange red solution of 47 mg (10%) of bisadduct (identified with DCI mass-spectrometry) was eluted with *n*-hexane / toluene 1:1.

EI-MS 70 kV (m/e ≥400 (%)): 919 (5; $MH^{\bullet+}$) 917 (3; $MH^{\bullet+}$), 721 (73), 720 (100; $M^{\bullet+}$ - C_7H_4NOBr). ^{1}H-NMR (360 MHz; $CS_2/(D_6)$acetone 10: 1): δ = 8.40 (m, 2 H), 7.83 (m, 2 H) ppm. ^{13}C-NMR (90,5 MHz; $CS_2/(D_6)$acetone 10: 1): δ = 169.29, 145.80, 145.70, 145.50, 145.40, 144.63, 144.35, 144.08, 143.73, 143.71, 143.40, 142.77, 142.65, 141.72, 140.67, 133.18, 131.33, 130.45, 130.20, 81.48 ppm. FT-IR (KBr): 1700sh, 1696s, 1586m, 1427w, 1395m, 1266s, 1253s, 1183w, 1172w, 1069w, 1041m, 1008s, 951w, 842w, 753w, 736w, 700w, 573w, 564w, 527ss, 525sh. UV/Vis λ_{max} (ε) in *n*-hexane: 211 (48000), 255 (43000), 318 (15000), 421 (1300).

1,2-[2-(4-methoxybenzoyl)-4,5-dihydrooxazolo]-[60]fullerene (**4a**).

A solution of 17.4 mg (0.02 mmol) of fulleroaziridine **3a** in 30 mL of acid free 1,1,2,2-tetrachloroethane (purified by column filtration on basic alumina) was boiled under reflux for 18 h. After cooling 200 mL of acetonitrile was added and then the resultant mixture was cooled and filtered. Elution of the residue with toluene followed by column chromatography on neutral alumina with toluene gave 16 mg (92 %) fullerooxazole **4a**.

DCI-MS (NH_3, m/e (%)): 872 (9), 871 (24), 870 (51; MH^+), 720 (100). Exact mass (EI) calc. for $C_{68}H_7NO_2^{\bullet+}$: 869.047676, found: 869.04531. ^{1}H-NMR (360 MHz; $CS_2/(D_6)$acetone 10: 1): δ = 8.37 (m, 2 H), 7.15 (m, 2 H), 3.99 (s, 3 H) ppm. ^{13}C-NMR (90,5 MHz; $CS_2/(D_6)$acetone 10: 1): δ = 165.41, 163.66, 149.10, 148.73, 148.32, 146.92, 146.89, 146.77, 146.63, 146.57, 146.25, 146.18, 146.04, 145.76, 145.64, 145.43, 145.16, 144.84, 144.57, 143.33, 143.32, 143.22, 142.98, 142.91, 142.82, 142.67, 142.58, 142.55, 140.96, 140.14, 138.41, 136.64, 131.64, 119.75, 114.83, 97.76, 92.95, 55.78 ppm. FT-IR (KBr): 1639s, 1607m, 1511s, 1420w, 1320br, 1172m, 1140w, 1088m, 1028m, 983s, 931m, 837m, 727m, 604w, 578w, 563m, 527ss. UV/Vis λ_{max} (ε) in *n*-hexane: 210 (83000), 257 (72000), 314 (25000); in toluene: 322 (33000).

1,2-[2-(4-cyanobenzoyl)-4,5-dihydrooxazolo]-[60]fullerene (**4b**).

22.6 mg (0.026 mmol) of **3b** was dissolved in 30 mL of 1,1,2,2-tetrachloroethane and refluxed for 3 h. Then 200 mL of acetonitrile was added, the resultant precipitation was isolated by filtration and the residue was eluted with trichloromethane. Finally the solvent was removed. **4b** was obtained as a brown powder in 20.5 mg (90 %) yield.

DCI-MS (NH_3, m/e (%)): 868 (5), 867 (31) 866 (72), 865 (100, MH^+), 721 (5), 720 (10). ^{1}H-NMR (360 MHz; $CS_2/(D_6)$acetone 10: 1): δ = 8.63 (m, 2 H), 8.01 (m, 2 H) ppm. ^{13}C-NMR (90,5 MHz; $CS_2/(D_6)$acetone 10: 1): δ = 164.64, 148.80, 148.39, 148.04, 147.01, 147.00, 146.87, 146.71, 146.65, 146.39, 146.06, 145.97, 145.84, 145.73, 145.27, 145.13, 144.84, 144.42, 143.43, 143.38, 143.32, 142.95, 142.87 (2x), 142.73, 142.59, 142.50, 141.08, 140.28, 138.39, 136.77, 133.13, 131.35, 130.31, 117.81, 117.15, 98.38, 92.79 ppm. FT-IR (KBr): 2230w, 1642s, 1408w, 1326m, 1262s, 1092s, 1020s, 982m, 929w, 849w, 803br, 658w, 603w, 577w, 563m, 527s, 525sh. UV/Vis λ_{max} (ε) in *n*-hexane: 210 (62000), 256 (50000), 314 (17000); in toluene: 321 (37000).

1,2-(2-benzoyl-4,5-dihydrooxazolo)-[60]fullerene (**4c**).

Refluxing of a wine-red solution of 33.8 mg (0.04 mmol) of fulleroaziridine **3c** in 40 mL 1,1,2,2-tetrachloroethane for 18 h gave a brown-red solution of **4c**. Precipitation with cooled acetonitrile and filtration gave a dark brown residue. The residue was washed thorougly with acetonitrile and eluted with trichloromethane. After evaporation of the solvent **4c** was obtained in 30.4 mg (90 %) yield.

DCI-MS (NH_3, m/e (%)): 842 (30), 841 (68), 840 (100; MH^+). ^{1}H-NMR (360 MHz; $CS_2/(D_6)$acetone 10 : 1): δ = 8.46 (m, 2 H), 7.71 (m, 1 H), 7.67 (m, 2 H) ppm. ^{13}C-NMR (90,5 MHz; $CS_2/(D_6)$acetone 10 : 1): δ = 165.73, 148.76 (2x), 148.35, 146.95, 146.94, 146.81, 146.66, 146.61, 146.31, 146.18, 146.04, 145.80, 145.68, 145.20, 145.16, 144.85, 144.43, 144.30, 143.37, 143.35, 143.26, 142.95, 142.94, 142.86, 142.71, 142.58, 141.01, 140.21, 138.41, 136.73, 133.13, 129.86, 129.44, 127.60, 97.92, 92.93 ppm. FT-IR (KBr): 1642s, 1511m, 1506sh, 1450w, 1326m, 1262s, 1181w, 1092s, 1026s, 983s, 933w, 804br, 773w, 690s, 660w, 576w, 563m, 527ss. UV/Vis λ_{max} (ε) in *n*-hexane: 212 (60000), 255 (49000), 315 (16000); in toluene: 322 (28000).

1,2-[2-(4-bromobenzoyl)-4,5-dihydrooxazolo]-[60]fullerene **(4d)**

14.0 mg (0.015 mmol) of **3d** was dissolved in 40 mL of 1,1,2,2-tetrachloroethane and refluxed for 15.5 h. Precipitation with cooled acetonitrile and filtration gave a dark brown residue. The residue was washed twice with acetonitrile and then eluted with trichloromethane. Finally the solvent was distilled of. **4d** was obtained as a brown powder in 13.6 mg (97 %) yield.

DCI-MS (NH_3, m/e (%)): 923 (5), 922 (24), 921 (63), 920 (100; MH^+), 919 (75), 918 (70), 722 (14), 721 (63), 720 (100). ^{1}H-NMR (360 MHz; $CS_2/(D_6)$acetone 10 : 1): δ = 8.36 (m, 2 H), 7.82 (m, 2 H) ppm. ^{13}C-NMR (90,5 MHz; $CS_2/(D_6)$acetone 10 : 1): δ = 165.15, 148.79, 148.47, 148.38, 146.98 (2x), 146.85, 146.70, 146.64, 146.35, 146.12, 146.02, 145.83, 145.71, 145.36, 145.16, 144.86, 144.03, 143.41, 143.37, 143.30, 142.95, 142.93, 142.87, 142.73, 142.59, 142.56, 141.05, 140.25, 138.42, 136.75, 132.82, 131.36, 128.47, 126.59, 98.15, 92.88 ppm. FT-IR (KBr): 1643s, 1632w, 1591w, 1485m, 1398m, 1384w, 1322m, 1261s, 1190w, 1181w, 1089s, 1012s, 983s, 931m, 798br, 723m, 657w, 603w, 563w, 527ss. UV/Vis λ_{max} (ε) in *n*-hexane: 210 (63000), 256 (36000), 315 (12000); in toluene: 320 (31000).

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19. C_{18}-reversed phase (Bischoff 250 x 4 mm, Merck LiChrosorb RP18, 7 μm), acetonitrile/toluol 1 : 1, UV/Vis detection at 300 nm (Kontron HPLC detector 432), 1.25 mL min^{-1} (Merck L-6000 pump).
20. In difference to the "aromatic" fullerene resonances with shorter relaxation times, the ^{13}C-NMR signals of the fullerene sp^3 carbons of **4a-4d** were only detected by using a relaxation delay of 10 sec. for **4a** and **4c** and 15 sec. for **4b** and **4d**.
21. C_{18}-reversed phase (250 x 20 mm, Merck LiChrosorb RP18, 7 μm), acetonitrile/toluol 1 : 1, UV/Vis detection at 300 nm (Abimed-Gilson Spectochrom detector), 9.5 mL min^{-1} (Kontron HPLC pump 420).
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