Preparation and Characterization of Sulfonyl-Azafulleroid and Sulfonylaziridino-Fullerene Derivatives

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Thermolysis of several sulfonyl azides in the presence of C_{60} leads either to aza[60]fulleroids or to mixtures of aza[60]-fulleroids and corresponding aziridino-fullerenes, depending on the substituent at the sulfonyl group. In all cases, 1,2-closed aziridino-fullerenes can be obtained from azafulleroids by irradiation. Addition of sulfonyl azides to C_{70} only yields azafulleroids with C_s-symmetry. Cyclic-voltammetric measurements revealed that there is no significant change of electrochemical properties compared to C_{60} and C_{70}.

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Introduction

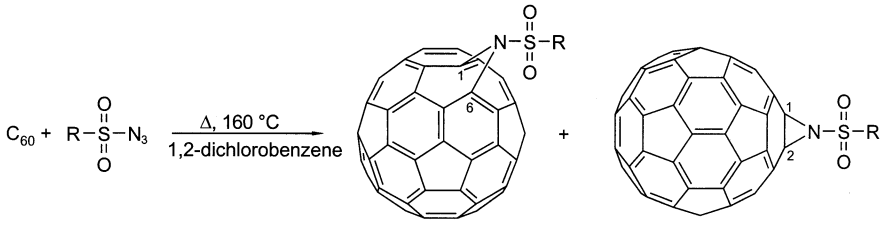
The thermal reaction of organic azides with fullerenes is a versatile route to provide stable cluster opened [5,6]-bridged iminofullerenes (azafulleroids).[1−12] Alternatively, cluster opened monofunctionalized fullerene derivatives (fulleroids) are accessible by thermal reactions of diazo compounds with fullerenes.[13−20] To the best of our knowledge, no other examples of cluster opened monoadducts of C_{60} and C_{70} are known. However, fulleroids containing at least one substituent such as a phenyl- or alkoxycarbonyl group are thermally convertible to the corresponding [6,6]-bridged isomers with closed fullerene framework.[2,5−8,11,13,17,21,22]

The synthesis of azafulleroids is achieved by [3+2] cycloadditions of azides to a [6,6] double bond of the fullerene with the formation of intermediate triazolines, followed by thermal cleavage of N_2. Depending on the nature of the substituent the nitrogen release affords different ratios of opened [5,6]-bridged azafulleroid to closed [6,6]-bridged aziridino-fullerene. Photochemical release of nitrogen predominantly leads to aziridino-fullerenes with closed fullerene framework.[2,9−11]

Nitrenes generated in situ by photolysis or thermolysis of azides add to fullerenes in [2+1] cycloadditons yielding exclusively closed [6,6]-bridged aziridino-fullerenes.[9,10,23]

Results and Discussion

We investigated addition reactions of several sulfonyl azides **1a−d** to C_{60} and C_{70}, photochemical rearrangements



1a-d **2a-d** **3a,b**

a: methyl, **b**: benzyl, **c**: tolyl, **d**: 4-methoxyphenyl

Scheme 1. Formation of (sulfonylimino)fullerenes by addition of sulfonyl azides to C_{60}

and the electrochemical properties of the synthesized fullerene derivatives.

The preparation of the sulfonylimino[60]fullerenes **2a−d, 3a−b** was achieved by thermal reaction of sulfonyl azides **1a−d** with C_{60} for 2 h as shown in Scheme 1. The sulfonyl

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azides were prepared by reaction of the corresponding sulfonyl chlorides with sodium azide.[24]

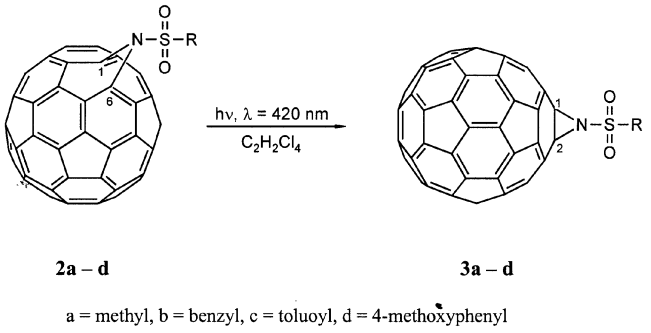
Chromatography on silica gel yielded unconverted C_{60} (1st fraction) and mixtures of azafulleroid/aziridino-fullerene (**2a/3a** and **2b/3b**) or only azafulleroids (**2c,d**) in > 25% yield, respectively. Separation of the azafulleroid/aziridino-fullerene mixtures has been accomplished by second chromatography on silica gel (**2a/3a**) or by HPLC (Bucky Clutcher I) (**2b/3b**). Azafulleroids are isolated in 11% (**2a**) and 7% (**2b**) yield and aziridino-fullerenes are isolated in 12% (**3a**) and 10% (**3b**) yield.

The structures of the [5,6]-opened azafulleroids **2a−d** have been identified by standard spectroscopic methods. MALDI-TOF mass spectra show for all monoadducts the molecular ion peaks at *m*/*z* = 813 (**2a/3a**), 889 (**2b/3b** and **2c/3c**) and 905 (**2d/3d**) together with peaks at *m*/*z* = 720 owing to the fragment C_{60}. The ^{13}C NMR spectra of **2a−d** show 32 signals at δ = 115−155 ppm for the sp^2 carbons of the C_{60} skeleton. The number of signals and the absence of signals in the range of δ = 60−80 ppm indicate both a [5,6]-opened structure without sp^3 carbons in the fullerene framework and C_s-symmetry. The remaining signals are attributed to the aromatic and aliphatic carbon atoms of the functional groups as well as the signals of the ^1H NMR spectra. Further evidence is obtained from the UV/Vis spectra which are similar to the spectrum of pure C_{60}. The characteristic absorption for [6,6]-closed fullerene derivatives at 420 nm are not observed.[14−17]

The ^{13}C NMR spectra of the aziridino-fullerenes **3a,b** show only 17 signals for the C_{60} skeleton [16 between δ = 115 and 155 ppm and one for the sp^3 hybridized carbons at δ = 79.48 ppm (**3a**) and 79.06 ppm (**3b**), respectively]. This indicates for both derivatives C_{2v}-symmetry with a [6,6] junction on the fullerene core. The UV/Vis spectra exhibits the typical bands of [6,6]-bridged dihydrofullerenes including the band at around 420 nm.

To synthesize the corresponding aziridino-fullerenes **3c** and **3d** solutions of the azafulleroids **2c** and **2d**, respectively, in oxygen free 1,1,2,2-tetrachloroethane were irradiated for 2 h in pyrex tubes (of, 10 mL) using a RPR 100 Rayonet Photochemical Chamber Reactor equipped with RPR-4190 Å lamps (Scheme 2). Chromatography on silica gel yielded small amounts of unconverted azafulleroid and the fulleroaziridine derivatives (**3c**, **3d**) in > 40% yield. The other azafulleroids (**2a**, **2b**) can be converted into the corresponding aziridino-fullerenes (**3a**, **3b**) by irradiation under same conditions as well. The ^1H, ^{13}C NMR and UV/Vis spectra of these compounds are identical to the ones described above.

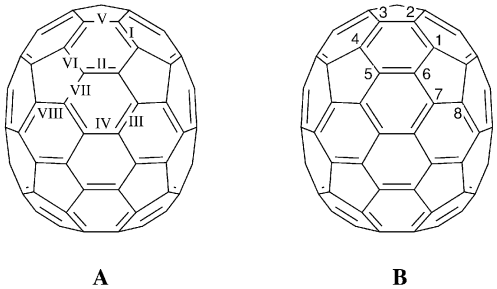
The ^{13}C NMR spectra of **3c** and **3d** show 16 signals at 120−150 ppm for the sp^2 carbons of the fullerene core and only one signal [δ = 80.01 ppm (**3c**) and δ = 80.17 ppm (**3d**)] for the sp^3 hybridized carbons in the fullerene framework, indicating C_{2v} symmetry with a [6,6] junction on the fullerene core. Further evidence is obtained from UV/Vis spectra which displays the characteristic absorption for 1,2 adducts at around 420 nm.



Scheme 2. Photochemical rearrangement of azafulleroids to aziridino-fullerenes

These results clearly show differences between reaction of alkylated (**1a**, **1b**) and arylated sulfonyl azides (**1c**, **1d**) with fullerenes. Addition of arylated sulfonyl azides exclusively results in the formation of azafulleroids whereas addition of alkylated sulfonylazides yields both, azafulleroids and aziridino-fullerenes in nearly the same ratio. The decisive step seems to be the nitrogen release from the intermediate triazoline. Luh et al. suggested the following mechanism for nitrogen release from triazolinofullerenes: homolytic cleavage of the N−N single bond of triazolines with formation of an amino/diazenyl diradical, which stabilizes by addition of the amino radical center to either C-6 or C-2 followed by N_2-release and electrocyclic ring opening.[11] Following this mechanism, differences in reactivity result from stabilizing effects in the diradical species. Ouchi, Ito and co-workers also observed a large substituent effect on the photochemical rearrangement of *N*-aryl-aza[60]fulleroids.[25]

In contrast to C_{60} monofunctionalization of C_{70} leads to mixtures of regioisomers due to lower symmetry and to differences in reactivity between the various double bonds. There are each four different [6,6] (I−IV) and [5,6] ring fusions (V−VIII) (Scheme 3). Double bonds in the pole region are more reactive (I, II) which is explained by the greater curvature and the resulting higher bonding tension. Therefore addition reactions theoretically could lead to eight regioisomeric monoadducts. Four of them have a [6,6] junction and four have a [5,6] junction. Additions to the [6,6] bonds result in closed structures which could be distinguished by ^{13}C NMR spectroscopy. Functionalization at bond I and II leads to C_s-symmetrical adducts with each



Scheme 3. A: Eight distinct sets of bonds of C_{70}: [6,6]- (I−IV) and [5,6] bonds (V−VIII). B: Partial numbering of some carbon atoms corresponding the IUPAC.[21]

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37 signals in the region for sp^2 hybridized fullerene carbon atoms. Due to different bridgehead atoms in the fullerene core it is possible to distinguish between these closed C_s-symmetrical adducts. 1,2 adducts (bond I) show two different signals for the two non equivalent sp^3 hybridized carbons while at [5,6] adducts (bond II) display only one signal for the two equivalent bridgehead atoms. ^{13}C NMR spectra of C_{70} derivatives functionalized at bond III show 70 signal because of the C_1-symmetry fullerene derivatives. Additions to bond IV result in C_{2v}-symmetrical adducts of which ^{13}C NMR spectra show only 21 signals for the fullerene carbons.[4,7,18,26−32]

C_{70} adducts with junctions to [5,6] ring fusions (V−VIII) can be synthesized accordingly to the [60]fulleroid derivatives. First, azides are added to C_{70} with formation of triazolino derivatives. Nitrogen release and a norcaradiene rearrangement leads now to aza[70]fulleroid. Depending on the first addition step, four different regioisomers are possible. Two of these isomers, the C2−C3 and the C7−C8 fulleroid, have a plane of symmetry whereas the two other ones, functionalized at bonds VI and VII, are C_1-symmetrical. The C_s- and the C_1-symmetrical fulleroids could not be distinguished from each other by ^{13}C NMR spectroscopy due to the same number of signals in the region for sp^2 hybridized fullerene carbon atoms.[4,7,18,26−32]

Thermolysis of sulfonyl azides **1a**, **1c**, and **1d** in the presence of C_{70} in 1,2-dichlorobenzene for 3 h at 160 °C leads to aza[70]fulleroids. In case of methylsulfonyl azide (**1a**) only one aza[70]fulleroid besides several by-products in < 3% was obtained whereas addition of **1c** and **1d** resulted in the formation of two isomeric azafulleroids (Scheme 4).

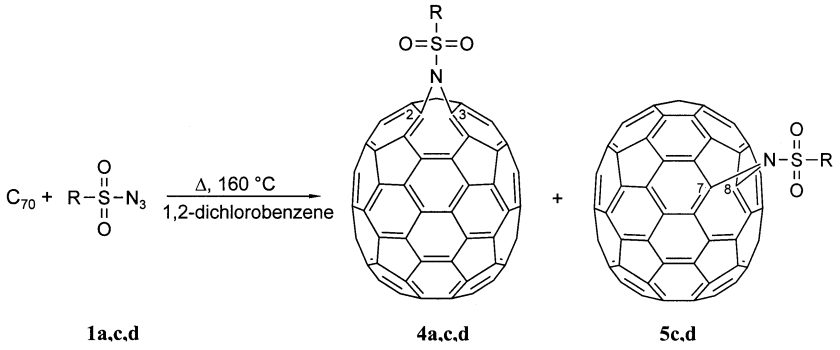
Chromatography on silica gel with toluene/cyclohexane yielded unconverted C_{70} (1st fraction) and mixtures of azafulleroids and by-products. Separation of the azafulleroids was carried out by second chromatography on silica gel with toluene/cyclohexane (1:2). Azafulleroids were isolated in 12% (**4a**), 9% (**4c**), 6% (**5c**), 10% (**4d**) and 7% (**5d**) yield, and their molecular formulae were confirmed by mass spectrometry.

Addition product **4a** displays a ^{13}C NMR spectrum comprised of 38 resonances, 37 sp^2 resonances in the region of δ = 115−155 ppm and 1 single intensity sp^3 resonance assigned to the methyl group. The presence of only one sp^3 resonance indicates that this isomer is a fulleroid, and the number of resonances indicates a structure with C_s-symmetry. There are two possible fulleroids with C_s-symmetry of **4a**: one formed by [3+2] cycloddition of methylsulfonyl azide to the C1−C2 double bond followed by nitrogen release and rearrangement to the C2−C3 position with an opened cluster structure. The second possible structure is formed by [3+2] cycloddition of methylsulfonyl azide to the C7−C21 double bond. Decomposition of the triazoline and rearrangement to the C7−C8 position leads also to an opened cluster structure. We tentatively assigned **4a** to a C2−C3 azafulleroid structure due to the higher reactivity of the C1−C2 double bond in the most curved surface.

The ^{13}C NMR spectra of **4c**, **5c**, **4d** and **5d** indicate fulleroid structures with a plane of symmetry for all as well. Each spectrum displays one single intensity sp^3 resonance assigned to the corresponding methyl group and 41 sp^2 resonances, four assigned to the phenyl group and 37 assigned to the fullerene carbons. These patterns are indicative of C_s-symmetrical fulleroid structures. Since the polar region of C_{70} is the more reactive area of the fullerene, we assume the major products **4c** and **4d** to be formed upon addition to the C2−C3 bond. Consequently, the minor products **5c** and **5d** must be functionalized at the C7−C8 bond. The UV/Vis spectra of the fulleroids **4a, 4c** and **4d** are similar to each other and the spectra of all five monofunctionalised aza[70]fulleroids are similar to the one of C_{70}.

These results suggest that sulfonyl azides are suitable to synthesize aza[70]fulleroids, with a C2−C3 junction as well as with a C7−C8 junction. There are only few examples of C_{70} derivatives containing a C7−C8 junction reported so far.[31,32]

The electrochemical behavior of the sulfonyliminofullerenes was studied by cyclic voltammetry and compared to that of C_{60} and C_{70} in order to determine the extent of electronic interaction between addend and fullerene core. The measurements were performed in *o*-dichlorobenzene with 0.1 M $(Bu_4N)BF_4$ as supporting electrolyte. The data for the C_{60} derivatives are listed in Table 1.



a: methyl, **c**: tolyl, **d**: 4-methoxyphenyl

Scheme 4. Formation of aza[70]fulleroids by addition of sulfonyl azides

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Table 1. $E_{1/2}$ values (mV vs. Fc/Fc^+) of C_{60} and several sulfonylimino[60]fullerenes ($E_{1/2} = (E_{red} + E_{reox})/2$, E_{red} and E_{reox} peak potentials; $\Delta E = E_{reox} + E_{red}$)

Compound	1st reduction potential, $E^1_{1/2}$ (ΔE)/[mV]	2nd reduction potential, $E^2_{1/2}$ (ΔE)/[mV]	3rd reduction potential, $E^3_{1/2}$ (ΔE)/[mV]
C_{60}	−1050 (63)	−1450 (67)	−1915 (65)
2a	−1086 (72)	−1464 (74)	−1930 (74)
3a	−1088 (82)	−1476 (82)	−1934 (86)
2c	−1084 (85)	−1460 (87)	−1922 (88)
3c	−1088 (76)	1466 (80)	−1932 (85)
2d	−1070 (85)	−1454 (90)	−1911 (90)
3d	−1080 (68)	−1470 (68)	−1926 (72)

Table 2. $E_{1/2}$ values (mV vs. Fc/Fc^+) of C_{60} and several sulfonylimino[70]fullerenes ($E_{1/2} = (E_{red} + E_{reox})/2$, E_{red} and E_{reox} peak potentials; $\Delta E = E_{reox} + E_{red}$)

Compound	1st reduction potential, $E^1_{1/2}$ (ΔE)	2nd reduction potential, $E^2_{1/2}$ (ΔE)	3rd reduction potential, $E^3_{1/2}$ (ΔE)
C_{70}	−1066 (63)	−1442 (67)	−1846 (65)
4a	−1070 (72)	−1428 (74)	−1846 (74)
4c	−1076 (85)	−1454 (87)	−1855 (88)
5c	−1064 (76)	−1412 (80)	−1832 (85)
4d	−1054 (85)	−1422 (90)	−1826 (90)
5d	−1066 (68)	−1430 (68)	−1840 (72)

All compounds exhibit three well defined, single electron, quasireversible waves[33,34] and retain the electronic properties of C_{60}. The reduction potentials are slightly shifted toward more negative values than in C_{60} itself. However, the effect of functionalization is large for the first reduction step for all derivatives. Among them the methoxy sulfonyl group causes the smallest effect. This behaviour is observed in most [60]fullerene derivatives, of which cyclic voltammograms are typically characterised by small shifts to more negative values of the reduction potentials due to an increase of electron density.[14−18,35−38]

The data for the C_{70} derivatives are listed in Table 2. These compounds exhibit three well defined, single electron, quasireversible reduction steps and retain the electronic properties of C_{70}. Though the effect of functionalization on the potentials is not uniform. These results are in agreement with other [70]fullerene derivatives.[39,40,41]

Conclusion

Thermolysis of sulfonyl azides has been shown to be a versatile procedure for the formation of monofunctionalized aza[60]fulleroids with an opened cluster structure. The corresponding aziridino-fullerenes are accessible by photochemical rearrangement. Addition of sulfonyl azides to C_{70} leads to the formation of fulleroid structures as well. Surprisingly, the functionalization occurs at the pole region with most curved surface as well as at the relatively flat midsection. The influence of sulfonylimino groups on the electronic properties of the fullerene seems to be small in the investigated region for both, the C_{60} and C_{70} derivatives.

Experimental Section

General Remarks: C_{60} and C_{70} were used in *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 (of, 10 mL) in a RPR-100 Rayonet Photochemical Chamber Reactor with RPR-4190 Å lamps. Analytical high performance liquid chromatography (HPLC) was performed by using a C_{18}-reversed phase column (Macherey ET 250/4 Nucleosil 100−5) and 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 decanting to remove the pentane soluble components. It was 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

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to solvent peak as reference. Fourier tranform infrared spectra were recorded with a Perkin−Elmer 1600-FTIR spetrometer. UV/Vis spectra were performed with a Perkin−Elmer Lambda 40 spectrophotometer.

Electrochemical Measurements: The electrochemical studies were carried out in *o*-dichlorobenzene (*per analysis* quality, water-free). The supporting electrolyte was $(Bu_4N)BF_4$ (0.1 M). All measurements were carried out using a K0264 three-electrode cell. The working electrode was a Pt-electrode (diameter 2 mm), the auxiliary electrode a Pt-wire, and the reference electrode a Ag-wire (pseudo-reference electrode). All potentials in the text are given vs. Fc/Fc^+ used as internal standard. The cell was connected to a computerized PAR 273 A (EG&G Princton Applied Research, USA).

Reaction of C_{60} with Methylsulfonyl Azide (1a): A solution of C_{60} (216 mg, 0.30 mmol) and methylsulfonyl azide (**1a**, 0.75 g, 6.2 mmol) in 50 mL 1,2-dichlorobenzene was heated at 160 °C for 2 h. The solvent was then evaporated under reduced pressure. Chromatography on silica gel 60 (toluene/cyclohexane, 1:1) gave 85 mg (39%) of unconverted C_{60} and 85 mg of a mixture of **2a** and **3a**. The solution of the mixture was reduced to 20 mL and second chromatography on silica gel 40 (toluene/cyclohexane, 1:1) gave 30 mg (12%) of **3a** (1st fraction) and 26 mg (11%) of **2a** (2nd fraction).

1st Fraction, *N*-(Methylsulfonyl)aziridino[2′,3′:1,2][60]fullerene: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 3.72 (s, 3 H, 5′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 145.47, 145.32, 145.25, 145.18, 144.68, 144.30, 144.15, 144.07, 143.41, 143.31, 143.28, 142.98, 142.35, 142.05, 141.16, 129.16 (16 C_{60} sp^2 signals), 79.48 (C-1, C-2), 43.08 (C-5′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2922 m (CH_3), 1348 s, 1161 s, 955 m, 816 m, 698 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 254 (90100), 323 (27700), 402 sh (2400), 410 (2100), 422 (1500), 484 (1100), 600 sh (450), 680 (130) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m*/*z* (%) = 813 (100) $[M]^-$ (calcd. 812.99), 720 (56) $[M - CH_3NO_2S]^-$.

2nd Fraction, 1,6-(*N*-Methylsulfonyl)aza[60]fulleroid: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 3.49 (s, 3 H, C-3′) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 147.86, 147.44, 144.72, 144.61, 144.46, 144.39, 144.38, 144.36, 144.29, 144.08, 143.91, 143.90, 143.70, 143.56, 143.21, 143.05, 142.00, 141.90, 141.20, 140.41, 140.11, 140.08, 138.99, 138.88, 138.81, 138.12, 135.86, 135.13, 133.87, 128.44, 127.19, 125.55 (32 C_{60} sp^2 signals), 41.36 (C-3′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2922 m (CH_3), 1357 s, 1162 s, 955 m, 769 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 258 (94000), 327 (30100), 525 (830), 595 sh (590) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m*/*z* (%) = 813 (100) $[M]^-$ (calcd. 812.99), 720 (45) $[M - CH_3NO_2S]^-$.

Reaction of C_{60} with Benzylsulfonyl Azide (1b): A solution of C_{60} (216 mg, 0.30 mmol) and benylsulfonyl azide (**1b**, 1.2 g, 6.0 mmol) in 70 mL 1,2-dichlorobenzene was heated for 15 min under reflux. The solvent was then evaporated under reduced pressure. Chromatography on silica gel 60 (toluene/cyclohexane, 1:1) gave 90 mg (42%) of unconverted C_{60} and 72 mg of a mixture of **2b** and **3b**. The solution of the mixture was reduced to 20 mL. Chromatography with HPLC (Bucky Clutcher I) (toluene/cyclohexane, 10:1) gave 18 mg (7%) of **2b** (1st fraction) and 26 mg (10%) of **3b** (2nd fraction).

1st Fraction, 1,6-(*N*-Benzylsulfonyl)aza[60]fulleroid: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 4:1): δ = 7.56−7.54 (m, 2 H, 6′-H, 8′-H), 7.47−7.45 (m, 3 H, 7′-H, 5′-H, 9′-H), 4.71 (s, 2 H, 3′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 147.35, 147.16, 144.78, 144.46, 144.38, 144.35, 144.33, 144.31, 144.28, 144.26, 144.16, 144.01, 143.82, 143.65, 143.51, 143.26, 143.24, 143.12, 143.07, 142.86, 141.96, 141.83, 140.36, 140.25, 139.81, 138.90, 138.85, 138.77, 138.10, 136.44, 135.07, 134.05 (32 C_{60} sp^2 signals), 131.47 (C-5′, C-9′), 129.40 (C-7′), 129.10 (C-6′, C-8′), 127.98 (C-4′) 60.85 (C-3′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2918 m (CH_2), 1508 s, 1355 s, 1153 s, 694 s, 528 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 240 nm, ε) = 260 (144000), 325 (48000) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m*/*z* (%) = 889 (100) $[M]^-$ (calcd. 889.03), 734 (25) $[M - C_7H_7NO_2S]^-$.

2nd Fraction, *N*-(Benzylsulfonylaziridino)[2′,3′:1,2][60]fullerene: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 4:1): δ = 7.78−7.77 (m, 2 H, 8′-H, 10′-H), 7.53−7.48 (m, 3 H, 7′-H, 9′-H, 11′-H), 4.83 (s, 3 H, 5′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 145.47, 145.32, 145.21, 144.68, 144.37, 144.13, 144.08, 143.39, 143.26, 143.25, 142.92, 142.38, 141.99, 141.23, 141.01 (15 C_{60} sp^2 signals), 131.61 (C-7′, C-11′), 129.60 (C-9′), 129.50 (C-8′, C-10′), 127.99 (C-6′) 61.95 (C-5′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2918 m (CH_2), 1341 s, 1152 s, 818 m, 696 m, 525 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 240 nm, ε) = 254 (106000), 322 (32000), 407 (200), 422 (1250) nm. MS (MALDI-TOF, pos. ion-mode, DCTB, 15 kV): *m*/*z* (%) = 889 (100) $[M]^+$ (calcd. 889.03).

Reaction of C_{60} with (4-Methylphenyl)sulfonyl Azide (1c): A solution of C_{60} (216 mg, 0.30 mmol) and (4-methylphenyl)sulfonyl azide (**1c**, 1.2 g, 6.0 mmol) in 50 mL 1,2-dichlorobenzene was heated at 160 °C for 2 h. The solvent was then evaporated under reduced pressure. Chromatography on silica gel 60 (toluene/cyclohexane, 1:1) gave 83 mg (38%) of unconverted C_{60} (1st fraction) and 75 mg (28%) of **2c** (2nd fraction).

2nd Fraction, 1,6-[*N*-(4′-Methylphenylsulfonyl)]aza[60]fulleroid: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 4:1): δ = 8.02 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, 4′-H, 8′-H), 7.42 (d, $^3J_{H,H}$ = 8.4 Hz, 2 H, 5′-H, 7′-H), 2.55 (s, 3 H, 9′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 148.20, 147.15, 144.68, 144.53, 144.14, 143.99, 143.96, 143.89, 143.81, 143.77, 143.62, 143.50, 143.45, 143.25, 143.04, 142.82, 142.79, 142.67, 142.52, 141.50, 141.46, 139.89, 139.54, 139.29, 138.40, 138.14, 137.71, 137.68, 135.31, 134.62, 133.69 (31 C_{60} sp^2 signals), 135.47 (C-6′), 129.68 (C-5′, C-7′), 128.77 (C-4′, C-8′), 21.66 (C-9′) ppm. FT-IR (KBr): nu(tilde = 2913 m (CH_3), 1508 s, 1338 s, 1261 m, 1165 s, 1086 s, 807 s, 644 m, 525 s cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 240 nm, ε) = 259 (56000), 326 (18250) nm. MS (MALDI-TOF, pos. ion-mode, DCTB, 15 kV): *m*/*z* (%) = 889 (100) $[M]^+$ (calcd. 889.03), 720 (46) $[M - C_7H_7NO_2S]^+$.

Reaction of C_{60} with (4-Methoxyphenyl)sulfonyl Azide (1d): A solution of C_{60} (216 mg, 0.30 mmol) and (4-methoxyphenyl)sulfonyl azide (**1d**, 1.3 g, 6.1 mmol) in 50 mL 1,2-dichlorobenzene was heated at 160 °C for 2 h. The solvent was then evaporated under reduced pressure. Chromatography on silica gel 60 (toluene/cyclohexane, 2:1) gave 75 mg (35%) of unconverted C_{60} and 90 mg of **2d** polluted with polar by-products. The solution of **2d** then was reduced to 20 mL. Chromatography on silica gel 40 (toluene/cyclohexane, 1:1) gave 84 mg (31%) of **2d**.

2nd Fraction, 1,6-[*N*-(4′-Methoxyphenylsulfonyl)]aza[60]fulleroid: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 8.02 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 4′-H, 8′-H), 7.05 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 5′-H, 7′-H), 3.95 (s, 3 H, 10′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 163.63 (C-6′), 148.19, 147.24, 144.56, 144.16, 144.05, 144.02, 143.94, 143.84, 143.82, 143.75, 143.66, 143.55, 143.50, 143.30, 143.08, 142.90, 142.89, 142.86, 142.85, 142.59, 142.53, 141.55, 141.50, 139.90, 139.60, 139.36, 138.48, 138.19, 137.80, 137.68, 135.33, 134.71, 134.11, 131.04 (32 C_{60} sp^2 signals, C-3′, C-

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4′, C-8′), 114.18 (C-5′, C-7′), 55.30 (C-10′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2930 s (CH_3), 1740 m, 1592 m, 1494 m, 1261 s, 1159 s, 1088 s, 1024 m, 803 m, 683 m, 612 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 258 (92500), 325 (33000) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m/z* (%) = 905 (100) $[M]^-$ (calcd. 905.02), 720 (20) $[M - C_7H_7NO_3S]^-$.

Photochemical Rearrangements of Azafulleroids to the Corresponding Aziridino-fullerenes

Synthesis of *N*-(Methylsulfonyl)aziridino[2′,3′:1,2][60]fullerene (3a): A solution of 1,6-(*N*-methylsulfonyl)aza[60]fulleroid (**2a**, 65 mg, 0.08 mmol) in 60 mL 1,1,2,2-tetrachlorethane was irradiated for 5 h. The solvent was evaporated under reduced pressure. Chromatography on silica gel 40 (toluene/cyclohexane, 1:2) gave 26 mg (40%) of **3a** (1st fraction) and 13 mg (20%) not consumed **2a**.

Synthesis of *N*-(Benzylylsulfonyl)aziridino[2′,3′:1,2][60]fullerene (3b): A solution of 1,6-(*N*-benzylsulfonyl)aza[60]fulleroid (**2b**, 15 mg, 0.02 mmol) in 20 mL 1,1,2,2-tetrachlorethane was irradiated for 4 h. The solvent was evaporated under reduced pressure, and the residue was filtered through silica gel with toluene. Chromatography with HPLC (Bucky Clutcher I) (toluene/cyclohexane, 10:1) gave 8 mg (53%) of **3b** (1st fraction) and 3 mg (20%) not consumed **2b** (2nd fraction).

Synthesis of *N*-(4′-Methylphenylsulfonyl)aziridino[2′,3′:1,2][60]fullerene (3c): A solution of 1,6-[*N*-(4′-methylphenylsulfonyl)]aza[60]fulleroid (**2c**, 75 mg, 0.08 mmol) in 60 mL 1,1,2,2-tetrachlorethane was irradiated for 6 h. The solvent was evaporated under reduced pressure, and the residue was filtered through silica gel with toluene. Chromatography with HPLC (Bucky Clutcher I) (toluene/cyclohexane, 8:1) gave 31 mg (41%) of **3c** (1st fraction) and 17 mg (23%) not consumed **2c** (2nd fraction).

1st Fraction, *N*-(4′-Methylphenylsulfonyl)aziridino[2′,3′:1,2][60]fullerene: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 4:1): δ = 8.24 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, 4′-H, 8′-H), 7.59 (d, $^3J_{H,H}$ = 8.5 Hz, 2 H, 5′-H, 7′-H), 2.66 (s, 3 H, 10′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 4:1): δ = 145.70, 145.48, 145.32, 145.23, 145.16, 144.69, 144.36, 144.17, 144.09, 143.49, 143.34, 143.29, 142.98, 142.37, 142.07, 141.51, 141.11 (16 C_{60} sp^2 signals, C-3′), 136.07 (C-6′), 130.34 (C-5′, C-7′), 128.77 (C-4′, C-8′), 80.01 (C-1,C-2), 22.19 (C-9′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2922 s (CH_3), 1636 s, 1508 m, 1344 s, 1166 s, 1085 m, 808 m, 674 m, 592 m, 526 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 231 (71000), 251 (94000), 321 (32000), 410 (2100), 422 (1500) nm. MS (MALDI-TOF, pos. ion-mode, DCTB, 15 kV): *m/z* (%) = 889 (100) $[M]^+$ (calcd. 889.03).

Synthesis of *N*-(4′-Methoxyphenylsulfonyl)aziridino[2′,3′:1,2][60]-fullerene (3d): A solution of 1,6-[*N*-(4′-methoxyphenylsulfonyl)]-aza[60]fulleroid (**2d**, 85 mg, 0.09 mmol) in 80 mL of 1,1,2,2-tetrachlorethane was irradiated for 6 h. The solvent was evaporated under reduced pressure. Chromatography on silica gel 40 (toluene/cyclohexane, 1:2) gave 36 mg (42%) of **3d** (1st fraction) and 16 mg (19%) not consumed **2d**.

1st Fraction, *N*-(4′-Methoxyphenylsulfonyl)aziridino[2′,3′:1,2][60]-fullerene: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 8.29 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 4′-H, 8′-H), 7.21 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 5′-H, 7′-H), 4.02 (s, 3 H, 10′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 164.47 (C-6′), 145.44, 145.27, 145.18, 145.11, 144.66, 144.30, 144.13, 144.05, 143.50, 143.30, 143.25, 142.95, 142.33, 142.00, 141.49, 141.06, 130.98, 129.63 (16 C_{60} sp^2 signals, C-3′, C-4′, C-8′), 114.81 (C-5′, C-7′), 80.17 (C-1,C-2), 55.75 (C-10′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2928 s (CH_3), 1738 m, 1594 m, 1344 s, 1261 s, 1159 s, 1088 s, 1024 m, 803 m, 683 m, 612 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 256 (91300), 323 (32600), 411 (2100), 423 (1400) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m/z* (%) = 905 (100) $[M]^-$ (calcd. 905.02), 720 (15) $[M - C_7H_7NO_3S]^-$.

Reaction of C_{70} with Methylsulfonyl Azide (1a): A solution of C_{70} (252 mg, 0.300 mmol) and methylsulfonyl azide (**1a**, 0.75 g, 6.2 mmol) in 70 mL 1,2-dichlorobenzene was heated at 160 °C for 3 h. The solvent was then evaporated under reduced pressure. Chromatography on silica gel 40 (toluene/cyclohexane, 1:1) gave unconverted C_{70} and a mixture of several products. The solution of the product mixture was reduced to 10 mL and flash chromatography on silica gel 40 (toluene/cyclohexane, 1:2) gave 34 mg (12%) of **4a** (4th fraction).

4th Fraction, 2,3-(*N*-Methylsulfonyl)aza[70]fulleroid: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 3.09 (s, 3 H, 3′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 151.65, 150.63, 149.92, 149.57, 149.50, 149.48, 148.73, 148.56, 148.38, 147.64, 147.53, 147.51, 147.47, 147.07, 146.03, 145.50, 145.24, 145.20, 145.12, 144.77, 144.63, 144.33, 144.32, 143.45, 139.99, 139.30, 138.62, 137.41, 131.95, 131.08, 130.99, 130.35, 128.86, 128.12, 127.47, 125.78, 116.84 (37 C_{70} sp^2 signals), 40.58 (C-3′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2927 s (CH_3), 1424 m, 1350 m, 1160 s, 958 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 242 (191000), 333 (36000), 366 (21000), 384 (35000), 485 (18000) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m/z* (%) = 933 (100) $[M]^-$ (calcd. 932.99), 840 (35) $[M - CH_3NO_2S]^-$.

Reaction of C_{70} with (4-Methylphenyl)sulfonyl Azide (1c): A solution of C_{70} (252 mg, 0.300 mmol) and (4-methylphenyl)sulfonyl azide (**1c**, 1.2 g, 6.0 mmol) in 70 mL 1,2-dichlorobenzene was heated at 160 °C for 3 h. The solvent was then evaporated under reduced pressure. Chromatography on silica gel 40 (toluene/cyclohexane, 1:1) gave unconverted C_{70} and a mixture of several products. The solution of the product mixture was reduced to 10 mL and flash chromatography on silica gel 40 (toluene/cyclohexane, 1:2) gave 19 mg (6%) of **5c** (3rd fraction) and 28 mg (9%) of **4c** (4th fraction).

3rd Fraction, 7,8-[*N*-(4′-Methylphenylsulfonyl)]aza[70]fulleroid: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 4:1): δ = 8.33 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, 4′-H, 8′-H), 7.62 (d, $^3J_{H,H}$ = 8.2 Hz, 2 H, 5′-H, 7′-H), 2.68 (s, 3 H, 9′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 4:1): δ = 151.93, 150.59, 150.45, 150.27, 148.59, 148.53, 148.12, 148.09, 147.98, 147.89, 147.56, 147.47, 147.35, 147.33, 147.31, 146.78, 146.26, 146.11, 145.41, 145.32, 145.21, 145.13, 144.86, 144.13, 144.02, 143.83, 143.41, 142.68, 140.37, 136.31, 134.96, 134.28, 133.02, 132.55, 132.43, 131.90, 128.72, 123.83 (37 C_{70} sp^2 signals, C-3′), 135.36 (C-6′), 130.37 (C-5′, C-7′), 129.83 (C-4′, C-8′), 22.28 (C-9′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2918 s (CH_3), 1654 s, 1261 s, 1165 w, 1090 s, 802 s cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 237 (183000), 333 (39000), 473 (20000) nm. MS (MALDI-TOF, pos. ion-mode, DCTB, 15 kV): *m/z* (%) = 1010 (100) $[M]^+$ (calcd. 1009.02).

4th Fraction, 2,3-(*N*-Methylsulfonyl)aza[70]fulleroid: ^{1}H NMR (500.13 MHz, CS_2/CD_2Cl_2, 4:1): δ = 7.81 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, 4′-H, 8′-H), 7.36 (d, $^3J_{H,H}$ = 8.1 Hz, 2 H, 5′-H, 7′-H), 2.55 (s, 3 H, 9′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 4:1): δ = 151.95, 150.88, 150.64, 150.27, 149.83, 149.80, 149.79, 149.10, 148.83, 148.68, 147.87, 147.86, 147.75, 147.66, 147.36, 146.33, 145.63, 145.48, 145.47, 145.34, 145.25, 145.10, 145.04, 144.90, 144.70, 144.58, 144.53, 143.74, 139.97, 138.88, 138.83, 138.48, 138.22, 132.24, 131.34, 131.27, 126.05, 117.36 (37 C_{70} sp^2 signals, C-3′), 135.13 (C-6′), 129.97 (C-5′, C-7′), 128.98 (C-4′, C-8′), 22.04 (C-9′)

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ppm. FT-IR (KBr): $\tilde{\nu}$ = 2922 s (CH_3), 1718 m, 1420 m, 1341 m, 1281 s, 1163 s, 1085 m, 793 m, 671 m, 656 m, 573 s, 562 s, 524 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 240 (235000), 333 (54000), 384 (49000), 486 (28000) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m/z* (%) = 1010 (100) $[M]^-$ (calcd. 1009.02), 854 (13) $[M - C_7H_7O_2S]^-$.

Reaction of C_{70} with (4-Methoxyphenyl)sulfonyl Azide (1d): A solution of C_{70} (252 mg, 0.300 mmol) and (4-methoxyphenyl)sulfonyl azide (**1d**, 1.3 g, 6.1 mmol) in 70 mL 1,2-dichlorobenzene was heated at 160 °C for 3 h. The solvent was then evaporated under reduced pressure. Chromatography on silica gel 40 (toluene/cyclohexane, 1:1) gave unconverted C_{70} and a mixture of several products. The solution of the product mixture was reduced to 20 mL and flash chromatography on silica gel 40 (toluene/cyclohexane, 1:2) gave 22 mg (7%) of **5d** (1st fraction) and 31 mg (10%) of **4d** (2nd fraction).

1st Fraction, 7,8-[*N*-(4′-Methoxyphenylsulfonyl)]aza[70]fulleroid: ^1H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 8.37 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 4′-H, 8′-H), 7.29 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 5′-H, 7′-H), 4.04 (s, 3 H, 10′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 163.95 (C-6′), 151.58, 150.24, 149.93, 148.25, 148.19, 147.79, 147.74, 147.63, 147.56, 147.23, 147.09, 147.00, 146.98, 146.95, 146.46, 145.92, 145.76, 145.05, 144.98, 144.79, 144.52, 143.68, 143.65, 143.49, 143.08, 142.34, 140.03, 136.01, 134.58, 132.69, 132.20, 132.08, 131.73, 131.55, 128.84, 128.38, 128.09, 125.19, 123.64 (37 C_{70} sp^2 signals, C-3′, C-4′, C-8′), 114.53 (C-5′, C-7′), 55.43 (C-10′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2925 s (CH_3), 1735 s, 1701 m, 1592 m, 1453 m, 1430 s, 1262 m, 1159 s, 1087 s, 672 m cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 240 (205000), 3343 (41000), 387 (38000), 460 (21000) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m/z* (%) = 1025 (100) $[M]^-$ (calcd. 1025.02), 840 (30) $[M - C_7H_7NO_3S]^-$.

2nd Fraction, 2,3-[*N*-(4′-Methoxyphenylsulfonyl)]aza[70]fulleroid: ^1H NMR (500.13 MHz, CS_2/CD_2Cl_2, 5:1): δ = 7.87 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 4′-H, 8′-H), 7.02 (d, $^3J_{H,H}$ = 9.0 Hz, 2 H, 5′-H, 7′-H), 3.96 (s, 3 H, 10′-H) ppm. ^{13}C NMR (125.76 MHz, CS_2/CD_2Cl_2, 5:1): δ = 163.73 (C-6′), 151.62, 150.54, 150.31, 149.95, 149.49, 149.47, 149.45, 148.78, 148.50, 148.34, 147.53, 147.42, 147.33, 147.03, 146.00, 145.30, 145.13, 145.02, 144.92, 144.78, 144.56, 144.38, 144.23, 144.18, 143.39, 139.51, 138.55, 138.43, 138.17, 137.85, 131.90, 131.00, 130.93, 130.92, 128.82, 128.06, 125.73, 125.16, 117.24 (37 C_{70} sp^2 signals, C-3′, C-4′, C-8′), 114.14 (C-5′, C-7′), 55.37 (C-10′) ppm. FT-IR (KBr): $\tilde{\nu}$ = 2926 s (CH_3), 1592 m, 1447 s, 1408 m, 1361 m, 1261 m, 1158 s, 1128 m, 1093 s, 1032 m, 832 m, 673 s cm^{-1}. UV/Vis (CH_2Cl_2): λ_{max} (> 220 nm, ε) = 242 (210000), 333 (42000), 367 (23000), 384 (41000), 486 (22000) nm. MS (MALDI-TOF, neg. ion-mode, DCTB, 15 kV): *m/z* (%) = 1025 (100) $[M]^-$ (calcd. 1025.02), 840 (45) $[M - C_7H_7NO_3S]^-$.

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