

Synthesis of the individual regioisomer of the bisadduct of fullerene C₆₀ with *tert*-butyl 11-azido-3,6,9-trioxaundecanoate*

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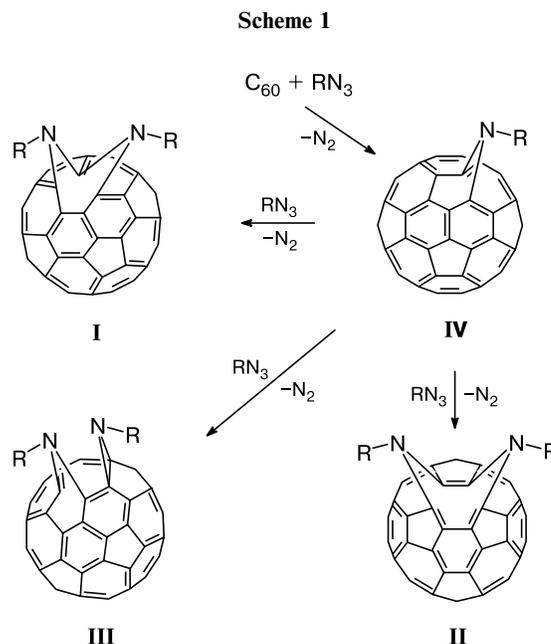
At 130 °C the reaction of fullerene C₆₀ with 1-azido-9-*tert*-butoxycarbonyl-3,6,9-trioxanonane occurs regioselectively affording one regioisomer of the bisadduct.

Key words: [60]fullerene, azides, cycloaddition reactions, monoadducts, bisadducts, structure, synthesis, electrochemical properties.

Fullerene chemistry is one of quickly developed areas of organic chemistry. Many diverse organofullerenes have been synthesized presently^{1–3}; due to higher solubility than that of fullerenes, they become more demanded, for instance, in producing polymeric voltaic cells, photo- and electroconducting films, nanoresistors, and various drugs.^{4–9} Among the diversity of organofullerenes, the number of polyadducts is much smaller than that of monoadducts. This is due to, first, difficulties in separation of regioisomeric mixtures. The reaction of azidoacetate with azahomofullerene affords only one regioisomer (I) of the bisadduct with C_s symmetry of the molecule.¹⁰ We found by the study of the reactions of fullerene C₆₀ with organic azides that the cycloaddition of nitropyrimidino- and several isocyanurato-substituted azides to a fullerene molecule is also regioselective but, along with the bisadducts with structure I, bisadducts of different structure (regioisomers II and III) can be formed.^{11–13} Regioisomers II and III, as well as regioisomers I (see Ref. 10), were assumed to be formed due to the addition of one more azide molecule to azahomofullerene IV (Scheme 1). This assumption was proved experimentally for 2-azido-5-nitropyrimidine.¹¹

Continuing investigation of the reactions of organic azides with fullerene C₆₀ as an approach to the synthesis of individual regiomers of bisadducts, we used *tert*-butyl 11-azido-3,6,9-trioxaundecanoate (I) in the reaction (Scheme 2). Compounds containing poly(ethylene glycol) fragments are widely used in the fullerene chemistry

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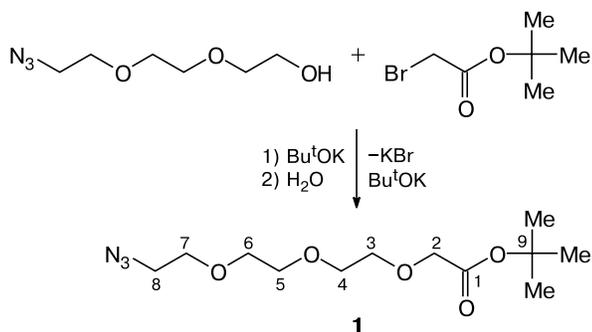


for the synthesis of amphiphilic molecules followed by producing related films, monolayers, composites,^{14–16} and spacers separating the fullerene sphere and donor fragments in molecules of covalently linked donor-acceptor dyads.^{17–19} The presence of the ester group in azide I also provides the subsequent functionalization of organofullerene.

Azide I was synthesized by the reaction of 8-azido-3,6-dioxaoctanol with *tert*-butyl bromoacetate in the presence of potassium *tert*-butoxide and characterized by

^1H and ^{13}C spectroscopy, and the composition was determined by elemental analysis.

Scheme 2



It is known that in the series of poly(ethylene glycol)-substituted azides 1-azido-3,6,9-trioxadecane and azides bearing calixarene or porphyrin substituents in the poly(ethylene glycol) fragments were used in the reaction with fullerene.^{20–23} These reactions were carried out in chlorobenzene at the boiling point of the solvent (132 °C), and all of them ceased by the formation of 5,6-opened monoadducts, *viz.*, azahomofullerenes.

Primarily we studied the reaction of fullerene C_{60} with azide **1** at 130 °C but in *o*-dichlorobenzene (*o*-DCB). This solvent makes it possible to vary more widely the temperature of the process. Adducts **2** and **3** were isolated from the reaction mixture using column chromatography. According to the data of elemental analysis and mass spectrometry, they were the mono- and bisadduct of fullerene and azide **1**, respectively, with the loss of nitrogen molecules. The yield of monoadduct **2** was 3–5% based on the reacted amount of fullerene, whereas the yield of bisadduct **3** reached 15–17%. The structure of the latter was proved by spectral methods, namely, ^1H and ^{13}C , IR, and UV spectroscopy.

Structure **3** was determined by a series of 2D NMR correlation experiments (COSY, HSQC, HMBC).^{24–26} The ^1H NMR spectrum of compound **3** exhibited four groups of lines in a region of 4.5–1.0 ppm characteristic of the polyethylene fragments. However, these lines were

strongly broadened, which prevented to distinguish any characteristic signal, beginning from which one could consecutively establish coupling between other nuclei according to the 2D NMR data. At the same time, the ^{13}C NMR spectrum of compound **3** contained the characteristic resonance of the C(1) carbonyl carbon atom with δ 169.58, beginning from which correlations with other nuclei were performed. The 2D HMBC spectrum exhibited the coupling between the C(1) carbon atom and hydrogen atoms of the C(2) H_2 group (δ 4.02), between the hydrogen atoms of C(2) H_2 (δ 4.02) and the C(3) carbon atom (δ 70.74). The resonance of the hydrogen atoms of the C(3) H_2 group (δ 3.74) was found from the 2D HSQC spectrum. In addition, the data of the 2D COSY spectrum made it possible to determine the bond between the hydrogen atoms of the adjacent C(3) H_2 and C(4) H_2 groups (Fig. 1). Similarly, the spin systems of the hydrogen atoms of other two $\text{CH}_2\text{—CH}_2$ fragments were distinguished on the basis of the 2D COSY spectrum, and the 2D HMBC spectral data confirmed the bond between these fragments (see Fig. 1). In addition, the 2D HMBC contains a cross peak between the signal of the hydrogen atom of three CH_3 groups (δ 1.47) and resonance of C(9) (δ 81.50), which made it possible to confirm the structure of the *tert*-butyl fragment. Thus, the experiments mentioned allowed us to determine the structure of the addend in a molecule of bisadduct **3**. The addition of the addend to the fullerene sphere follows unambiguously from the data of the 2D HMBC spectrum, which demonstrated the bond between the hydrogen atoms of C(8) H_2 (δ 4.31) and two carbon atoms (δ 163.55 and 141.40) of the fullerene sphere (see Fig. 1). However, it is noteworthy that the signal intensities of these carbon atoms relate to each other as 1 : 2. This is possible only for a symmetrical system with two added addends, and the first carbon atom is common for them.

The detailed analysis of the ^{13}C NMR spectrum showed that the fullerene sphere of bisadduct **3** is characterized by signals, whose number and intensity (24 signals with the intensity 2C, two signals 4C, and four signals 1C) indicates the C_s symmetry of the sphere. A comparison of the signal intensities with δ 163.55 and 141.40 and the signal from C(1) showed that the last resonance corre-

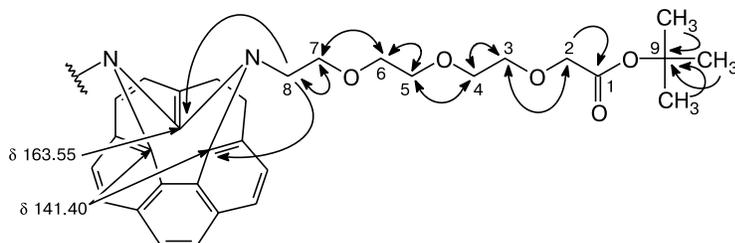
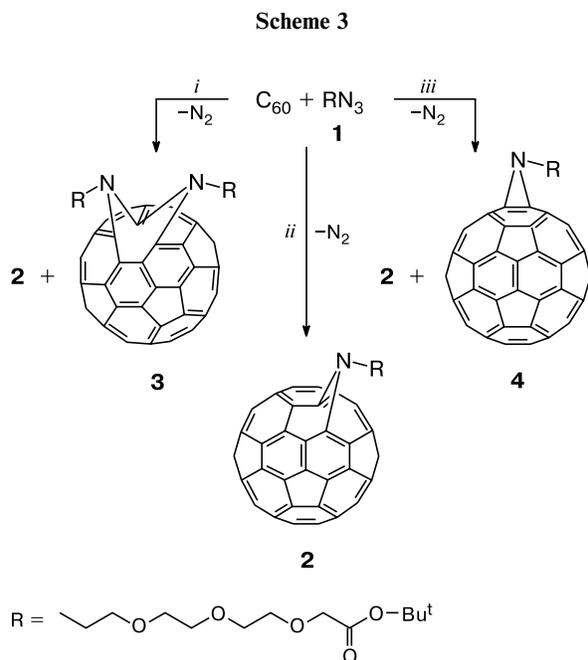


Fig. 1. Principal COSY (curved arrows) and HMBC (curved arrows from hydrogen atoms to carbon atoms) correlations for compound **3**.

sponds to two carbon atoms (this comparison is valid, because the signals from the carbon atoms with close relaxation times are compared).²⁶ Based on the presented facts, we can conclude that two addends are added to the fullerene sphere.

The chemical shifts of the carbon atoms of the fullerene sphere (δ 163.55 and 141.40), to which the addends have added, indicated the open character of cycloaddition and suggested that bisadduct **3** is a regioisomer of type **I** (see Refs 10 and 13; Scheme 3).



Reagents and conditions: *o*-DCB, 3 h; $T = 130^\circ\text{C}$ (i); 180°C (ii); 100°C (iii).

Since the result obtained differed from the published data,^{17–19} we carried out the reaction of fullerene with azide **1** rising the temperature to 180°C in one experiment and decreasing it to 100°C in another entry.

According to the MALDI data, the monoadduct with m/z 981 and trisadduct with m/z 1503 are formed along with unreacted fullerene in the reaction mixture formed upon the reaction of fullerene with azide **1** at 180°C . According to the TLC data, the fractions containing the trisadduct, which were obtained by the separation of the reaction mixture using column chromatography, represented mixtures of regioisomers that we failed to separate.

The monoadduct, whose R_f value and the UV and IR spectra coincided with the data for adduct **2**, was isolated in the individual state in 20% yield based on the reacted amount of fullerene. Thus, an increase in the temperature of the reaction of fullerene with azide **1** to 180°C decreased substantially the yield of bisadduct **3** (or results in its absence in the reaction mixture) and

increases the yield of monoadduct **2**. The UV spectrum of adduct **2** is typical of monoazahomofullerenes.^{27,28} The characteristic bands in the IR spectrum indicated that a molecule of monoadduct **2** bears the fullerene fragment and functional groups related to the addend. The final structure of compound **2** was determined from the data of 2D NMR spectroscopy (see below).

The decrease in the temperature of the reaction of fullerene with azide **1** to 100°C allowed us to isolate two monoadducts in the individual state and an unseparated mixture of regioisomers of polyadducts. One of the monoadducts is compound **2**, but its yield decreased to 1–3%. At the same time, the yield of the second monoadduct **4** was 20% based on the reacted amount of fullerene. The IR spectra of monoadducts **2** and **4** did not differ. However, the NMR spectra differed substantially (especially the ¹³C NMR spectrum). The structures of compounds **2** and **4** were determined by the NMR method according to the scheme analogous to that used for compound **3**. As a result, it was found that in all cases the addend is the fragment of *tert*-butyl 3,6,9-trioxaundecanoate and the structures of compounds **2** and **4** differ only by the mode of fixation of the addend on the fullerene sphere. This was unambiguously shown by the 2D HMBC method, which confirmed the addition of the addend to the carbon atoms of the fullerene sphere in both compounds (Fig. 2). In turn, the chemical shifts of the signals from the carbon atoms of the sphere suggested the character of addition of the addend: monoadduct **2** has 5,6-opened structure and monoadduct **4** is characterized by the 6,6-closed type of addition.

Thus, the reaction of fullerene with azide **1** is a complicated temperature-dependent process, and we failed to determine unambiguously which compound is intermediate in the synthesis of bisadduct **3**. For example, at 100°C the highest yield was observed for 6,6-closed monoadduct **4**, at 130°C 5,6-opened bisadduct **3** had the highest yield, and at 180°C 5,6-opened monoadduct **2** was formed in the highest yield. Based on the order of product formation, one could assume that diazadihomofullerene **3** is formed due to the addition of azide **1** to 6,6-closed monoadduct **4** (Scheme 4). Monoazahomofullerene **2** could be formed as a result of the thermal isomerization of 6,6-closed monoadduct **4**. However, the heating for 20 h of a solution of monoadducts **2** and **4** in boiling *o*-DCB showed that these compounds underwent no mutual thermal transformations and no decomposition to the initial C₆₀. It is most likely that the reaction of fullerene with azide **1** occurs regardless of the temperature as [2+3] cycloaddition, whose first step is the formation of thermally unstable fullerenetriazoline **5**. Quantum chemical calculations suggest that triazolinofullerenes decompose *via* the synchronous mechanism for which the direct 6,6-closed structures cannot be formed.²⁹ However, calculations were performed for azide with the donor radi-

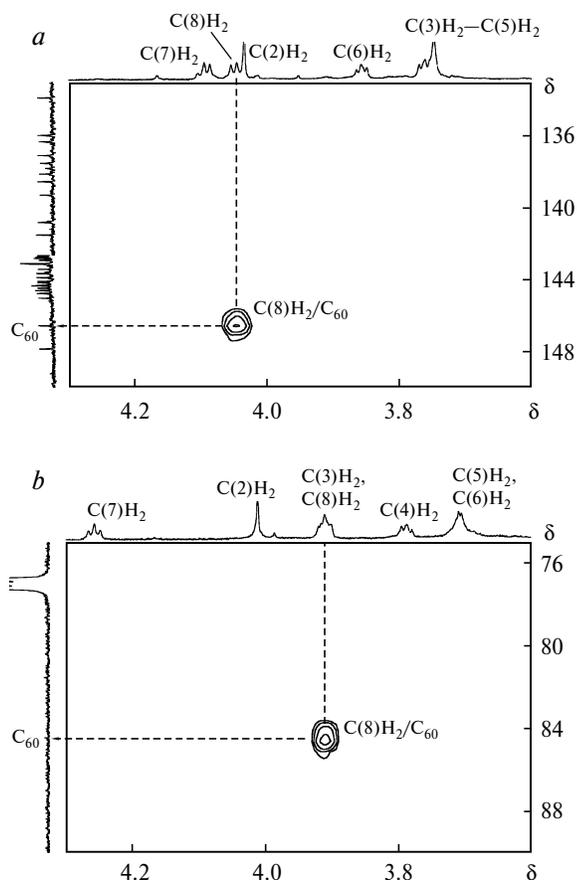


Fig. 2. Fragments of the 2D HMBC spectra for monoadducts **2** (a) and **4** (b).

cal (MeN₃). In the case of acceptor radicals, as for azide **1**, it is quite probable that the asynchronous decomposition of triazolinofullerene **5** affords bipolar ion **6** from which

Table 1. Potentials (E_p^{red}) of the peaks detected in the cyclic voltammograms of C₆₀, monoadducts **2** and **4**, and bisadduct **3***

Compound	$-E_p^{\text{red}}/\text{V}$			
	E_1	E_2	E_3	E_4
C ₆₀	0.83	1.24	1.70	2.16
2	0.89	1.29	1.75	2.20
4	0.87	1.27	1.76	2.23
3	0.96	1.30	1.75	2.28

* Conditions: *o*-DCB–MeCN (3 : 1) mixture at 25 °C; supporting electrolyte 0.1 M Bu₄NBF₄; glassy carbon as cathode ($S_{\text{work}} = 3.14 \text{ mm}^2$), Ag/0.01 M AgNO₃ in MeCN as reference electrode, $v_{\text{sweep}} = 50 \text{ mV s}^{-1}$.

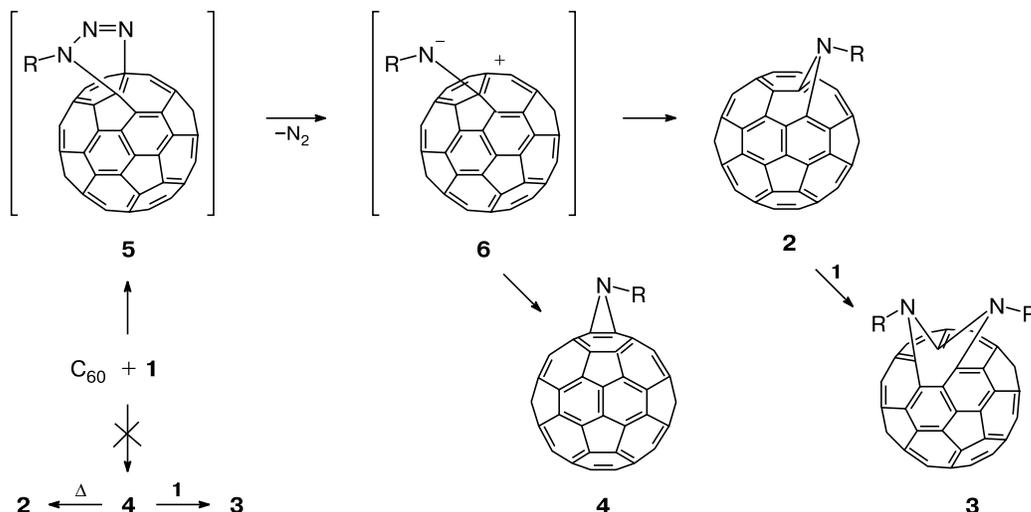
both 5,6-opened monoadduct **2** and 6,6-closed monoadduct **4** can be formed simultaneously, and the latter is formed at 100 °C in a larger amount.

The temperature increase favors the formation of 5,6-opened adduct **2** via this route. Adduct **2** easily adds azide **1** to form bisadduct **3** at 130 °C, whereas tris- and polyadducts are formed at higher temperature.

One of the practically significant characteristics of fullerenes and their derivatives is the ability to accept electrons. The electrochemical properties of monoadducts **2** and **4** and bisadduct **3** were studied by cyclic voltammetry (CV). The experimental results were compared to the data for the starting C₆₀. Azide **1** was not reduced in the potential interval from 0 to –2.5 V.

The cyclic voltammograms of organofullerenes **2–4**, as well as the CV curve of fullerene C₆₀, exhibited four reversible one-electron reduction peaks each corresponding to the reduction of the fullerene sphere. The reduction of both monoadducts **2** and **4** and bisadduct **3** was more difficult than that for unmodified fullerene (Table 1),

Scheme 4



which agrees with saturation of the C=C bonds of the fullerene sphere. It should be mentioned that, unlike the 6,6-closed bisadducts,³⁰ the reduction of 5,6-opened bisadduct **3** is reversible, which is characteristic, in principle, of this type of bisadducts.^{11–13}

Thus, depending on the temperature, the reaction of fullerene C₆₀ with azide **1** can afford both monoadducts and one regioisomer of the bisadduct. The latter, most likely, is the product of cycloaddition of one more molecule of azide **1** to the intermediate 5,6-opened monoadduct.

Experimental

IR spectra were recorded on a Bruker IFS-113V FTIR spectrometer in KBr pellets. 1D and 2D NMR experiments were carried out in CDCl₃ solutions on a Bruker Avance-600 NMR spectrometer (600 MHz (¹H) and 150.926 MHz (¹³C)) at 30 °C. NMR spectra for azide **1** were recorded on a Bruker AMX 500 spectrometer (500 MHz (¹H) and 125.77 MHz (¹³C)). The residual signal of CDCl₃ (δ_H 7.26 and δ_C 77.0) was used as the internal signal. UV spectra were recorded on a Specord UV-VIS instrument. Mass spectra were obtained on a MALDI TOF MS instrument (Dynamo). In the CV studies, a stationary glassy carbon disc electrode with a working surface of 3.14 mm² was used as the working electrode. Voltammograms (CV curves) were recorded using a PI-50-1 potentiostat with a PR-8 programmer when switching the electrochemical cell according to the three-electrode scheme. CV curves were recorded on a two-coordinate recorder with a potential sweep rate of 50 mV s⁻¹. CV curves were obtained in an *o*-DCB : MeCN (3 : 1) mixture vs Bu₄NBF₄ (0.1 M). The reference electrode was an Ag/0.01 M AgNO₃ system in MeCN. A Pt wire served as the auxiliary electrode. Measurements were carried out in a temperature-controlled (25 °C) cell under argon. The concentration of C₆₀ in solution was 2 · 10⁻³ mol L⁻¹, and that of the adducts was 1 · 10⁻³ mol L⁻¹. Elemental analysis was carried out on an Analyzer CHN-3 instrument. Anhydrous *o*-DCB and MeCN were distilled above P₂O₅, and THF was distilled above KOH. [60]Fullerene was received from the G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences (Nizhny Novgorod). The starting 8-azido-3,6-dioxaoctanol was synthesized according to an earlier published procedure.³¹ *tert*-Butyl bromoacetate and potassium *tert*-butoxide are commercial preparations (Aldrich).

tert-Butyl 11-azido-3,6,9-trioxaundecanoate (**1**). Potassium *tert*-butoxide (800 mg, 7.14 mmol) was added at 0 °C and stirring to a solution of 8-azido-3,6-dioxaoctanol (500 mg, 2.85 mmol) and *tert*-butyl bromoacetate (0.7 mL, 4.74 mmol) in anhydrous tetrahydrofuran (5 mL). The mixture was stirred for 30 min, after which water was added, and organic compounds were extracted with ethyl acetate. The organic phase was separated, washed with water and a saturated NaCl solution, and dried by filtration through anhydrous sodium sulfate. The solvent was removed *in vacuo* using a water-jet pump. The residue was chromatographed on a column packed with silica gel using a toluene–acetone (5 : 1) mixture as eluent. Azidoester **1** was obtained in a yield of 553 mg (67%). Found (%): C, 49.93; H, 7.95; N, 14.41. C₁₂H₂₃N₃O₅. Calculated (%): C, 49.81;

H, 8.01; N, 14.52. TLC (Sorbfil, toluene–acetone (2 : 1) mixture as eluent): R_f 0.52. ¹H NMR (CDCl₃), δ: 1.48 (s, 9 H, 3 Me); 3.40 (t, 2 H, C(8)H₂, ³J_{H,H} = 4.6 Hz); 3.65–3.72 (m, 10 H, C(3)H₂–C(7)H₂); 4.02 (s, 2 H, C(2)H₂). ¹³C NMR (CDCl₃), δ: 28.1 (3 CH₃); 50.7 (C(8)); 69.0, 70.0, 70.6, 70.65, 70.68, 70.7 (C(2)–C(7)); 81.5 (C(9)); 169.7 (C(1)).

Reaction of fullerene C₆₀ with 1-azido-10-*tert*-butoxycarbonyl-3,6,9-trioxaundecanone (1**) (general procedure).** A mixture of C₆₀ (0.132 mmol), azide **1** (0.198 mmol) and anhydrous degassed *o*-DCB (25 mL) was heated with stirring for 3 h at 100, 130, or 180 °C. The solvent was removed *in vacuo*, and the residue was chromatographed on a column packed with silica gel.

Method A (*T* = 100 °C). When toluene was used as the eluent, unreacted fullerene was isolated in an amount of 42 mg (44%). The fraction containing adduct **4** and fractions of the polyadducts were separated with a mixture of toluene and CH₃CN (50 : 1). Repeated chromatography gave 14 mg (20% based on the amount of reacted fullerene) of *tert*-butyl 11-((C₆₀-I_h)fullereno[*b*]aziridinyl)-3,6,9-trioxaundecanoate (**4**). Found (%): C, 87.47; H, 2.09; N, 1.37. C₇₂H₂₃NO₅. Calculated (%): C, 88.07; H, 2.34; N, 1.42. TLC (Sorbfil, toluene–CH₃CN (5 : 1) mixture as eluent): R_f 0.55. MS, *m/z*: 720 (C₆₀); 981 (C₇₂H₂₃NO₅). UV (CH₂Cl₂), λ_{max}/nm: 259, 328, 437 (narrow), 477, 722. IR (KBr), ν/cm⁻¹: 526 (fullerene fragment), 1118 (C–O), 1744 (C=O), 2855, 2922 (C–H). ¹H NMR (CDCl₃), δ: 1.47 (s, 9 H, 3 Me); 3.71 (t, 4 H, C(5)H₂, C(6)H₂, ³J_{H,H} = 2.2 Hz); 3.78 (m, 2 H, C(4)H₂); 3.9 (m, 4 H, C(8)H₂, C(3)H₂); 4.01 (s, 2 H, C(2)H₂); 4.26 (m, 2 H, C(7)H₂). ¹³C NMR (CDCl₃), δ: 28.00 (3 CH₃); 50.30 (C(8)); 70.20 (C(4)); 70.60 (C(7)); 70.70 (C(3)); 71.00 (C(5), C(2)); 71.10 (C(6)); 81.40 (C(9)); 169.20 (C(1)). C₆₀N: 84.40 (2 C); 140.81 (4 C); 142.16 (4 C); 142.35 (4 C); 142.89 (2 C); 143.10 (8 C); 143.11 (8 C); 143.21 (2 C); 143.84 (4 C); 144.59 (4 C); 144.61 (4 C); 144.67 (4 C); 145.17 (6 C); 145.21 (4 C).

Method B (*T* = 130 °C). Using toluene as the eluent, we isolated unreacted fullerene in an amount of 24 mg (25%). Adduct **2** (5 mg, 5%), adduct **3** (18 mg, 15%), and the fraction of the polyadducts were separated with a mixture of toluene and CH₃CN (50 : 1).

***N,N'*-Bis(11-*tert*-butoxycarbonyl-3,6,9-trioxaundecyl)-{1'*a*H,2'*a*H-1'*a*,2'*a*-diaz-1'(2')a,2'(3')a-dihomo(C₆₀-I_h)-[5,6]fullerene} (**3**).** Found (%): C, 80.73; H, 3.85; N, 2.15. C₈₄H₄₆N₂O₁₀. Calculated (%): C, 81.16; H, 3.70; N, 2.25. No mass spectrum was obtained because of low volatility of the compound. TLC data (Sorbfil, toluene–CH₃CN (5 : 2) as eluent): R_f 0.42. UV (CH₂Cl₂), λ_{max}/nm: 258, 326, 540. IR (KBr), ν/cm⁻¹: 524 (fullerene fragment), 1116 (C–O), 1743 (C=O), 2854, 2922 (C–H). ¹H NMR (CDCl₃), δ: 1.48 (br.s, 18 H, 6 Me); 3.78, 4.06, 4.31 (m, 28 H, 2 C(2)H₂–C(7)H₂). ¹³C NMR (CDCl₃), δ: 28.13 (6 Me); 51.43 (C(8)); 69.07, 70.38, 70.70, 70.73, 70.82, 70.99 (C(2)–C(7)); 81.49 (C(9)); 169.20 (C(1)). C₆₀N: 130.68 (2 C); 131.16 (1 C); 132.90 (2 C); 134.57 (2 C); 135.14 (2 C); 137.29 (2 C); 138.88 (2 C); 138.97 (2 C); 139.33 (2 C); 139.53 (2 C); 142.02 (2 C); 141.40 (2 C); 141.59 (4 C); 142.69 (2 C); 143.30 (2 C); 143.56 (2 C); 143.71 (2 C); 143.91 (2 C); 144.04 (1 C); 144.12 (4 C); 144.21 (2 C); 144.57 (2 C); 144.61 (2 C); 144.89 (2 C); 144.97 (2 C); 145.12 (2 C); 145.48 (1 C); 146.87 (2 C); 147.63 (2 C); 163.65 (1 C).

Method C (*T* = 180 °C). Unreacted fullerene (24 mg, 25%) was isolated using toluene as the eluent. The elution with

a toluene—CH₃CN (50 : 1) mixture gave adduct **2** (19 mg, 20%) and the fractions containing the polyadducts.

tert-Butyl 11-(1'-a-aza-1'(2')-homo(C₆₀-I_h)[5,6]fullerenyl)-3,6,9-trioxaundecanoate (2). Found (%): C, 87.45; H, 2.08; N, 1.35. C₇₂H₂₃NO₅. Calculated (%): C, 88.07; H, 2.34; N, 1.42. MS. Found: *m/z* (%): 723 (C₆₀); 984. Calculated: 981. TLC data (Sorbfil, toluene—CH₃CN (5 : 1) as eluent): R_f 0.64 UV (CH₂Cl₂), λ_{max}/nm: 264, 332, 426 (broad), 555. IR (KBr), ν_{max}/cm⁻¹: 525 (fullerene fragment), 1119 (C—O); 1742 (C=O); 2854, 2922 (C—H). ¹H NMR (CDCl₃), δ: 1.46 (s, 9 H, 3 Me); 3.76 (m, 6 H, C(3)H₂—C(5)H₂); 3.86 (m, 2 H, C(6)H₂); 4.04 (s, 2 H, C(2)H₂); 4.06 (m, 2 H, C(8)H₂); 4.11 (m, 2 H, C(7)H₂). ¹³C NMR (CDCl₃), δ: 28.16 (3 Me); 50.82 (C(8)); 69.12 (C(2)); 70.45 (C(7)); 70.82 (C(5)); 70.84 (C(4)); 70.88 (C(3)); 70.99 (C(6)); 81.53 (C(9)); 169.63 (C(1)). C₆₀N: 133.86 (2 C); 135.95 (2 C); 136.32 (2 C); 137.07 (2 C); 137.51 (2 C); 137.79 (1 C); 138.11 (2 C); 138.54 (2 C); 139.28 (2 C); 140.75 (1 C); 140.80 (2 C); 141.51 (2 C); 142.67 (2 C); 142.74 (2 C); 142.81 (2 C); 142.92 (2 C); 143.23 (1 C); 143.42 (2 C); 143.57 (1 C); 143.65 (2 C); 143.88 (2 C); 144.10 (2 C); 144.17 (2 C); 144.31 (2 C); 144.33 (2 C); 144.47 (2 C); 144.60 (2 C); 144.75 (2 C); 145.03 (2 C); 146.55 (2 C); 147.85 (2 C); 143.11 (2 C).

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