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Synthesis and electrochemical properties of individual isomers of isocyanurate-substituted bis-organodiazadihomofullerenes

I. P. Romanova, **G. G. Yusupova, O. A. Larionova, A. A. Balandina, Sh. K. Latypov, D. G. Yakhvarov, V. V. Zverev, and O. G. Sinyashin***

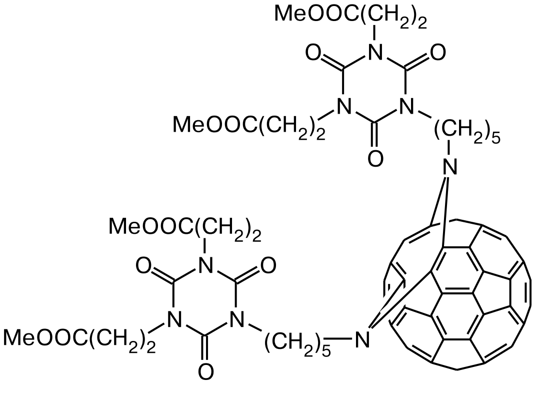
A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 73 2253. E-mail: romanova@iopc.knc.ru

The reactions of fullerene C_{60} with isocyanurate-substituted azides afforded individual regioisomers of bis-adducts. The structures of the regioisomers depend on the structure of the organic fragment in azide and are determined primarily by the bulkiness of this fragment.

Key words: [60]fullerene, bis-adducts, cycloaddition, structure, synthesis, electrochemical properties.

Cycloaddition of several organic fragments to the fullerene cage provides a unique way to construct three-dimensional stereochemically definite structures, in which the fullerene cage serves as a terminal for the attachment of various organic substituents. The resulting molecules retain the unique properties of fullerenes. For example, polyadducts also stepwise accept several electrons during electrochemical reduction but, unlike fullerenes, are more readily soluble in organic solvents, some of polyadducts possessing film-forming, liquid-crystalline, or amphiphilic properties or blocking viruses.[1—7] However, in spite of these interesting properties, polyadducts are less well studied than fullerenes and their monoadducts. This is due primarily to the fact that the isolation of individual regioisomers presents difficulty. For example, cycloaddition of the second addend to the best studied 6,6-closed monoorganofullerenes affords nine isomers of bis-adducts. Subsequent reactions lead to a substantial increase in the number of regioisomers.[8] Two approaches were developed for the regioselective cycloaddition of addends to fullerenes. One of these methods is based on the ability of fullerenes to be involved in retro reactions, due to which the cyclic fragments on the surface of the fullerene cage can undergo a rearrangement to form predominantly one thermodynamically most stable isomer.[1] In addition, the so-called "tether controlled synthesis" is used.[9] This method involves addends, whose functional groups are separated by a bridge of a particular length.

Reactions with organic azides are of interest from the viewpoint of the development of new approaches to the regioselective addition of addends to the fullerene cage. It is known that the reactions of fullerenes with azides can produce 5,6-open adducts, *viz.*, azahomofullerenes. Data on the reactivity of the latter compounds are scarce. For instance, the addition of the azide molecule to azahomofullerenes was demonstrated[10] to be accompanied by the predominant formation of one regioisomer. Besides, we have demonstrated[11] that the reaction of fullerene C_{60} with 1,3-di(2-methoxycarbonylethyl)-substituted isocyanuratopentylazide **1** produces regioisomer **2** in high yield.



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It should be noted that the structure of the fullerene cage of the regioisomer described in the literature differs from that synthesized by us. In this connection, it was important to reveal the factors responsible for the regioselectivity of cycloaddition of addends to fullerene C_{60} in reactions proceeding through the formation of 5,6-open structures and examine the possibility of developing a new approach to the synthesis of individual regioisomers based on these compounds. In the present study, we performed reactions of fullerene C_{60} with isocyanurate-substituted azides **3—5**, in which both the structure of the substituents in the isocyanuric ring and the length of the methyl-

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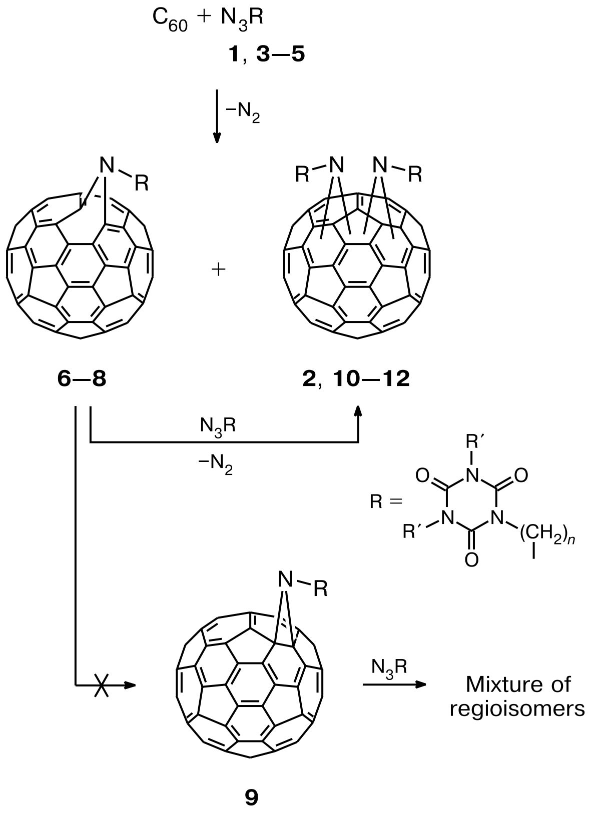
ene chain between the isocyanuric fragment and the azido group were varied (Scheme 1).

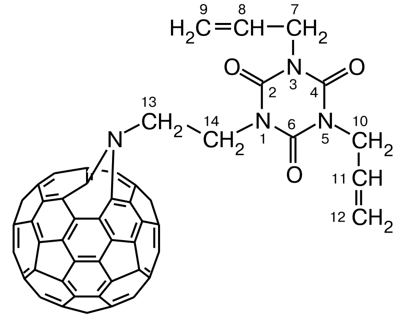
Scheme 1



1, 2: R′ = MeOOCCH$_2$CH$_2$—, *n* = 5
3, 6, 10: R′ = CH$_2$=CH—CH$_2$—, *n* =2
4, 7, 9, 11: R′ = CH$_2$=CH—CH$_2$—, *n* = 5
5, 8, 12: R′ = NC—CH$_2$—CH$_2$—, *n* = 5

First, we chose the optimal temperature of the processes. Earlier, we have been demonstrated[12,13] that under the reaction conditions, azahomofullerene **8** gradually decomposes to give the starting fullerene, whereas azahomofullerene **7** (the 5,6-open adduct) is transformed into fullereno[1,2-*b*]aziridine **9** (the 6,6-closed adduct) upon heating in boiling *o*-dichlorobenzene (*o*-DCB). In this case, the latter transformation is undesirable because it can give rise to an unseparable mixture of 6,6-closed regioisomers. Because of this, we found conditions ensuring the existence of 5,6-open structures, *viz*., azahomofullerenes **6—8**, in the reaction mixture.

The reactions of fullerene C_{60} with azides **3—5** were carried out in *o*-DCB. The reaction of di(allyl)isocyanurate-substituted azide **4** was performed at 180 °C, whereas the temperature of the reactions of di(cyanoethyl)-substituted azides **3** and **5** was lowered to 130 °C. The reaction products and unconsumed fullerene were separated by column chromatography. As a result, both azahomofullerenes **6—8** and individual isomers of bis-organofullerenes **10—12** were isolated from each reaction mixture. After double chromatographic purification, the yields of the latter products were 10—15% with respect to the starting fullerene C_{60}. Azahomofullerenes **7** and **8** have been characterized in our earlier studies.[12,13] The structures of azahomofullerene **6** and bis-organofullerenes **10—12** were established by IR, UV, and ^{1}H and ^{13}C NMR (1D and 2D) spectroscopy. The compositions were determined by elemental analysis. The molecular ion peak was obtained for azahomofullerene **6** by MALDI, whereas the molecular ion peaks were not observed in the mass spectra of bis-organofullerenes **10—12** because of their low volatility.[14]



6

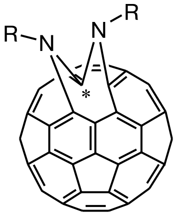
The fact that compound **6** is azahomofullerene is evidenced primarily by its ^{13}C NMR spectrum. The fullerene cage is characterized only by signals at δ 133—146, *i.e.*, the signals belonging to the sp^3-hybridized carbon atoms of the fullerene cages of 5,6- and 6,6-closed structures are absent in the spectrum.[1—3] In addition, the narrow low-intensity band at λ_{max} = 420 nm characteristic of 6,6-closed structures is absent in the UV spectrum of compound **6**, but the spectrum shows low-intensity broad bands in the 400—800 nm region typical of 5,6-open structures.[1—3] The IR and ^{1}H NMR spectroscopic data for compound **6** provide evidence that the structure of the isocyanuric fragment is retained in the course of the reaction of azide **3** with fullerene C_{60}.

According to the elemental analysis data, products **10—12** are adducts generated by the addition of two molecules of the corresponding azides **3—5** to fullerene C_{60}, which is accompanied by elimination of N_2 molecules. The IR spectra of these compounds show, in addition to the bands of the organic fragment, a band at 526—527 cm^{-1} characteristic of organofullerenes. However, it should be noted that the intensity of this band in the spectra of bis-organofullerenes **10—12** is much lower than that in the spectra of monoadducts **6—8**. Earlier, we have observed an analogous distinguishing feature for phosphorylated bis-adducts[15] and bis-adduct **2**.[11]

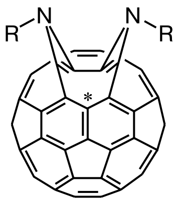
The ^{1}H NMR spectra of bis-adducts **10—12** do not differ substantially from the spectra of the starting azides

3—5 and azahomofullerenes **6—8**,[12,13] which indicates that the structure of the organic fragment is retained and two organic fragments in the isocyanuric ring are magnetically equivalent. It should be noted that all homofullerenes are characterized by low-field shifts of the signals for the hydrogen atoms, which are in the direct vicinity of the addition site of the addend, relative to their positions in the spectra of the starting azides. The UV spectra of isocyanurate-substituted bis-adducts **10—12** show no absorption bands in the 400—800 nm region characteristic of organofullerenes.

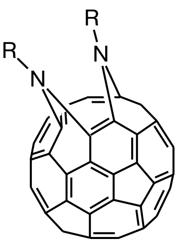
The regioselectivity of the addition of two azide molecules to the C_{60} fullerene cage was determined based on ^{13}C NMR spectroscopic data. The ^{13}C NMR spectra of all bis-adducts **10—12** show no signals at δ 70—90 typical of resonances of the sp^3-hybridized carbon atoms of the fullerene cages of 6,6-closed mono- and polyadducts.[1—3] The region characteristic of the sp^2-hybridized carbon atoms of the fullerene cage (δ 133—146) contains signals, whose number and relative intensities provide evidence that bis-organofullerene molecules have the C_s symmetry. Earlier,[11] we have demonstrated that ten structures correspond to this set of lines in the ^{13}C NMR spectrum. Of these structures, three 5,6-open structures **I—III** and one 6,6-open structure **IV** are most probable (the carbon atoms, whose signals in the ^{13}C NMR spectra are outside the region δ 133—146, are marked with an asterisk).



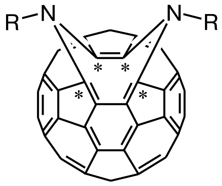
I



II



III

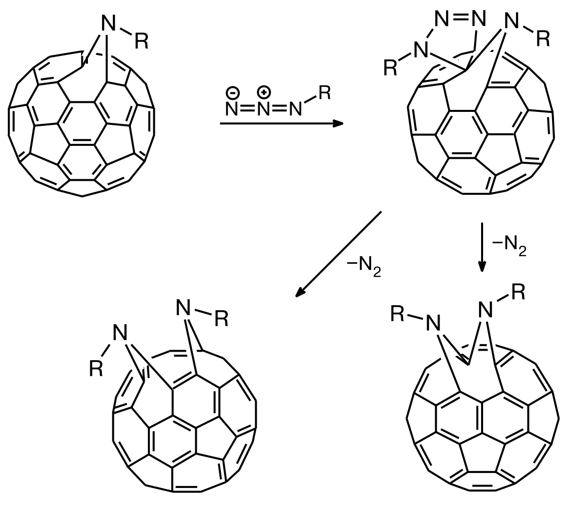


IV

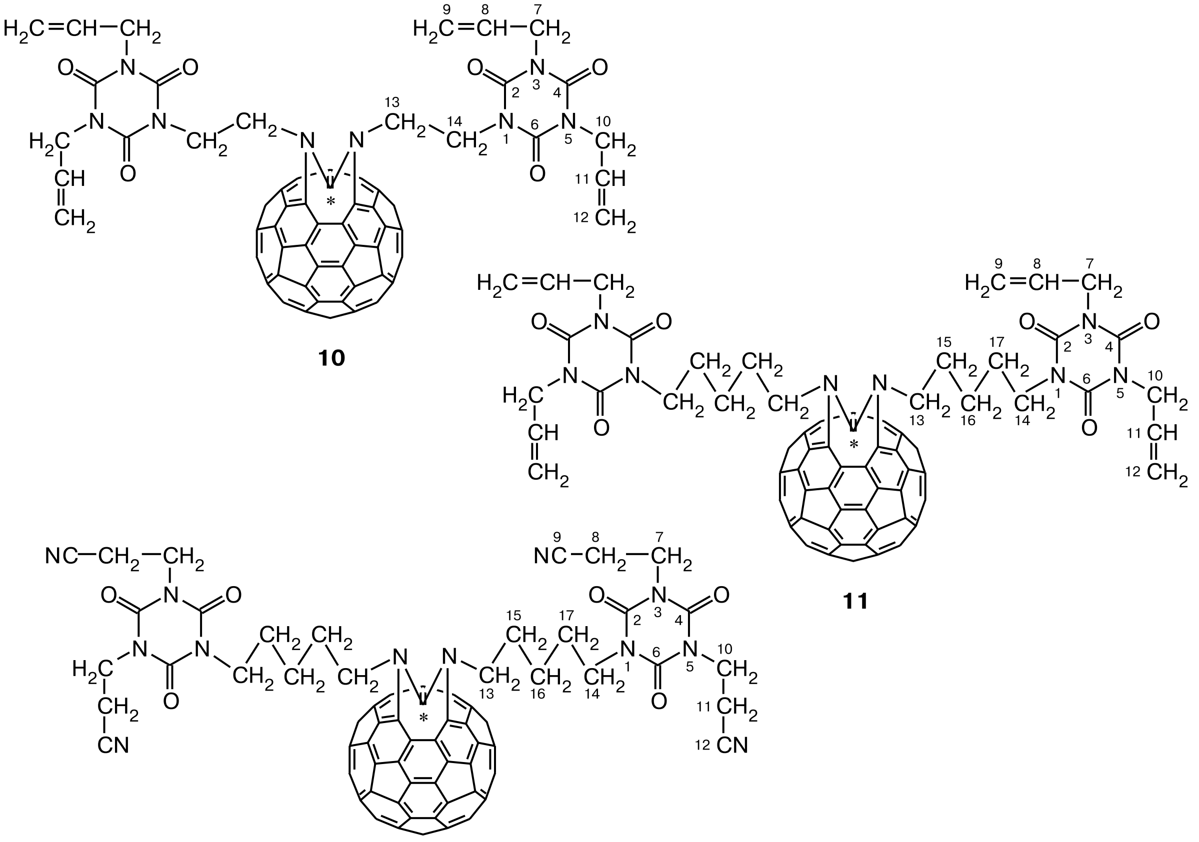
A few representatives of bis-adducts of all possible structures were documented.[10,16—19] In these studies, the data on these structures were compared with related organic compounds, and it was concluded that only structure **III** contains no carbon atoms, whose signals would appear in the ^{13}C NMR spectra outside the region δ 133—146. Based on this conclusion, we have assigned[11] the structure of regioisomer **III** to compound **2**. For regioisomer **I**, the carbon atom directly bound to two nitrogen atoms was demonstrated[10] to give a signal at δ ~160. Unlike the ^{13}C NMR spectrum of compound **2**, the NMR spectra of products **10—12** show such signals. Hence, we assigned the structure of regioisomer **I** to these products. It should be noted that the latter structure exists regardless of the nature of the substituent in the isocyanuric ring and the length of the methylene chain between the isocyanuric ring and the azido group in azides **3—5**.

Therefore, the investigation of the reactions of fullerene C_{60} with organic azides **1** and **3—5** demonstrated that the reactions of organic azides with fullerene can be used as a procedure for the preparation of individual isomers of bis-organofullerenes. We performed calculations of the total and relative energies of regioisomers **I—IV** with R = H by the density functional theory method (DFT/PBE/TZ2P) with the nonempirical exchange-correlation potential PBE (Perdew—Burke—Ernzerhof),[20] the triple-zeta basis set, and two polarization functions (TZ2P) using the PRIRODA program[21] (Table 1). These calculations demonstrated that regioisomer **IV** and regioisomer **II** are the thermodynamically least and most stable structures, respectively. Based on these calculations and the data on the reactions of fullerene C_{60} with azides containing linear organic fragments,[10] *viz.*, with 1,3-di(2-methoxycarbonylethyl)-substituted isocyanuratopentylazide **1** and azides **3—5**, it can be concluded that regioisomers **I** and **III** are, apparently, products generated in the reactions of azides with azahomofullerenes under kinetic control (Scheme 2), whereas the existence of a particular structure, most likely, depends on the bulkiness of the organic fragment in azide molecules.

Scheme 2



III **I**



10

11

12

Table 1. Total (*E*) and relative energies (Δ*E*) of regioisomers **I**—**IV** (R = H) calculated by the DFT method

Regioisomer	−*E*/au	Δ*E*/kcal mol^{-1}
I	2394.86898	17.70
II	2394.89719	0.00
III	2394.88480	7.77
IV	2394.86062	22.95

The ability of fullerenes and their derivatives to accept electrons is a practically important feature of these compounds. The cyclic voltammetric study demonstrated that the successive saturation of the bonds in fullerenes hinders electrochemical reduction of polyadduct molecules, and each subsequent C=C bond cleavage in the C_{60} fullerene cage makes reduction of polyadducts irreversible[22,23] and is accompanied by the shift of the reduction peaks toward cathodic potentials by 0.1—0.15 V. However, this conclusion is true only for 6,6-closed adducts. To our knowledge, data on electrochemical reduction of 5,6-open polyadducts are lacking in the literature.

The electrochemical properties of monoadduct **6** and bis-adducts **2** and **10—12** were studied by cyclic voltammetry. The experimental results were compared with the cyclic voltammetric data for unsubstituted C_{60}. In the potential range from 0 to −2.5 V, the starting azides **1** and **3—5** are not reduced. The cyclic voltammograms of all the organofullerenes under study, as well as the CV curve of fullerene C_{60}, show several reversible one-electron peaks corresponding to reduction of the fullerene cage. It should be noted that it is more difficult to reduce both monoadduct **6** and bis-adducts **2** and **10—12** compared to the nonmodified fullerene (Table 2). It was found that the closer the electron-withdrawing isocyanuric fragment to the fullerene cage, the easier the reduction of the bis-adduct. For example, reduction of bis-adduct **10** occurs more readily than reduction of bis-adducts **11** and **12**. Reduction of bis-adduct **10** occurs at potentials, which are close to the reduction potentials of monoadduct **6**. This is the difference between the 5,6-open structures of bis-adducts and the 6,6-closed regioisomers. It should also be noted that reduction of bis-adducts **2** and **10—12** occurs in a similar fashion in spite of the different structures of the fullerene cages in the molecules of these compounds.

To summarize, the reactions of fullerene C_{60} with isocyanurate-substituted azides provide evidence that the reactions of fullerene C_{60} with organic azides can be used as a procedure for the regioselective addition of two

Table 2. Potentials of peaks observed in the cyclic voltammograms* of C_{60}, monoazahomofullerene **6**, and bis-adducts **2** and **10—12**

Compound	$-E_1$	$-E_2$	$-E_3$	$-E_4$
	V			
C_{60}	0.83	1.24	1.70	2.16
2	0.95	1.26	1.73	—
6	0.89	1.30	1.75	2.20
10	0.90	1.33	1.73	2.25
11	0.94	1.34	1.76	—
12	0.98	1.37	1.78	—

* A 3 : 1 *o*-DCB—MeCN mixture at 25 °C; 0.1 *M* Bu_4NBF_4 as the supporting electrolyte; a glassy-carbon electrode as the cathode ($S_{work} = 3.14$ mm^2), Ag/0.01 *M* $AgNO_3$ in MeCN as the reference electrode, $\nu_{scan} = 50$ mV s^{-1}.

addend molecules to the fullerene cage giving rise to structures in which two 5,6-bonds in the fullerene cage are cleaved. The structures of the resulting regioisomers are, most likely, determined by the steric effects of the substituents at the bridging nitrogen atoms. Unlike the 6,6-closed bis-adducts, the 5,6-open bis-adducts undergo electrochemical reversible reduction, the ability to accept electrons being independent of the structure of the fullerene cage of the regioisomer.

Experimental

The IR spectra were measured on a Bruker IFS-113V Fourier-transform spectrometer in KBr pellets. The assignment of the lines in the ^{1}H and ^{13}C NMR spectra of compounds **6** and **10—12** was made based on 1D and 2D NMR experiments (DEPT, 2D COSY, 2D HSQC, and 2D HMBC).[24,25] The ^{1}H and ^{13}C NMR spectra were recorded on an Avance-600 instrument (Bruker) (600.00 MHz for ^{1}H and 150.864 MHz for ^{13}C). The UV spectra were measured on a Specord UV—Vis instrument. The mass spectra were obtained on a MALDI TOF MS instrument (Dynamo). In the cyclic voltammetric studies, a stationary disk glassy-carbon electrode with the working surface area of 3.14 mm^2 was used as the working electrode. The cyclic voltammograms (CV curves) were measured on a PI-50-1 potentiostat equipped with a PR-8 programmer and an electrochemical cell according to a three-electrode scheme. The CV curves were recorded with the use of an XY recorder at a potential scan rate of 50 mV s^{-1} in a 3 : 1 *o*-DCB—MeCN mixture with the use of Bu_4NBF_4 (0.1 *M*) as the supporting electrolyte. An Ag/0.01 *M* $AgNO_3$ system in MeCN served as the reference electrode, and a platinum wire was used as the auxiliary electrode. The measurements were carried out in a temperature-controlled (25 °C) cell under an argon atmosphere. The concentration of the solutions of C_{60} and azide **1** was $2 \cdot 10^{-3}$ mol L^{-1}, and the concentration of the solutions of the adducts was $1 \cdot 10^{-3}$ mol L^{-1}. Anhydrous *o*-DCB and MeCN were prepared by distillation over P_2O_5. [60]Fullerene was synthesized at the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences (Nizhnii Novgorod). Azides **3—5** were prepared according to a procedure described earlier.[11—13] Elemental analysis was carried out on an Analizator CHN-3 instrument.

Reactions of fullerene C_{60} with azides 3—5. A mixture of C_{60} (0.143 mmol) and the corresponding azide (0.429 mmol) in dry degassed *o*-dichlorobenzene (25 mL) was stirred at 130 °C (with azides **3** or **5**) or 180 °C (with azide **4**) for 4 h. The solvent was removed from the reaction mixture *in vacuo*. The residue was chromatographed on a silica gel column to isolate unconsumed fullerene (toluene as the eluent), monoadducts **6—8** (toluene as the eluent), and bis-adducts **10—12**.

1a-[2-(3,5-Diallyl-2,4,6-trioxo-1,3,5-triazin-1-yl)ethyl]-1a-aza-1(2)a-homo(C_{60}-*I_h*)[5,6]fullerene (6), was isolated by column chromatography, R_f 0.17, toluene as the eluent (Sorbfil). Found (%): C, 87.00; H, 1.66; N, 5.63. $C_{71}H_{14}N_4O_3$. Calculated (%): C, 87.84; H, 1.44; N, 5.77. MS, *m/z*: 970. UV (CH_2Cl_2), λ_{max}/nm: 263, 333, 430, 545. IR (KBr), ν/cm^{-1}: 1645, 1693, 526. ^{1}H NMR ($CDCl_3$), δ: 5.91 (ddt, 2 H, C(8)H_2, C(11)H_2, $^3J_{H,H}$ = 17.1 Hz, $^3J_{H,H}$ = 10.9 Hz, $^3J_{H,H}$ = 6.1 Hz); 5.35 (d, 2 H, C(9)H_{trans}, C(12)H_{trans}, $^3J_{H,H}$ = 17.1 Hz); 5.23 (d, 2 H, C(9)H_{cis}, C(12)H_{cis}, $^3J_{H,H}$ = 10.9 Hz); 4.56 (d, 4 H, C(7)H_2, C(10)H_2, $^3J_{H,H}$ = 6.1 Hz); 4.53 (t, 2 H, C(13)H_2, $^3J_{H,H}$ = 5.7 Hz); 4.01 (t, 2 H, C(14)H_2, $^3J_{H,H}$ = 5.7 Hz). ^{13}C—{^{1}H} NMR ($CDCl_3$), δ: 148.94 (C(4), C(6)); 148.49 (C(2)); 130.90 (C(9), C(12)); 119.19 (C(8), C(11)); 48.78 (C(14)); 45.11 (C(7), C(10)); 41.81 (C(13)); **C_{60}N**: 133.75, 135.78, 136.29, 137.05, and 137.29 (all, 2 C each); 137.87 (1 C); 138.14, 138.56, and 139.39 (all, 2 C each); 140.56 (1 C); 140.88, 141.52, 142.71, 142.79, 142.84, 142.99, and 143.21 (all, 2 C each); 143.27 (1 C); 143.45 (2 C); 143.57 (1 C); 143.67, 143.86, 144.01, and 144.18 (all, 2 C each); 144.33 (4 C); 144.49, 144.60, 144.70, 145.03, 145.49, and 147.72 (all, 2 C each).

1a,5a-Bis-[2-(3,5-diallyl-2,4,6-trioxo-1,3,5-triazin-1-yl)ethyl]-1a,5a-diaza-1(2)a,1(5)a-dihomo(C_{60}-*I_h*)[5,6]fullerene (10) was isolated by column chromatography, toluene—Et_2O as the eluent (50 : 1); R_f 0.21, toluene—Et_2O as the eluent, 10 : 1 (Sorbfil). Found (%): C, 79.84; H, 2.51; N, 9.09. $C_{82}H_{28}N_8O_6$. Calculated (%): C, 80.66; H, 2.29; N, 9.18. IR (KBr), ν/cm^{-1}: 1692 (C=O); 762 (isocyanuric ring); 527 (fullerene fragment). ^{1}H NMR ($CDCl_3$), δ: 5.85 (ddt, 4 H, C(8)H_2, C(11)H_2, $^3J_{H,H}$ = 17.1 Hz, $^3J_{H,H}$ = 10.9 Hz, $^3J_{H,H}$ = 6.1 Hz); 5.32 (d, 4 H, C(9)H_{trans}, C(12)H_{trans}, $^3J_{H,H}$ = 17.1 Hz); 5.21 (d, 4 H, C(9)H_{cis}, C(12)H_{cis}, $^3J_{H,H}$ = 10.1 Hz); 4.65 (dt, 2 H, C(13)H_2, $^2J_{H,H}$ = 13.5 Hz, $^3J_{H,H}$ = 6.1 Hz); 4.54 (dd, 4 H, C(14)H_2, $^3J_{H,H}$ = 6.1 Hz); 4.49 (d, 8 H, C(7)H_2, C(10)H_2, $^3J_{H,H}$ = 6.1 Hz); 4.10 (dt, 4 H, C(13)H_2, $^2J_{H,H}$ = 13.5 Hz, $^3J_{H,H}$ = 6.1 Hz). ^{13}C—{^{1}H} NMR ($CDCl_3$), δ: 148.74 (C(4), C(6)); 148.46 (2 C(2)); 130.82 (C(9), C(12)); 119.39 (C(8), C(11)); 47.74 (2 C(14)); 45.12 (C(7), C(10)); 41.89 (2 C(13)); **C_{60}N**: 130.69 and 132.34 (both, 2 C each); 134.02 (1 C); 134.66, 135.37, 136.65, 139.04, 139.20, 139.55, 139.72, 141.46, 141.65, 142.04, 142.61, 143.42, 143.58, 143.80, and 143.98 (all, 2 C each); 144.06 (1 C); 144.14 and 144.20 (both, 4 C each); 144.57, 144.62, 144.82, 144.98, and 145.17 (all, 2 C each); 145.39 (1 C); 146.85 and 147.45 (both, 2 C each); 160.13 (1 C).

1a,5a-Bis-[5-(3,5-diallyl-2,4,6-trioxo-1,3,5-triazin-1-yl)pentyl]-1a,5a-diaza-1(2)a,1(5)a-dihomo(C_{60}-*I_h*)[5,6]fullerene (11) was isolated by column chromatography, toluene—Et_2O as the eluent (50 : 1); R_f 0.69, toluene—Et_2O as the eluent, 5 : 1 (Sorbfil). Found (%): C, 79.77; H, 2.92; N, 8.41. $C_{88}H_{40}N_8O_6$.

Calculated (%): C, 80.98; H, 3.07; N, 8.59. IR (KBr), ν/cm^{-1}: 1691 (C=O); 762 (isocyanuric ring); 526 (fullerene fragment). ^{1}H NMR (CDCl$_3$), δ: 5.87 (ddt, 4 H, C(8)H$_2$, C(11)H$_2$, $^3J_{\mathrm{H,H}}$ = 17.21 Hz, $^3J_{\mathrm{H,H}}$ = 10.9 Hz, $^3J_{\mathrm{H,H}}$ = 5.8 Hz); 5.32 (d, 4 H, C(9)H$_{trans}$, C(12)H$_{trans}$, $^3J_{\mathrm{H,H}}$ = 17.2 Hz); 5.25 (d, 4 H, C(9)H$_{cis}$, C(12)H$_{cis}$, $^3J_{\mathrm{H,H}}$ = 10.9 Hz); 4.50 (d, 8 H, C(7)H$_2$, C(10)H$_2$, $^3J_{\mathrm{H,H}}$ = 5.8 Hz); 4.05 (m, 4 H, C(13)H$_2$); 3.91 (m, 4 H, C(14)H$_2$); 2.06 (m, 4 H, C(15)H$_2$); 1.85 (m, 4 H, C(17)H$_2$); 1.71 (m, 4 H, C(16)H$_2$). ^{13}C—{^{1}H} NMR (CDCl$_3$), δ: 148.76 (C(4), C(6)); 148.48 (2 C(2)); 130.99 (C(9), C(12)); 119.07 (C(8), C(11)); 51.31 (2 C(13)); 44.98 (C(7), C(10)); 43.02 (2 C(14)); 28.89 (2 C(17)); 27.71 (2 C(15)); 24.44 (C(16)); **C$_{60}$N**: 130.51 (2 C); 132.26 (1 C); 132.86, 134.59, 135.24, 137.10, 138.83, 139.02, 139.36, 139.58, and 141.06 (all, 2 C each); 141.59 (4 C); 142.03 and 142.68 (both, 2 C each); 143.08 (1 C); 143.34, 143.57, 143.73, 143.97, 144.10, 144.14, 144.19, 144.55, 144.61, 144.87, 144.96, and 145.12 (all, 2 C each); 145.44 (1 C); 146.84 and 147.61 (both, 2 C each); 163.77 (1 C).

1a,5a-Bis{5-[3,5-di(2-cyanoethyl)-2,4,6-trioxo)-1,3,5-triazin-1-yl]pentyl}-1a,5a-diaza-1(2)a,1(5)a-dihomo(C$_{60}$-*I$_h$*)[5,6]fullerene (12) was isolated by column chromatography, toluene—MeCN as the eluent (10 : 1); R_f 0.32, toluene—MeCN as the eluent, 5 : 1 (Sorbfil). Found (%): C, 76.98; H, 2.98; N, 11.60. $C_{88}H_{36}N_{12}O_6$. Calculated (%): C, 77.88; H, 2.65; N, 12.38. IR (KBr), ν/cm^{-1}: 1692 (C=O); 762 (isocyanuric ring); 527 (fullerene fragment). ^{1}H NMR (CDCl$_3$), δ: 4.25 (dd, 8 H, C(7)H$_2$, C(10)H$_2$, $^3J_{\mathrm{H,H}}$ = 6.6 Hz, $^3J_{\mathrm{H,H}}$ = 7.0 Hz); 4.06 (m, 4 H, C(13)H$_2$); 4.03 (m, 4 H, C(14)H$_2$); 2.81 (dd, 8 H, C(8)H$_2$, C(11)H$_2$, $^3J_{\mathrm{H,H}}$ = 6.6 Hz, $^3J_{\mathrm{H,H}}$ = 7.0 Hz); 2.08 (m, 4 H, C(17)H$_2$); 1.87 (m, 4 H, C(15)H$_2$); 1.74 (m, 4 H, C(16)H$_2$). ^{13}C—{^{1}H} NMR (CDCl$_3$), δ: 148.24 (C(4), C(6)); 148.29 (2 C(2)); 116.53 (C(9), C(12)); 51.29 (2 C(13)); 43.41 (2 C(14)); 38.37 (C(7), C(10)); 28.87 (2 C(17)); 27.45 (2 C(15)); 24.32 (2 C(16)); 16.52 (C(8), C(11)); **C$_{60}$N**: 130.46 (2 C); 132.20 (1 C); 132.82, 134.57, 135.23, 137.08, 138.81, 139.00, 139.36, 139.57, 141.05, 141.54, 141.57, 142.03, 142.66, 143.35, 143.53, 143.74, and 143.94 (all, 2 C each); 144.03 (1 C); 144.10, 144.13, 144.19, 144.55, 144.60, 144.85, 144.98, and 145.12 (all, 2 C each); 145.43 (1 C); 146.77 and 147.55 (both, 2 C each); 163.60 (1 C).

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