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Proton-Acceptor Properties of Azahomofullerene and Fullerenoaziridine Containing a Cyanuric Acid Fragment

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Abstract—^{13}C and ^{1}H NMR and UV spectral studies on 1,3-diallyl-5-[4-(azahomo[60]fullereno)butyl]hexahydro-1,3,5-triazine-2,4,6-trione ([5,6]-open isomer) and 1,3-diallyl-5-[4-(aziridino[60]fullereno)butyl]hexahydro-1,3,5-triazine-2,4,6-trione ([6,6]-closed isomer), as well as quantum-chemical calculations, showed that only the latter possesses weakly basic properties.

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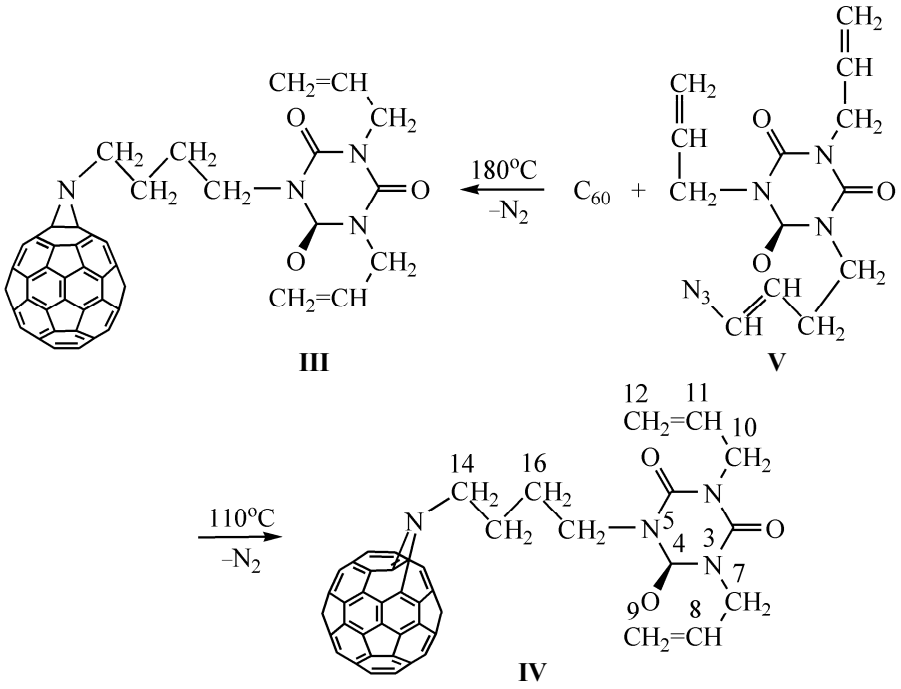
Oxygen-containing fullerene derivatives, e.g., fullerols and phosphorylated methanofullerenes, are promising as materials for the design of proton conductors [1, 2]. Available data on proton-acceptor properties of nitrogen-containing fullerene derivatives are few in number. It is known that fulleropyrrolidines are weaker bases than pyrrolidines, which is generally attributed to interaction between the lone electron pair (LEP) on the nitrogen atom and π-system of the fullerene sphere [3]. Protonation–deprotonation processes were also studied for dimethylaminophenyl-substituted fullerenoaziridine **I** and azahomofullerene **II**; it was found that only the latter exhibits very weak basicity and that the protonation involves the electron-donor dimethylamino group rather than exohedral nitrogen atom in the fullerene fragment [4]. In the present article we report on the results of our study on proton-acceptor properties of 1,3-diallyl-5-{4-([60]fullero[1,2-*b*]aziridino)butyl}hexahydro-1,3,5-triazine-2,4,6-trione (**III**) and 1,3-diallyl-5-[4-(azahomo[60]fullero)butyl]hexahydro-1,3,5-triazine-2,4,6-trione (**IV**). It is known that organic acids are incapable of protonating cyanuric acid derivatives and that mineral acids promote their decomposition [5]. Therefore, unlike compounds **I** and **II**, only the exohedral nitrogen atom in molecules **III** and **IV** can take up a proton.

Fulleroaziridine **III** was synthesized by us previously via reaction of C_{60} with azide **V** in *o*-dichlorobenzene at 180°C [6]. Azahomofullerene **IV** was synthesized in the present work from the same initial compounds but at a lower temperature, at 110°C. Compound **IV** was isolated from the reaction mixture by column chromatography. Its structure was determined using a series of two-dimensional NMR correlation techniques (COSY, HSQC, HMBC) [7, 8]. In the ^{1}H NMR spectrum of **IV** we observed a number of multiplet signals in the region δ 6–2 ppm. The 2D COSY data allowed us to distinguish spin systems corresponding to the tetramethylene moiety and allyl groups. Analysis of signal intensities in the ^{1}H NMR spectrum showed the presence of two equivalent allyl fragments. The corresponding carbon atoms were identified with account taken of the 2D HSQC data. Finally, the structure of these fragments was determined on the basis of the 2D HMBC spectrum which displayed couplings between the $C^{7}H_2/C^{10}H_2$ protons (δ 4.52 ppm) and quaternary carbon atoms resonating at δ_C 148.84 and 148.5 ppm (Fig. 1). The intensity ratio of the latter signals was 2:1, so that we assigned the signal at δ_C 148.84 ppm to C^4 and C^6, and the signal at δ_C 148.5 ppm, to C^2. Thus we have proved that the allyl fragments are attached to the triazine ring.

It is often difficult to identify signals from protons in the terminal methylene groups in compounds containing polymethylene bridges. As applied to molecule **IV**, these are the $C^{13}H_2$ and $C^{14}H_2$ groups. Their signals were assigned on the basis of 2D HMBC



experiment. The HMBC spectrum of **IV** displayed a cross peak between C^4 (C^6) (δ_C 148.84 ppm) and methylene protons resonating at δ 4.11 ppm. This means that the latter signal corresponds to the terminal $C^{13}H_2$ group which is linked to the triazine ring (Fig. 1). The presence of a cross peak between protons of the other terminal CH_2 group of the spacer (δ 3.85) and ^{13}C resonance at δ_C 146.54 ppm arising from carbon nucleus in the fullerene sphere (Fig. 1) allowed us to assign the signal at δ 3.85 ppm to the $C^{14}H_2$ group attached to the fullerene sphere. The chemical shift of the bridging carbon atoms (δ_C 146.54 ppm) corresponds to the open mode of cycloaddition.

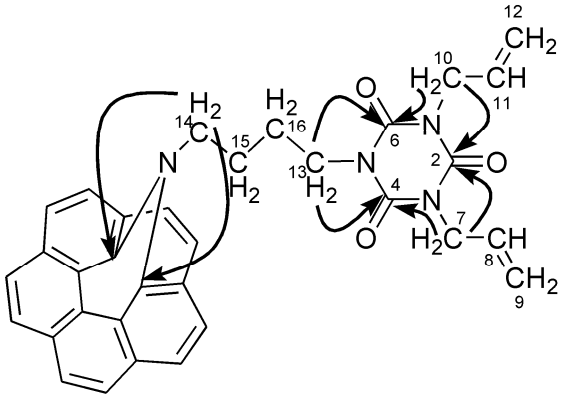


Fig. 1. Principal correlations in the HMBC spectrum of compound **IV**.

The UV spectrum of **IV** was typical of azahomofullerenes ([5,6]-open isomers of fullerene monoadducts). The spectrum lacked low-intensity absorption band in the λ region 420–430 nm, which could indicate [6,6]-closed structure of fullerene monoadducts [6, 9].

Basic properties of isomers **III** and **IV**, as well of initial azide **V**, were studied by ^1H NMR and UV spectroscopy using trifluoroacetic acid as protonating agent. Initially, the ^1H NMR and UV spectra of solutions of pure compounds **III**–**V** were recorded, and then trifluoroacetic acid in the same solvent was added. Experiments were performed at a concentration of **III**–**V** and trifluoroacetic acid of 3×10^{-4} M.

Gradual addition of trifluoroacetic acid to azide **V** and [5,6]-open isomer **IV** (the acid-to-substrate ratio was varied from 1:1 to 100:1) did not change the ^1H spectrum. In the case of [6,6]-closed isomer **III**, appreciable changes in the ^1H NMR spectrum were

Table 1. ^{13}C NMR spectra of isomers **III** and **IV** and azide **V** in the absence and in the presence of 100 equiv of trifluoroacetic acid (TFA)

Comp. no.	δ, ppm ($^3J_{HH}$, Hz)							
	C^7H_2, $S^{10}H$, 4H	C^8H, $C^{11}H$, 2H	$(C^9H_2, C^{12}H_2)_{trans}$, 2H	$(C^9H_2, C^{12}H_2)_{cis}$, 2H	$C^{13}H_2$, 2H	$C^{14}H_2$, 2H	$C^{15}H_2$, $C^{16}H_2$, 4H	TFA
III	4.52 d (6.2)	5.89 d.d.t	5.32 d (18.5)	5.26 d (10.0)	4.15 m	3.72 m	2.17 m	
III + TFA	4.52 d (6.2)	5.87 d. d. t	5.32 d (18.5)	5.26 d (10.0)	4.17 m	3.81 m	2.12 m	10.25 s
IV	4.48 d (6.0)	5.86 d. d. t	5.31 d (18.0)	5.24 d (10.8)	3.93 m	3.43 m	1.86 m	
IV + TFA	4.52 d (6.0)	5.85 d. d. t	5.30 d (17.0)	5.27 d (10.0)	3.96 m	3.43 m	1.87 m	10.25 s
V	4.48 d (6.0)	5.86 d. d. t	5.31 d (18.0)	5.24 d (10.8)	3.93 m	3.43 m	1.86 m	
V + TFA	4.52 d (6.0)	5.85 d. d. t	5.30 d (17.0)	5.27 d (10.0)	3.96 m	3.43 m	1.87 m	10.25 s

observed only after addition of 100-fold excess of the acid (Table 1). The $C^{14}H_2$ signal was displaced downfield by 0.1 ppm relative to the corresponding signal of pure compound **III**, and the other signals in the ^1H NMR spectrum were slightly broadened.

The observed variations in ^1H NMR spectrum may be attributed to protonation of the nitrogen atom in the aziridine ring of molecule **III**. However, the site of protonation cannot be determined unambiguously on the basis of proton chemical shifts. Here, ^{15}N NMR spectra would be most informative, but low sensitivity of this method restricts its application. Alternatively, ^{13}C NMR spectroscopy may be used [10, 11]. Although its sensitivity is lower than that of ^{15}N NMR, but the results are much more reliable than the ^1H NMR data. Therefore, we analyzed the ^{13}C NMR spectra to determine the site of proton addition.

Addition of trifluoroacetic acid to a solution of [6,6]-closed isomer **III** to a ratio of 100:1 resulted in upfield displacement of carbon signals from the polymethylene spacer, while the chemical shifts of the other carbon nuclei changed insignificantly (Table 2). Presumably, the observed pattern corresponds to protonation of the aziridine nitrogen atom which is linked to the tetramethylene spacer. In order to verify this assumption we performed RB3LYP/6-31G(*d*)//RHF/6-31G calculations of the ^{13}C chemical shifts for neutral molecule **III** and that protonated at the aziridine nitrogen atom. In fact, the calculation results were consistent with the experimentally observed upfield shift of ^{13}C signals from all CH_2 groups in the bridge (Fig. 2).

It should be noted that the spectrum of isomer **III** in neutral medium showed equivalence of symmetric (with respect to the axis passing through C^2 and N^5)

Table 2. ^{13}C NMR spectra of isomer **III** in the absence and in the presence of 100 equiv of trifluoroacetic acid (TFA)

Atom	δ_C, ppm	
	III	**III** + TFA
C^2	148.51	148.70
C^4, C^6	148.86	149.18, 149.36
C^7, C^{10}	45.03	45.44, 45.52
C^8, C^{11}	130.98	130.03, 130.17
C^9, C^{12}	119.13	119.48, 119.65
C^{13}	43.05	42.21
C^{14}	50.45	48.56
C^{15}	25.77	25.35
C^{16}	26.72	24.70
$C_{60}N$	(C_{2v}) 2C: 85.05; 145.25 8C: 145.19; 144.70; 144.61; 143.13; 140.85 4C: 143.84; 142.93; 142.33; 142.18	(*Cs*) 2C: 81.5; 146.67; 145.42; 144.06; 143.98; 143.96; 143.23; 143.09; 142.58; 142.15; 141.91; 141.74; 141.25; 141.22;140.89; 140.52 4C: 145.27; 143.28; 142.91; 142.18; 142.00;141.19 1C: 146.77; 145.50; 142.25; 142.23

carbon nuclei in the triazine ring (C^4/C^6) and in the corresponding allyl fragments (C^7/C^{10}, C^8/C^{11}, and C^9/C^{12}), while they became nonequivalent upon protonation. The number of spectral lines is likely to increase as a result of deceleration of some exchange process. Fast inversion of the aziridine nitrogen atom in unprotonated isomer **III** gives rise to exchange between two main molecular conformations shown in Fig. 3, where R^1 is lone electron pair: as a result, the triazine fragment appears at one or another side of the

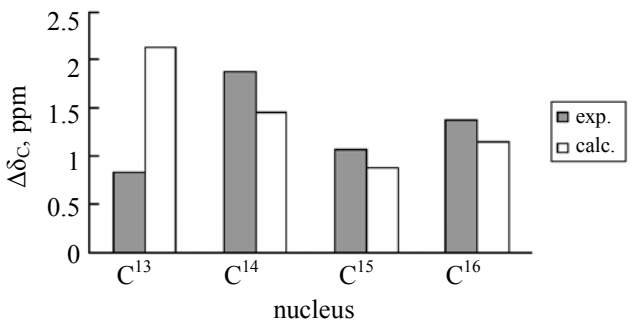


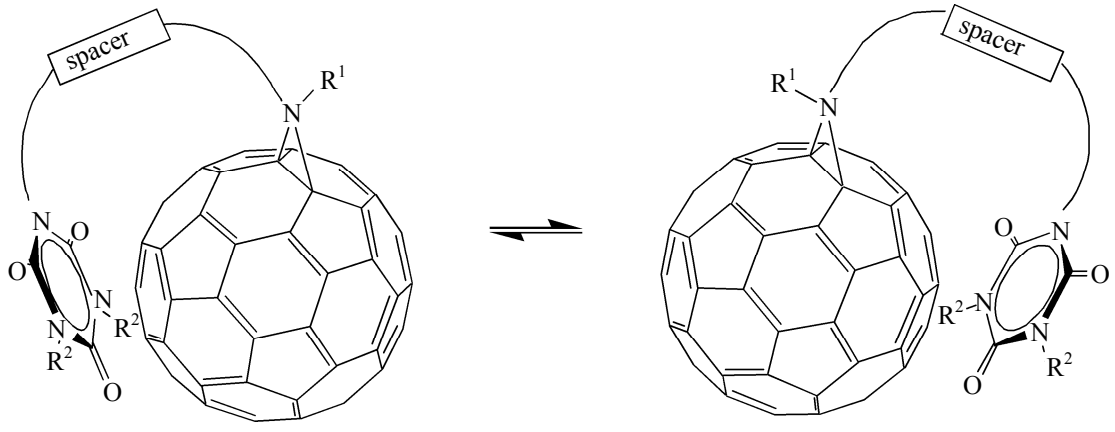
Fig. 2. Experimental and calculated ^{13}C chemical shifts for the unprotonated and protonated forms of isomer **III**.

fullerene sphere, and signals from the above carbon atoms are averaged. Protonation (Fig. 3, R^1 = H) makes the inversion slower, and the triazine fragment appears preferentially only at one side of the fullerene sphere. It might be expected that the presence of four single bonds in the spacer should ensure free rotation about these bonds, thus ensuring effective signal averaging in the ^{13}C NMR spectrum. However, nonequivalence of the corresponding carbon nuclei, observed experimentally in the spectrum of protonated compound **III** suggests conformational preference of some orientation of the substituent. Most probably, this pattern is governed by steric factors: either rotation of fairly bulky substituent at the end of the spacer is restricted due to proximity to the fullerene fragment or some interactions exist between the substituent and the fullerene sphere.

Thus analysis of the ^{13}C NMR data led us to conclude that compound **III** in the presence of 100 equiv of trifluoroacetic acid is protonated at the aziridine nitrogen atom. Presumably, the predominant conformation in solution is that in which the triazine fragment is fairly close to the fullerene sphere.

Analogous conclusions can be drawn from the results of UV titration of solutions of isomers **III** and **IV**. At a substrate-to-acid ratio of 1:1 to 1:50, in the spectra of both isomers we observed only decrease in the absorption intensity due to dilution (Fig. 4a, b). The same pattern was observed in the spectrum of [5,6]-open isomer **IV** in the presence of 100-fold excess of trifluoroacetic acid. The UV spectrum of isomer **III** in the presence of 100 equiv of trifluoroacetic acid was characterized by considerable increase in intensity and broadening of the originally narrow absorption band at λ_{max} 428 nm (Fig. 4c).

Our experimental data on the basicity of of azahomofullerene and fullerenoaziridine are very consistent with the corresponding proton affinities calculated in terms of the density functional theory (DFT) using Perdew–Burke–Ernzerhof exchange-correlation potential [12] and triple zeta basis set supplemented by two polarization functions (TZ2P); the calculations were performed using PRIRODA software [13]. The calculated proton affinity of trimethylamine (Me_3N, **VI**) is 233 kcal mol^{-1}, and that of *N*-methylaziridine (C_2H_4NMe, **VII**) is 229 kcal mol^{-1}. The corresponding values for model fullerenoaziridine ($C_{60}NMe$, **VIIIa**, [6,6]-closed isomer) and azahomofullerene ($C_{60}NMe$, **VIIIb**, [5,6]-open isomer)



R^1 = LEP, H; R^2 = CH_2CHCH_2.

Fig. 3. Schematic representation of two conformers of compound **III**.

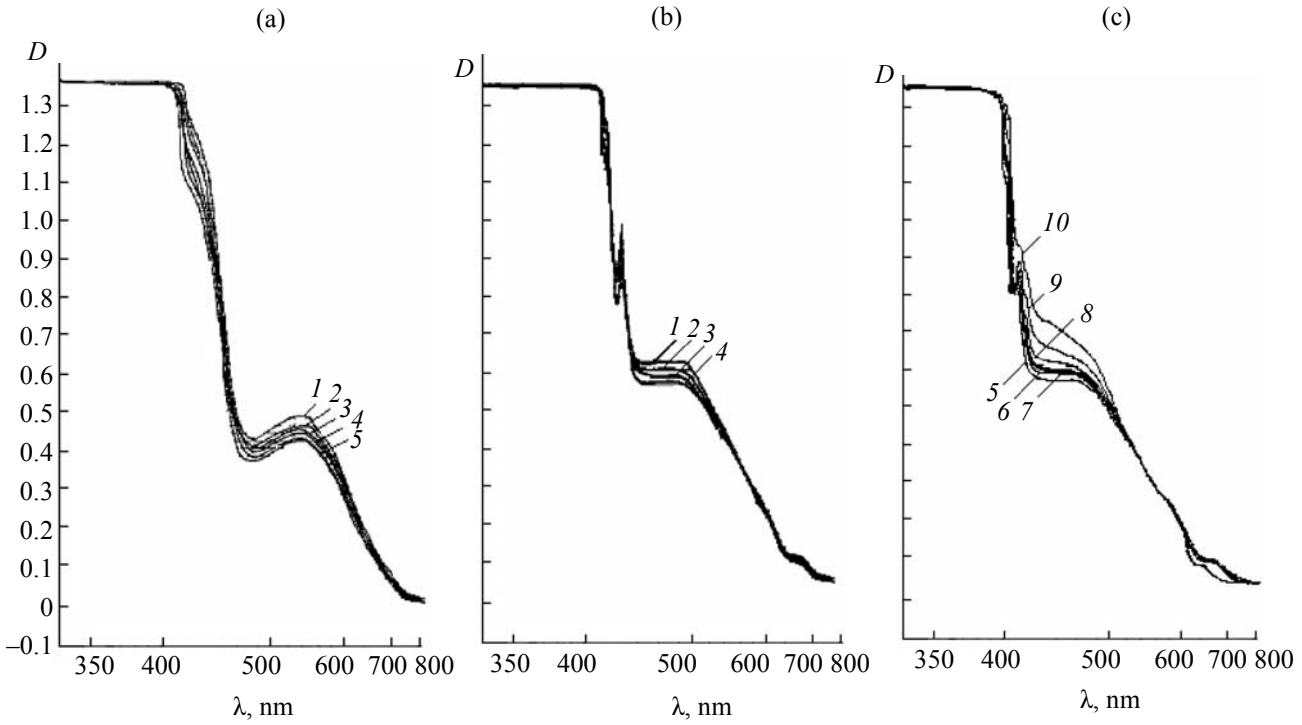


Fig. 4. UV spectra of isomers (a) **IV** and (b, c) **III** in methylene chloride at a substrate-to-trifluoroacetic acid ratio of (*1*) 1 : 10, (*2*) 1 : 20, (*3*) 1 : 30, (*4*) 1 : 40, (*5*) 1 : 50, (*6*) 1 : 60, (*7*) 1 : 70, (*8*) 1 : 80, (*9*) 1 : 90, and (*10*) 1 : 100.

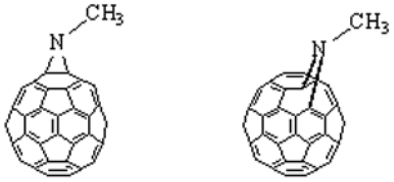
are 225 and 221 kcal mol^{-1}, respectively. The data in Table 3 also show that the total energies of protonated species **VIIIa**$^+$ and **VIIIb**$^+$ differ by 4 kcal mol^{-1}, while the total energies of the initial neutral structures **VIIIa** and **VIIIb** are almost equal. A conclusion may be drawn that difference in the proton affinities of isomers **VIIIa** and **VIIIc** results from interaction of the lone electron pair on the nitrogen atom in **VIIIc** with the fullerene π-system. This interaction reduces the basicity of the nitrogen atom and hinders its protonation.

Thus our results show that azahomofullerenes ([5,6]-open isomers) possess no basic properties and that fullerenoaziridines are extremely weak proton acceptors. Like fullerenopyrrolidines [3], the lone electron pair on the nitrogen atom in molecules **III** and **IV** is most likely to be involved in interaction with π-electron system of the fullerene sphere.

EXPERIMENTAL

The NMR spectra were recorded at 30°C on a Bruker Avance-600 spectrometer at 600 MHz for ^{1}H and 150.926 MHz for ^{13}C using $CDCl_3$ as solvent and reference (δ 7.26 ppm, δ_C 77.0 ppm). The UV spectra were measured on a Specord UV-Vis spectrophotometer from solutions in methylene chloride. The mass spectrum was obtained on a MALDI TOF MS instrument (Dynamo). The IR spectrum was recorded in KBr on a Vruker IFS-113V spectrometer with Fourier transform. The elemental composition of **IV**

Table 3. Total (*E*) and relative energies (Δ*E*) of isomers **VIIIa** and **VIIIb** and their protonated forms **VIIIa**$^+$ and **VIIIb**$^+$, calculated at the DFT/PBE/TZ2P level



VIIIa **VIIIb**

Comp. no.	*E*, au	Δ*E*, kcal mol^{-1}
VIIIa	–2378.84182	0.0
VIIIb	–2378.84105	0.5
(VIIIa)$^+$	–2379.20038	0.0
(VIIIb)$^+$	–2379.19409	4.0

was determined using an Analizator CHN-3 instrument. Quantum-chemical calculations were performed at the Supercomputer Center, Kazan Research Center, Russian Academy of Sciences. *o*-Dichlorobenzene was dehydrated by distillation over P_2O_5. Fullerene C_{60} was synthesized at the Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences (Nizhnii Novgorod, Russia). Azide **V** was synthesized according to the procedure described in [14].

1,3-Diallyl-5-{4-[1a*H*-1a-aza-1(9)a-homo(C_{60}-I_h)[5,6]fulleren-1a-yl]butyl}hexahydro-1,3,5-triazine-2,4,6-trione (IV). Azide **V**, 0.199 mmol, was added to a solution of 0.132 mmol of C_{60} in 25 ml of anhydrous *o*-dichlorobenzene, and the mixture was stirred for 4.5 h at 110°C. The solvent was removed under reduced pressure, and the residue was subjected to column chromatography on silica gel. Elution with toluene gave C_{60} (30%) and monoadduct **IV**. Yield 25%. R_f 0.56 (toluene–Et_2O, 10:1). For ^{1}H NMR spectrum, see Table 1. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 148.50 (C^2), 148.84 (C^4, C^6), 45.03 (C^7, C^{10}); 130.98 (C^8, C^{11}), 119.14 (C^9, C^{12}); 42.93 (C^{13}); 51.19 (C^{14}); 26.76 (C^{16}), 25.70 (C^{15}); C_{60}N: 147.81 (2C), 146.54 (2C), 144.75 (2C), 144.59 (2C), 144.51 (2C), 144.28 (2C), 144.23 (2C), 144.20 (2C), 144.18 (2C), 143.88 (2C), 143.68 (2C), 143. 49 (2C), 143.21 (1C), 143.15 (2C), 143.12 (4S), 142.98 (2C), 142.91 (1C), 142.81 (2C), 142.75 (2C), 141.47 (2C), 140.89 (1C), 140.81 (2C), 139.30 (2C), 138.58 (2C), 138.55 (2C), 138.13 (2C), 137.91 (1C), 137.48 (2C), 137.12 (2C), 135.88 (2C), 133.78 (2C). UV spectrum, λ_{max}, nm ($\varepsilon\times10^{-4}$): 263 (5.62), 333 (5.04), 430 br (4.02), 545 (3.63). IR spectrum, ν, cm^{-1}: 1693 (C=O), 1648 (C=C), 2968, 2766, 991, 931 (C–H), 1457 (C–N), 526 (fullerene sphere). Mass spectrum (MALDI): *m*/*z* 720 (C_{60}); 998 ($C_{73}H_{18}N_4O_3$). Found, %: C 87.60; H 1.34; N 5.63. $C_{71}H_{14}N_4O_3$. Calculated, %: C 87.78; H 1.80; N 5.61.

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