Synthesis, electrochemical properties, and thermal transformations of 1-(5-nitropyrimidin-2-yl)[60]fullereno[1,2-*b*]aziridine

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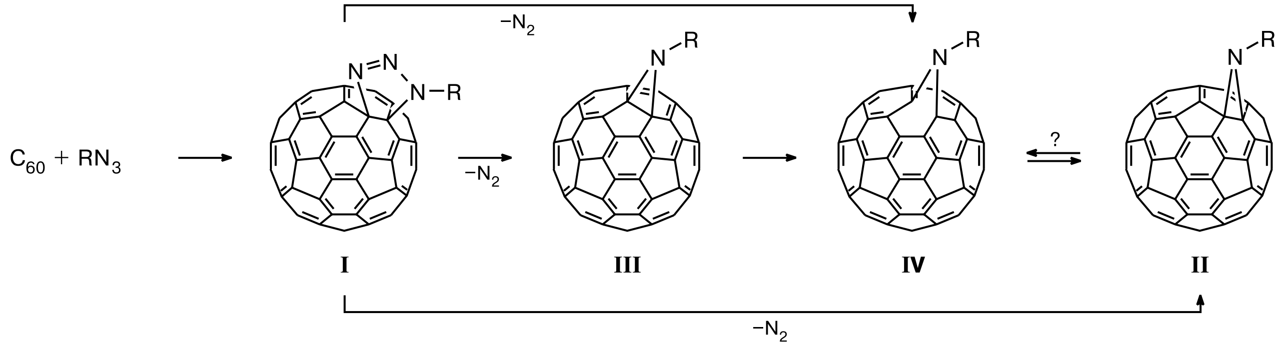
The reaction of fullerene C_{60} with 2-azido-5-nitropyrimidine afforded 1-(5-nitropyrimidin-2-yl)[60]fullereno[1,2-*b*]aziridine, whose electrochemical reduction proceeds more easily than the reduction of nonmodified C_{60}.

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

Reactions of fullerenes with organic azides are widely used to attach organic fragments to the carbon cage of fullerenes due to accessibility of a broad range of aliphatic and aromatic azides and variety of types of organofullerenes that formed.[1,2] Monoadducts of such reactions are [60]fullereno[1,2-*c*]triazolines (**I**), [60]fullereno[1,2-*b*]aziridines (**II**), [60]fullereno[1,6-*b*]aziridines (**III**), and azahomo[60]fullerenes (**IV**), which are prone to mutual thermal transformations. [60]Fullereno[1,2-*c*]triazolines (**I**) are the least thermally stable, and their decomposition depends on the structure of organic fragment R and conditions of the process. For instance, phenyl- and *para*-cyanophenyl-substituted fullerenotriazolines decompose upon irradiation to form the corresponding fullerenoaziridines **II** (Scheme 1),[3,4a] while the same fullerenotriazolines are thermally transformed into azahomofullerenes **IV**. Series of aryl-, methoxycarbonylmethyl-, and trimethylsilylethoxymethyl-substituted fullerenotriazolines undergo similar thermal transformations.[4b] The thermal decomposition of fullerenotriazolines **I** is considered[5] to proceed through the formation of 5,6-closed structures, namely, [60]fullereno[1,6-*b*]aziridines (**III**), which are transformed, in turn, into azahomofullerenes **IV**. The step of transformation of fullerenotriazolines **I** into fullereno[1,6-*b*]aziridines **III** was not directly confirmed experimentally so far. We proved the transformations of [60]fullereno[1,6-*b*]aziridines (**III**) into azahomofullerenes **IV** for isocyanurato-substituted adducts.[6,7] In addition, we have shown[7] for the first time that, as in the case of carbocyclic organofullerenes, azahomofullerenes **IV** can thermally convert to fullereno[1,2-*b*]aziridines **II**, which were earlier considered[2]

Scheme 1



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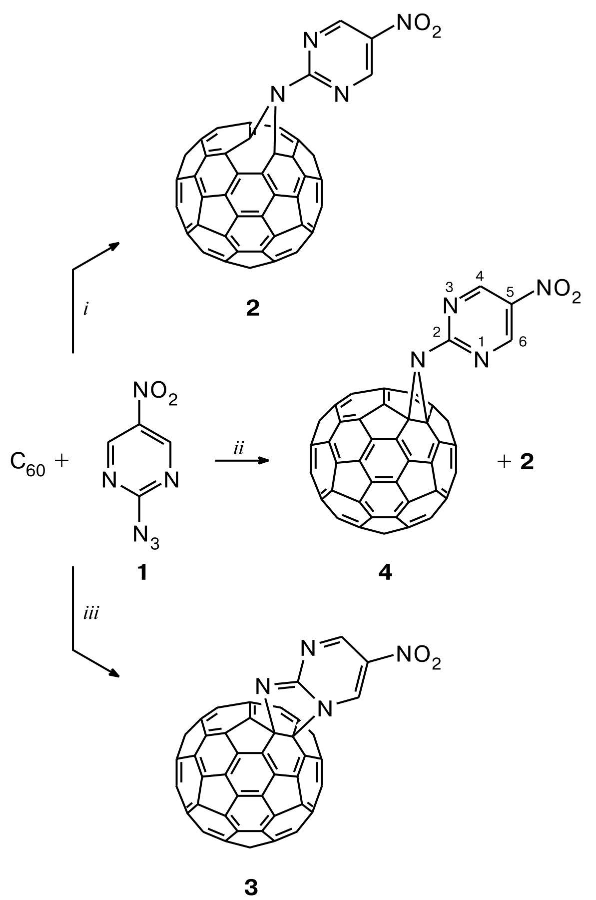
to be only the addition products of nitrenes to C_{60}. Later the thermal transformation of azahomofullerenes **IV** into fullereno[1,2-*b*]aziridines **II** was carried out[8] for the 2,6-bis(acylamino)pyrimidinyl-substituted adducts. However, this scheme of thermal transformations is not universal. For instance, we found[7] that isocyanurato-substituted fullereno[1,2-*c*]triazoline, under fairly mild conditions, thermally decomposes immediately to the corresponding fullereno[1,2-*b*]aziridines, omitting the step of fullereno[1,6-*b*]aziridine and azahomofullerene formation.

The study of the reaction products of fullerene C_{60} with 2-azido-5-nitropyrimidine (**1**) provided unusual data on the sequence of mutual transformations. We have previously shown[9] that at 180 °C this reaction affords (5-nitropyrimidin-2-yl)azahomofullerene (**2**), which did not transform into other products upon refluxing of its solution in *o*-dichlorobenzene (*o*-DCB) and decomposed to the starting fullerenes after 20 h. The temperature decrease to 100 °C resulted in the formation of an unexpected product, *viz*., 4-nitro-[60]fullereno[1´,2´:4,5]imidazo-[1,2-*b*]pyrimidine (**3**), which also decomposed to fullerene under the same conditions.[10] Both products of this reaction manifested unusual electrochemical properties. According to the cyclic voltammetry data, they were reduced more easily than the starting fullerene C_{60}. Therefore, it was of interest to obtain 1-(5-nitropyrimidin-2-yl)[60]fullereno[1,2-*b*]aziridine (**4**), which was expected in this type of reactions, to study its ability to accept electrons, and determine the sequence of product formation in this reaction. Based on the data on thermal transformations of compounds **2** and **3**, we decreased the temperature of the reaction of fullerene C_{60} with azide **1** from 180 °C to 160 °C (Scheme 2).

Scheme 2



Reagents and conditions: *o*-DCB, 4 h; *T* = 180 (*i*), 160 (*ii*), 100 °C (*iii*).

The separation of the components of the reaction mixture by column chromatography gave unreacted fullerene and already prepared earlier azahomofullerene **2** along with new compound **4** and trace amounts of bisadducts. The data of elemental analysis and MALDI mass spectra of compound **4** show that its formation was accompanied by the addition of one azide molecule to the fullerene cage followed by nitrogen molecule elimination. The ^{1}H NMR spectrum of compound **4** contains a singlet at δ 9.48, indicating that the hydrogen atoms of the pyrimidine ring are magnetically equivalent. Similar pattern was observed in the ^{1}H NMR spectrum of azahomofullerene **2** (singlet at δ 9.38),[9] while the spectrum of fullerenoimidazopyrimidine **3** exhibited two singlets at δ 9.38 and 9.54 corresponding to the hydrogen atoms at the carbon atoms of the pyrimidine ring.[10] The IR spectrum of compound **4**, as well as the IR spectrum of azahomofullerene **2**, contains absorption bands of both the fullerene fragment (absorption band at 526 cm^{-1} characteristic of the starting C_{60} and all types of organofullerenes) and bands of the nitropyrimidine fragment. The latter underwent shifts in the spectrum of compound **4** over their positions in the spectra of azahomofullerene **2** and starting azide **1** (data for compound **4** are given in Experimental; for compound **2** (see Ref. 9): 1575, 1332, 849 (NO_2), 1456, 645 (pyrimidine ring); for azide **1** (see Ref. 9): 1571, 1331, 873 (NO_2), 1417, 639 (pyrimidine ring)). Thus, according to the ^{1}H NMR and IR spectral data, the nitropyrimidine ring retains its structure in a molecule of compound **4**.

Important information on the structure of the fullerene sphere in monoorganofullerenes can be obtained from their UV spectra. The UV spectra of 5,6- and 6,6-organofullerenes are known[8] to differ substantially, and the spectra of the 6,6-adducts contain a narrow low-intensity band at 420 nm. The same band was observed in the UV spectrum of compound **4**, whereas this band was absent from the spectrum of azahomofullerene **2** (see Ref. 9).

The final conclusion on the structure of compound **4** is based on the heterocorrelation 2D NMR experiments.

The signals in the ^{13}C NMR spectrum of compound **4** were assigned on the basis of the 2D HSQC ($^1J_{\mathrm{H,C}}$) and 2D HMBC ($^{2,3}J_{\mathrm{H,C}}$) experiments.[12,13] In the 1D spectrum, the fullerene sphere was characterized by 14 signals at δ 145.2—139.8 and one signal at δ 82.57, which are ascribed to the sp^3-hybridized carbon atoms of the fullerene sphere and indicate the addition of the addend to the bond, which is common for the two six-membered rings of the carbon cage. The number and relative intensities of these resonances agree with the high C_{2v} symmetry of a molecule of compound **4**. The signal of the C(4) and C(6) carbon atoms at δ 154.56 corresponded to the nitropyrimidine fragment in the 1D ^{13}C NMR spectrum. The signals of the quaternary C(2) and C(5) carbon atoms were not manifested. Chemical shifts of these atoms were determined from the 2D HMBC spectrum, which contains cross-peaks between the H(4) and H(6) atoms (δ 9.48) and between the carbon atoms at δ 164.92 and 138.50 (Fig. 1). A more intense cross-peak is observed for the signal at δ 164.92. Taking into account that the spin-spin coupling constant ^3J is higher than $^{2,4}J$ (see Ref. 14), the higher intensity of the cross-peak indicates its correspondence to a correlation of the H(4)/H(6) atoms with the C(2) atom (δ 164.92), and the second, less intense cross-peak corresponds to a correlation of H(4)/H(6) and C(5) (δ 138.50).

Thus, the physicochemical data indicate that compound **4** is the expected 1-(5-nitropyrimidin-2-yl)[60]fullerene[1,2-*b*]aziridine, *viz*., the closed adduct of fullerene C_{60} and azide **1**.

As in the case of azahomofullerene **3**, thermal transformations of fullerenoaziridine **4** were studied by heating of its solution in *o*-DCB at the boiling point of the solvent (180 °C). According to the TLC data, compound **4** was not detected in the heated solution and no formation of compounds **2** and **3** was observed already after 2 h. The separation of the mixture by column chromatography gave only a powdered light brown product **5** (R_f = 0.17, toluene—MeCN (1 : 1) as eluent). However, the upper part of the column remained strongly colored, which indicated that high-polarity components of the mixture retained. A gradual increase in the fraction of MeCN in the eluent did not allow us to extract these products from the column. Compound **5** was studied by the MALDI, UV, and IR spectroscopic methods. Since the volatility of compound **5** is low, the peak of its molecular ion was not detected, and no peaks of other compounds were found in the spectrum. Note that the low volatility is characteristic of poly(organo)fullerenes. The UV spectrum of compound **5** exhibited no absorption bands at 400—800 nm, *i.e.*, the bands characteristic of compound **4** with $\lambda_{\max}$ 420 (narrow band) and 494 (broad low-intensity band) disappeared. High-intensity bands at 1083, 1639, and 1731 cm^{-1} appeared in the IR spectrum. Based on these data, we believe that the heating of fullerenoaziridine **4** resulted in the oxidation of the fullerene sphere of this compound due to trace amounts of oxygen to form products with C=O bonds, unlike azahomofullerene **2** and fullerenoimidazopyrimidine **3**. Despite this, we assume that fullerenoaziridine **4** is transformed during the reaction into azahomofullerene **2**, which is isolated from the reaction mixture obtained at 180 °C.

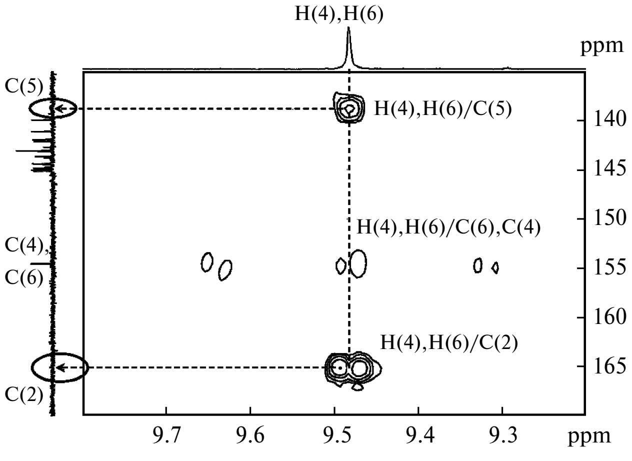


Fig. 1. Fragment of the 2D HMBC spectrum of compound **4** ($^3J_{\mathrm{CH}}$ = 8 Hz).

The structures and relative stability of 6,6-closed structures **II** and 5,6-open structures **IV** (R = Me, Ph, 5-nitropyrimidin-2-yl) (compounds **4** and **2**) were studied by the DFT/PBE/TZ2P density functional method using the PRIRODA program.[15,16] Structures **IV** have two nonequivalent inversion forms differing by orientation of the R substituent, which lies above the six-membered (**IVa**) or five-membered (**IVb**) ring of the fullerene sphere. For R = Me and Ph, structures **IVa** are approximately 1—2 kcal mol^{-1} more stable than structures **IVb**. At the same time, for nitropyrimidine-substituted compound **2**, the energies of inversion forms **IVa** and **IVb** are equivalent. In addition, it was found that, in the case of R = Me and Ph, 6,6-closed aziridine structures **II** are more stable than 5,6-open azahomofullerene structures **IV**. At the same time, the nitropyrimidinyl-substituted compounds manifest an opposite order of stability, *i.e.*, the azahomofullerene structure of compound **2** is by 2 kcal mol^{-1} more preferential than the fullerenoaziridine structure of compound **4** (Table 1).

Stabilization of the azahomofullerene structure of compound **2** (structures **IVa** and **IVb**) compared to the aziridine structure of compound **4** is explained by the direct polar conjugation of the nitropyrimidine fragment with the fullerene sphere. This is more pronounced for the azahomofullerene structure, which is indicated by a considerable shortening of the N—C bond in compound **2** (see Table 1).

We studied the electrochemical properties of fullereneaziridine **4** by cyclic voltammetry (CV). The electrochemi-

Table 1. Relative energies of the structures (ΔE/kcal mol^{-1}) and the N—C bond lengths (d/Å) in structures **II**, **IVa**, and **IVb** (R = Me, Ph, $C_4H_2N_3O_2$) calculated by the DFT/PBE/TZ2P method

R	**II**		**IVa**		**IVb**	
	ΔE	d	ΔE	d	ΔE	d
Me	0.00	1.4675	0.63	1.4655	2.58	1.4703
Ph	0.00	1.4235	0.71	1.4207	1.35	1.4207
$C_4H_2N_3O_2$	2.00	1.3895	0.04	1.3771	0.00	1.3780

cal data were compared with the CV data for fullerene C_{60}, starting azide **1**, and compounds **2** and **3** (Table 2). Under the studied conditions in the potential interval from −0.8 to −2.5 V, the voltammograms of both C_{60} and azide **1** exhibited[9] four reduction peaks. In the case of fullerene, all peaks are reversible, while azide **1** is reduced irreversibly with the first peak corresponding to the reduction of the nitro group and other peaks corresponding to both the subsequent reduction of the nitro group and pyrimidine ring (C=N bond opening followed by protonation[17]). The reduction of compounds **2** and **3** was more complicated, and each cyclic voltammogram exhibited already six reduction peaks corresponding to the reduction of both the fullerene sphere and nitropyrimidine fragment.[10] On the contrary, the CV curve of fullerenoaziridine **4** contained only four reduction peaks. For the potential reverse at the end of the first reduction wave, the first reduction peak is reversible, and the subsequent potential sweep is accompanied by reversibility loss of reduction of both the first and subsequent reduction peaks. A comparison of the reduction potentials of fullerene C_{60} and compounds **1—4** indicates that the first reduction peak of fullerenoaziridine **4** corresponds to the transfer of an electron to the fullerene sphere. As in the case of compounds **2** and **3**, this reduction proceeds more easily than the reduction of nonmodified fullerene C_{60}.

Table 2. Potentials (E_p^{red}) at the wave peaks in the cyclic voltammograms of C_{60} and compounds **1—4**[a]

Compound	$-E_p^{red}$/V					
	E_1	E_2	E_3	E_4	E_5	E_6
C_{60}	0.83[b]	1.24[b]	1.70[b]	2.16[b]	—	—
1	1.11	1.51	2.02	2.20	—	—
2	0.75[b]	1.11	1.22	1.68	1.88	2.18
3	0.73[b]	1.07	1.20	1.68	1.82	2.21
4	0.79[b]	1.15	1.75	2.23	—	—

[a] Conditions: *o*-DCB—MeCN (3 : 1) mixture at 25 °C; concentrations of solutions $2 \cdot 10^{-3}$ mol L^{-1} (C_{60}, **1**) and $1 \cdot 10^{-3}$ mol L^{-1} (**2—4**); supporting electrolyte 0.1 *M* Bu_4NBF_4; glassy-carbon (GC) cathode (S_{work} = 3.14 mm^2), reference electrode Ag/0.01 *M* $AgNO_3$ in MeCN, ν_{sweep} = 50 mV s^{-1}.

[b] Reversible wave.

Thus, the reaction of fullerene C_{60} with 2-azido-5-nitropyrimidine **1** afforded the product with the 6,6-closed structure of the fullerene sphere, namely, 1-(5-nitropyrimidin-2-yl)[60]fullereno[1,2-*b*]aziridine (**4**), at a lower temperature (160 °C) than that of the synthesis of azahomofullerene **2**. This suggests that 6,6-closed adduct **4** is transformed during the reaction into 5,6-open adduct **2**. As products **2** and **3**, which have been earlier obtained in this reaction, compound **4** is a stronger electron-acceptor than the starting fullerene C_{60}.

Experimental

IR spectra were recorded on a Bruker IFS-113V FTIR spectrometer in KBr pellets. 1D and 2D NMR spectra were obtained on a Bruker AVANCE-600 FTIR spectrometer with working frequencies of 600.00 (^{1}H) and 150.86 (^{13}C) MHz in $CDCl_3$ at 30 °C. UV spectra were recorded on a Specord UV-VIS instrument. Mass spectra were obtained on a MALDI TOF MS instrument (Dynamo). Elemental analysis was carried out on a CHN-analyzer. A stationary disk glassy-carbon electrode with a working surface of 3.14 mm^2 was used as the working electrode in CV studies. Voltammograms (CV curves) were recorded using a PI-50-1 potentiostat with a PR-8 programmer and an electrochemical cell switched-on *via* the three-electrode scheme. The CV curves were detected on a two-coordinate recorder with a linear potential sweep rate of 50 mV s^{-1}. The CV curves were obtained in an *o*-DCB : MeCN (3 : 1) mixture *vs.* Bu_4NBF_4 (0.1 *M*). An Ag/0.01 *M* $AgNO_3$ system in MeCN served as the reference electrode. A Pt wire was used as the auxiliary electrode. Measurements were carried out in a temperature-controlled (25 °C) cell in an argon atmosphere. The concentration in solutions of C_{60} and azide **1** was $2 \cdot 10^{-3}$ mol L^{-1}, and that in solutions of the adducts was $1 \cdot 10^{-3}$ mol L^{-1}. Anhydrous *o*-DCB and MeCN were prepared by distillation above P_2O_5. [60]Fullerene was synthesized at the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences (Nizhnii Novgorod, Russia). Azide **1** was synthesized according to a previously described procedure.[18]

Reaction of C_{60} with 2-azido-5-nitropyrimidine (1). A mixture of C_{60} (0.132 mmol) and azide **1** (0.164 mmol) in anhydrous degassed *o*-DCB (25 mL) was heated at 160 °C with stirring for 4 h. The solvent was removed *in vacuo*, and the residue was chromatographed on a column packed with silica gel. Using a mixture of toluene and petroleum ether, C_{60} (19 mg, 20%) and fractions containing mono- and polyadducts were isolated. The fraction containing monoadducts was chromatographed two times and gave compound **2** (12 mg, 11%) and 1-(5-nitropyrimidin-2-yl)[60]fullereno[1,2-*b*]aziridine (**4**) (14 mg, 11%). Compound 4. Found (%): C, 88, 82; H, 0.26; N, 5.96. $C_{64}H_2N_4O_2$. Calculated (%): C, 89.51; H, 0.23; N, 6.52. TLC data (Sorbfil, toluene—petroleum ether (5 : 3) system as eluent): R_f 0.82. Mass spectrum, *m/z*: 858. UV (CH_2Cl_2), λ_{max}/nm: 255, 324, 420 (narrow), 490, 664. IR (KBr), ν/cm^{-1}: 1573, 1341, 806 (NO_2), 2961, 2923, 2852, 1434, 669 (pyrimidine ring), 526 (fullerene fragment). ^{1}H NMR ($CDCl_3$), δ: 9.48 (s, 2 H, C(4)H, C(6)H). ^{13}C NMR, δ: 164.92 (C(2)), 154.56 (C(4), C(6)), 138.50 C(5); $C_{60}N$: 82.57 (2C), 144.73 (2C), 143.75 (2C), 142.70 (2C), 145.12 (4C), 145.05 (4C), 144.83 (4C), 144.44 (4C), 144.37 (4C), 143.66 (4C), 143.11 (4 C),142.12 (4C), 141.92 (4C), 141.11 (4C), 139.92 (4C), 143.08 (8C).

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