Synthesis of new carbazole-containing fullerenopyrrolidines

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The reactions of fullerene C_{60} and *N*-methylglycine with 3-formyl-9-isoamylcarbazole or 3,6-diformyl-9-isoamylcarbazole afforded new carbazole-containing fullerenopyrrolidines. Their structures were established by spectroscopic methods. Electrochemical reduction and oxidation of the resulting compounds were studied by cyclic voltammetry and ESR spectroscopy. The three-dimensional structures were determined by the quantum-chemical PM3 and DFT/PBE/TZ2P methods.

Key words: fullerene C_{60}, fullerenopyrrolidines, 3-formyl-9-isoamylcarbazole, 3,6-diformyl-9-isoamylcarbazole, HPLC, ^{1}H and ^{13}C NMR spectroscopy, UV spectroscopy, IR spectroscopy, MALDI-TOF mass spectrometry, cyclic voltammetry, ESR spectroscopy.

Carbazole and its derivatives are widely used in fullerene chemistry as electron-donating amines.[1,2] Doping of polyvinylcarbazole films with fullerene C_{60} affords photoconducting materials. Composite materials based on polyvinylcarbazole and fullerene hexaadducts exhibit unique optical and physical properties.[3—5] The synthesis of C_{60}-based donor-acceptor carbazole-containing diads exhibiting interesting optical and physical properties was described in the study.[6] The above-mentioned properties stimulate researchers to synthesize new fullerene-containing carbazole derivatives.

In the present study, we synthesized a new type of carbazole-containing fullerene derivatives and studied their electrochemical properties and three-dimensional structures by quantum-chemical methods.

Results and Discussion

Functionalization of fullerenes by cycloaddition of azomethine ylides to C_{60} (Prato reaction) is widely used in fullerene chemistry.[7,8] We studied the reactions of carbazole-containing aldehydes, *viz.*, 3-formyl-9-isoamylcarbazole (**1**) and 3,6-diformyl-9-isoamylcarbazole (**2**), with *N*-methylglycine and fullerene C_{60}.

Refluxing of a mixture of fullerene C_{60}, *N*-methylglycine, and carbazole **1** in chlorobenzene under dry argon for 3.5 h led to consumption of the major portion of fullerene to form the monoadduct and a mixture of bis-adducts. Column chromatography on SiO_2 afforded monofullerenopyrrolidine **3** (in a yield of 55.7% with respect to the fullerene consumed) and bis-fullerenopyrrolidine **4** (8% yield) (Scheme 1). Compound **3** partially precipitated from the eluent as brown-black crystals, which were identified as a monoaddition product by X-ray diffraction analysis.[9]*

The purity of compounds **3** and **4** was confirmed by HPLC data (Fig. 1).

The molecular ion mass of compound **3** determined by MALDI-TOF mass spectrometry** confirmed the composition of **3**. The mass spectrum shows a molecular ion peak at *m/z* 1012.98 (calculated for $C_{80}H_{24}N_2$: M = 1013.08). The UV spectrum of compound **3** has absorption bands at 258, 326, 432, and 704 nm characteristic of fullerene derivatives.[10—12] The IR spectrum of fullerenopyrrolidine **3** shows absorption bands at 526 and 1180 cm^{-1} belonging to stretching vibrations of the fullerene cage and a series of other absorption bands belonging to stretching vibrations of the carbazole fragment.

The structure of compound **3** was also confirmed by ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR spectrum of compound **3** shows signals for the carbon atoms of the fullerene cage and the attached fragment. The signals of the latter fragment are observed at δ 119—128 and 140.3 (aromatic C atoms of carbazole) and at δ 22.55 ($C\underline{Me}_2$), 26.33 ($\underline{C}Me_2$), 37.56 ($C\underline{C}H_2C$), and 41.39 ($N\underline{C}H_2C$) (C atoms of the isoamyl group). The signals for the C atoms of the pyrrolidine ring appear at δ 39.99 (NMe), 69.99 (NCH_2), and 84.05 (NCH), which are characteris-

* The results of X-ray diffraction study of this compound will be published elsewhere.

** Matrix-assisted laser desorption ionization time-of-flight mass spectrometry.

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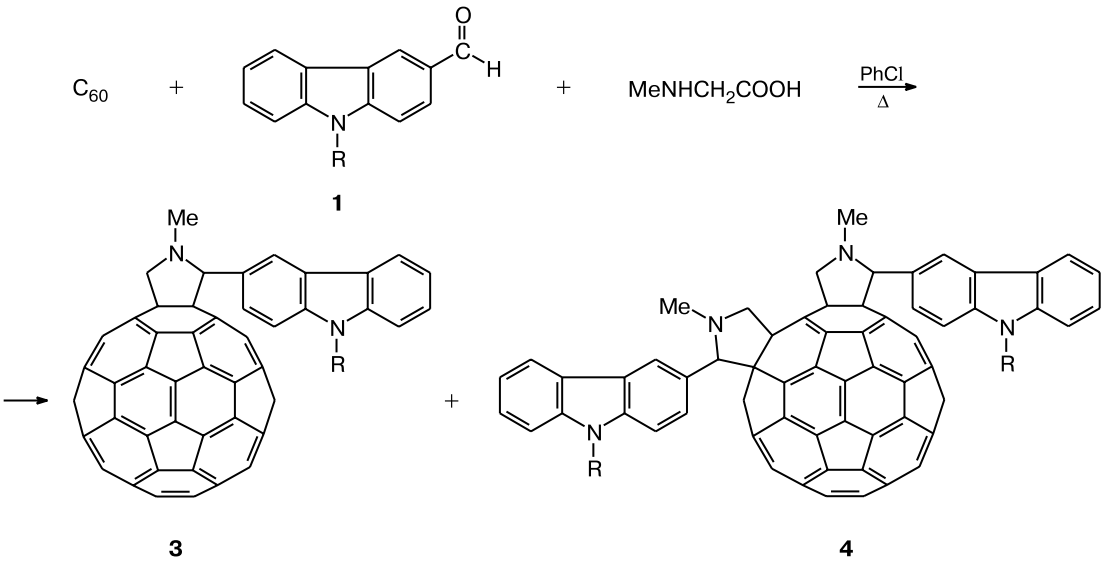
Scheme 1



tic of other fullerenopyrrolidines.[7—12] The signals for the sp^3-hybridized C atoms of the fullerene cage are observed at δ 68.82 and 77.78. The signals for virtually all sp^2-hybridized C atoms of the fullerene cage are present at δ 135.62—156.23. In our opinion, this is evidence that the asymmetric substituent in compound **3** has a strong effect on the electronic structure of the fullerene cage resulting in the nonequivalence of all sides of the latter.

The ^{1}H NMR spectra of compound **3** show signals for the protons of the NMe (δ 2.87), CH (δ 5.07), and CH_2 groups (δ 5.12) of the pyrrolidine fragment. The signals for the protons of the carbazole fragment are observed at δ 7.13—8.03 (H arom.), 4.35 (NCH_2), 1.76 (CH_2), 1.26 (CH), and 1.06 (Me) (protons of the isoamyl group).

The molecular weight of compound **4** determined by MALDI-TOF mass spectrometry is 1305.94 *m/z* (calculated for $C_{100}H_{48}N_4$: M = 1305.53) and corresponds to the bis-fullerenopyrrolidine structure. Earlier,[13] it has been demonstrated that the 400—800 nm region of UV spectra of regioisomeric methanofullerene bis-adducts can serve

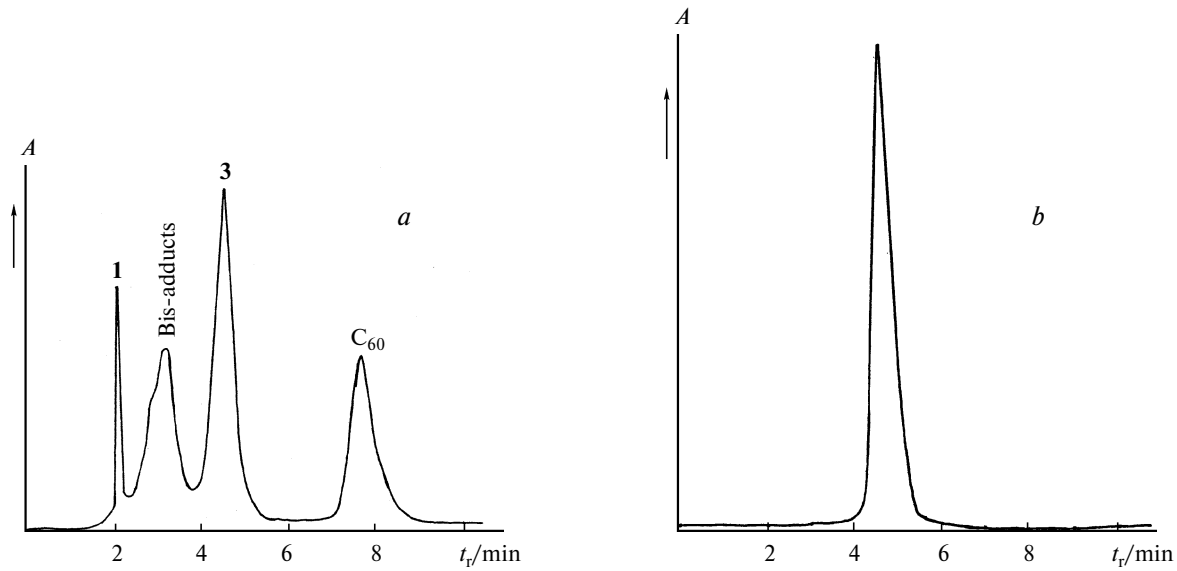


Fig. 1. HPLC data for the mixture prepared by the reaction of C_{60}, *N*-methylglycine, and carbazole **1** (*a*) and compound **3** (*b*). The chromatographic conditions: C_{18} reversed-phase column (250×4.6 mm, Partisil-5 ODS-3), toluene—MeCN (1 : 1, v/v) as the eluent, the elution rate was 1.5 mL min^{-1}, UV detection at λ = 328 nm.

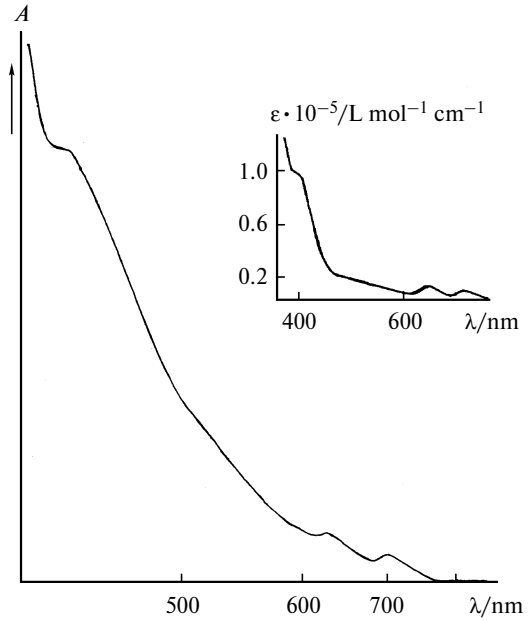


Fig. 2. UV spectrum of compound **4** (UV spectrum of bis-fullerenopyrrolidine with the *cis*-3 arrangement of the addends (see Ref. 15) is shown in the inset).

for recognition of the spatial arrangement of addends at the fullerene cage (the so-called fingerprint method). It appeared that this rule is valid for both bis-methanofullerenes and bis-fullerenopyrrolidines.[14,15] A comparative analysis of the UV spectrum of compound **4** and the spectra of other fullerenopyrrolidines published in the literature[15] (Fig. 2) demonstrated that the spectrum of **4** is indicative of the addition of the second addend at the *cis*-3 position. The results of quantum-chemical calculations are consistent with this assignment (see below).

In the ^{1}H NMR spectrum of compound **4**, the signals at δ 1.05—1.19 belong to the protons of the Me groups, the signals at δ 1.22—1.27 correspond to the protons of the CH groups, and the signal at δ 1.73 is assigned to the protons of the CH_2 groups of the isoamyl fragments. The signals at δ 7.12—8.47 belong to the aromatic protons of the carbazole fragments. The protons of the NMe groups of the pyrrolidine rings are observed at δ 2.88 and 2.90, and the signals of the CH and CH_2 groups appear at δ 4.91 and 5.30, respectively.

The ^{13}C NMR spectrum of compound **4** shows signals at δ 108.27—128.78 belonging to the aromatic C atoms of the carbazole fragments and signals at δ 22.55, 26.33, 37.59, and 41.29 corresponding to the C atoms of the isoamyl group. The signals at δ 37.59 and 39.97 are assigned to the NMe groups of the pyrrolidine rings, the double signals at δ 68.41 and 72.45 belong to the C_{sp^3} atoms of the fullerene cage, and 28 signals of different intensities at δ 135.57—155.61 correspond to 56 sp^2-hybridized C atoms of the fullerene cage.

3,6-Diformyl-9-isoamylcarbazole (**2**) reacts with fullerene C_{60} under analogous conditions. The presence of two reactive aldehyde groups in the starting compound **2** provides a possibility to prepare three types of fullerene derivatives, *viz.*, monofullerenopyrrolidine **5** containing the free aldehyde group, the bis-adduct of fullerene with two pyrrolidine fragments linked by a bridge (**6**), and the dumbbell-shaped bis-fullerene adduct (**7**) (Scheme 2). A large number of bis-adducts containing the free aldehyde group can also be produced. Refluxing of the starting compounds in chlorobenzene for 5 h afforded monofullerenopyrrolidine **5** and a mixture of bis-adducts. Column chromatography on SiO_2 gave compound **5** (14% yield) and bis-adduct **6** (2.8% yield).

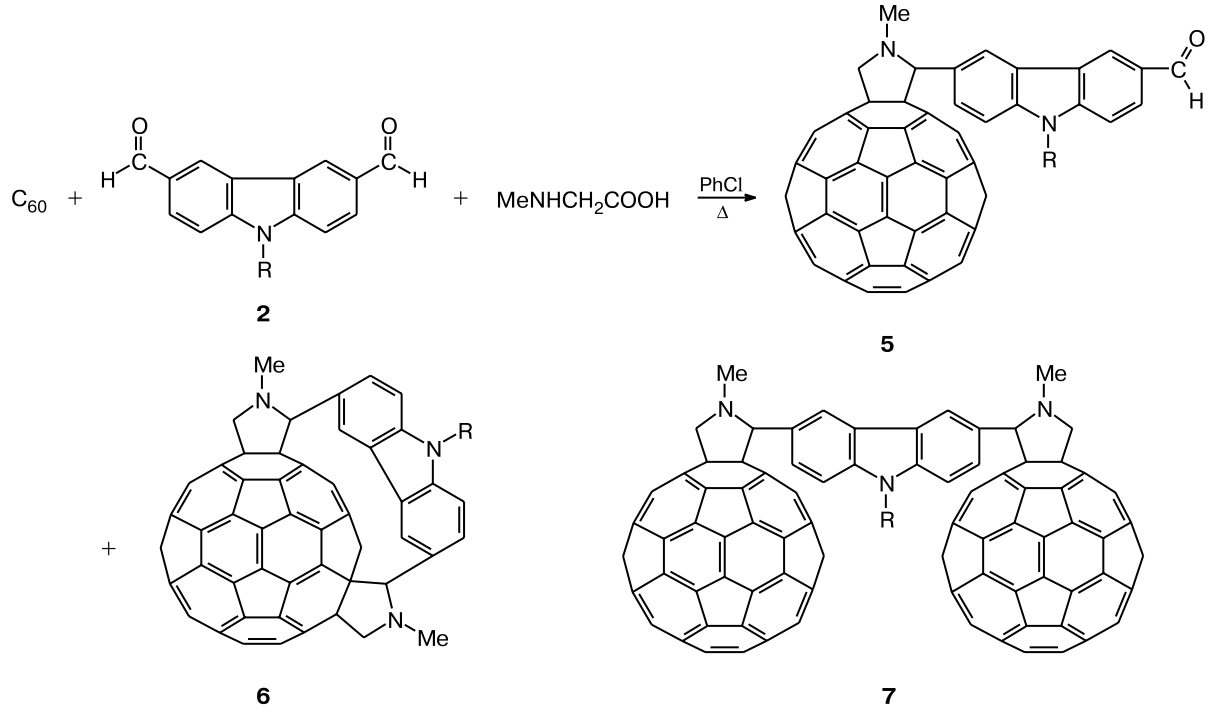
The reaction with the use of the starting components in the same ratio, which was carried out until fullerene C_{60} was virtually completely consumed, afforded monoadduct **5** in lower yield (1.8%) and compound **6** in higher yield (19.8%); other bis-adducts were also obtained in higher yields (total yield was 80%). The structure of compound **5** was established by spectroscopic methods. The mass spectrum of compound **5** shows a molecular ion peak at *m/z* 1041.14 (calculated for $C_{81}H_{24}N_2O$: M = 1041.09). Other spectroscopic characteristics are virtually analogous to those of monoadduct **3**, except for the signals assigned to the aldehyde group in compound **5**. These are the characteristic band of the C=O group in the IR spectrum (1687 cm^{-1}), the signal for the aldehyde proton in the ^{1}H NMR spectrum (δ 10.07), and the signal for the C atom of the C(O)H group in the ^{13}C NMR spectrum (δ 191.2).

Very low solubility of compound **6** in all available solvents did not allow us to record high-quality ^{1}H and ^{13}C NMR spectra. The mass spectrum of compound **6** shows a peak at *m/z* 1068.91 (calculated for $C_{83}H_{30}N_3$: M = 1068.17), which corresponds to the proposed structure of the bis-adduct closed at the fullerene cage. The IR spectrum of compound **6** shows absorption bands at 526 and 1179 cm^{-1} belonging to stretching vibrations of the fullerene cage. It should be noted that the absorption band of the aldehyde group at 1687 cm^{-1} is absent in the IR spectrum of compound **6**, which also confirms the proposed structure.

We did not observe the formation of dumbbell-shaped compound **7** in this synthesis.

The electrochemical properties of fullerene derivatives are widely used, because they allow one to reveal new electron-donor and electron-acceptor compounds suitable for the design of modern materials and devices for nanoengineering. We studied electrochemical reductions of newly synthesized fullerenopyrrolidines **3—5** by cyclic voltammetry (CV) at a glassy-carbon electrode in a *o*-dichlorobenzene (DCB)—DMF (3 : 1, v/v)/0.1 *M* Bu_4NBF_4 solvent mixture.

Scheme 2



R = $CH_2CH_2CHMe_2$

The characteristic feature of the compounds under consideration is that they are adsorbed on a glassy-carbon electrode, resulting in the appearance of adsorption peaks in cyclic voltammograms. All these peaks are irreversible and are recorded at cathodic potentials lower than the potentials of the first main reduction peaks (Table 1). These peaks appear upon storage of the electrodes in solution, whereas they were absent in cyclic voltammograms, which were rapidly recorded immediately after the electrode was dipped in the solution.

Otherwise electrochemical reduction of fullerenopyrrolidines **3—5** occurs analogously to that of other representatives of this class studied earlier.[11,16] In the medium under study, the cyclic voltammograms show three reduction peaks, and three conjugated oxidation peaks are observed on the reverse scan of the cyclic voltammograms (see Table 1). The heights of the reduction peaks correspond to the one-electron level. For compounds **3** and **5**, the difference between the reduction peak potentials and the corresponding oxidation peak potentials is virtually equal to the theoretical value for reversible one-electron transfer[17] $\Delta E_p = E^m_{p,ox} - E^m_{p,red} \approx 60$ mV ($m = 1—3$). Consequently, in the available potential range,

Scheme 3

$$A + e \overset{E^1_{p,red}}{\rightleftharpoons} A^{\bullet -} + e \overset{E^2_{p,red}}{\rightleftharpoons} AA^{2-} + e \overset{E^3_{p,red}}{\rightleftharpoons} AA^{3\bullet -}$$

Table 1. Cyclic voltammetric data (reduction peak potentials ($E_{p,red}$), oxidation peak potentials ($E_{p,ox}$), and adsorption peak potentials ($E_{p,ads}$)) for electrochemical reduction of fullerenopyrrolidines **3—5** and fullerene C_{60} in the DCB—DMF (3 : 1, v/v)/0.1 *M* Bu_4NBF_4 solution system at a glassy-carbon electrode[a]

Compound	$E_{p,ads}$	$E^1_{p,red}$	$E^1_{p,ox}$	$E^2_{p,red}$	$E^2_{p,ox}$	$E^3_{p,red}$	$E^3_{p,ox}$
	V						
C_{60}[b]	—	−0.96	−0.90	−1.40	−1.34	−1.90	−1.84
3	−0.86	−1.07	−1.00	−1.50	−1.43	−2.09	−2.01
4	−0.79	−1.23	−1.00	−1.69	−1.59	−2.41[c]	−2.31[c]
5	−0.94	−1.07	−1.12	−1.50	−1.43	−2.08	−2.01

[a] [**3**] = [**5**] = $5 \cdot 10^{-4}$ mol L^{-1}, [**4**] = $7 \cdot 10^{-4}$ mol L^{-1}, υ = 20 mV s^{-1}, T = 22 °C; the potentials were measured relative to E_0 of the Fc/Fc^+ system using the $Ag/AgNO_3$ reference electrode in MeCN.

[b] The fourth reversible peak with $E_{p,red} = -2.40$ V was recorded.

[c] At υ = 20 mV s^{-1}, the peak is masked by the background discharge current and, consequently, is not recorded; hence, the value measured at υ = 100 mV s^{-1} is given.

fullerenopyrrolidines **3** and **5** reversibly and stepwise accept three electrons per molecule to form finally the radical trianions (Scheme 3).

For bis-adduct **4**, the difference ΔE_p is slightly larger (see Table 1). In the second reduction step, the larger

difference ΔE_p has been observed earlier[18,19] for phosphorylated methanofullerenes, which was associated with elimination of the methyl group. The *N*-methylated pyrrolidine ring is stable in reduction of fullerenopyrrolidines, and there is no reason to expect that this ring will be opened with elimination of the addend or migration of the latter over the fullerene cage in [60]fullerenobis(pyrrolidine). We hypothesized that reduction of compound **4**, like that of fullerenopyrrolidines **3** and **5**, involves reversible stepwise transfer of three electrons to the molecule, and an overestimation of ΔE_p compared to the theoretical value is due to a different reason. Since the pyrrolidine substituent is asymmetric and the fullerene molecule has four *cis*-3 positions, the synthesis of the *cis*-3 isomer can afford ten diastereomers. Apparently, the small difference in their reduction potentials is responsible for a slight increase in the slope of the log*i*—*E* plot compared to the Nernst potential and, as a consequence, to an increase in ΔE_p compared to the theoretical value for reversible one-electron transfer.

Fullerenopyrrolidines **3—5** are more difficult to reduce than [60]fullerene. The potentials of the first peak for monoadducts **3** and **5** are shifted to more cathodic potentials by 110 mV, and the potential of the first peak for bis-adduct **4** is shifted by 270 mV. The difference in the potentials of the second electron transfer is approximately the same. By contrast, the difference in the potentials of the third reduction peaks is much larger, which is particularly pronounced for the bis-adduct ($\Delta E^3_{p,red} = E^3_{p,red}(C_{60}) - E^3_{p,red}$(**4**) = 0.51 V). For this compound, the third peak appears already at the potentials of the fourth peak of C_{60}. In other words, the presence of two pyrrolidine rings in the *cis*-3 position of the fullerene cage in the step of third electron transfer is equivalent to the insertion of an additional electron into the fullerene molecule. The above-mentioned results suggest that disruption of the π-conjugated system of C_{60} upon introduction of the pyrrolidine ring reduces the electron affinity (to a larger extent for the bis-adducts), and this effect is most pronounced in the step of third electron transfer.

The ESR spectra, which were measured upon electroreduction of fullerenopyrrolidines **3** and **5** in a special electrochemical cell directly in a resonator used in an ESR spectrometer (Fig. 3), are identical in the characteristics to the spectra of fullerenopyrrolidines studied earlier.[11,16] At potentials of the first peak, the radical anions are generated (g = 2.0000, ΔH = 0.08 mT). At potentials of the third peak, the radical trianions are produced (g = 2.0015, ΔH = 0.15 mT). As has been hypothesized earlier,[11,16] the dianionic states are diamagnetic. The spectrum, which was measured after electrolysis of compound **4** at the potential of the first peak, is complicated and partially unresolved, and it can be described as a superposition of the spectra of at least two types of particles (see Fig. 3). The spectra of these particles differ in the linewidth and g factor. Each spectrum shows splitting of two N nuclei. The spectrum remains unchanged in a wide temperature range (from 243 to 343 K). It is impossible to perform precise analysis of the spectra due to the presence of satellites from the ^{13}C nuclei of the fullerene cage at the wings of the spectra. The ESR spectrum of the radical trianion of compound **4** is also a superposition of at least two lines with the g factors of 2.0015 and 2.0018 without hyperfine structure with the N nuclei. For compounds **3—5**, the reverse scan from the potential of the third reduction peak to the first peak again leads to the spectrum of the radical anion, which is indicative of reversibility of all three steps of electron transfer.

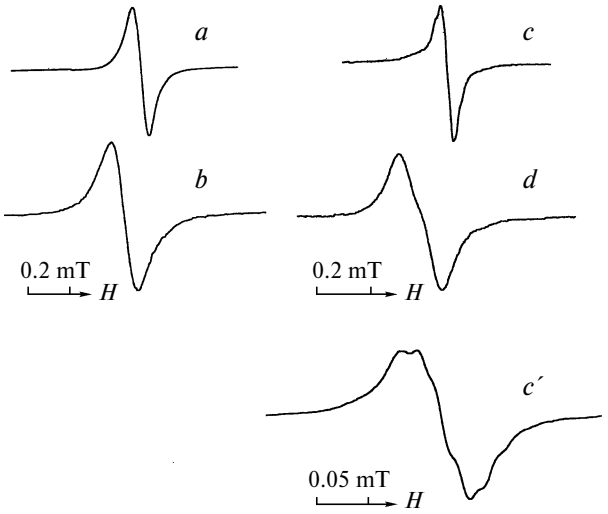


Fig. 3. ESR spectra of the radical anions (*a*, *c*, *c*′) and radical trianions (*b*, *d*) of fullerenopyrrolidines **3**, **5** (*a*, *b*), and **4** (*c*, *c*′, *d*) generated at the Pt electrode in a DCB—DMF (3 : 1, v/v)/Bu_4NBF_4 (0.1 mol L^{-1}) mixture at C = $5 \cdot 10^{-4}$ mol L^{-1} and T = 263 K.

The results of our investigation of the electronic and spatial structures of carbazole derivatives of fullerene **3** and **4** (*cis*-3) by the quantum-chemical PM3 and DFT/PBE/TZ2P methods are consistent with the results of electrochemical study. For comparison, we studied the *cis*-2 isomer. Calculations by the PM3 and DFT/PBE/TZ2P methods demonstrated that the *cis*-3 isomer is more stable than the *cis*-2 isomer (by 1.0 and 6.7 kcal mol^{-1}, respectively). The heats of formation of fullerene C_{60} and compounds **3** and **4** (*cis*-3) change nonadditively, and their differences for compounds **3** and C_{60} and for compounds **4** (*cis*-3) and **3** are 29.07 and 31.85 kcal mol^{-1}, respectively (PM3 method). The electron affinities (EA) of the compounds under study also change nonadditively. The experimental data on $E^1_{p,red}$ show that the introduction of one pyrrolidinocarbazole group leads to a decrease in the electron affinity of the

Table 2. Heats of formation (H), the total energies of the molecules (E) and the radical anions ($E(B^-)$), and the electron affinities (EA) of mono- and bis-fullerenopyrrolidines **3** and **4**

Compound	H^a /kcal mol^{-1}	$-E^b$	$-E(B^-)^b$	EA^a	EA^b
		a.u.		eV	
C_{60}	811.75	2284.29541	2284.40217	2.65	2.65
3	840.82	3012.48932	3012.58936	2.51	2.48
4 (*cis*-3)	872.67	3740.66481	3740.75498	2.28	2.21
4 (*cis*-2)	873.75	3740.65412	3740.74664	2.36	2.27

[a] Calculations by the PM3 method.
[b] Calculations by the DFT/PBE/TZ2P method.

solvated molecule by 0.11 eV, and the introduction of the second group decreases the affinity by 0.16 eV (*i.e.*, the decrease is larger by a factor of 1.5). The electron affinities in the gas phase estimated by the PM3 and DFT/PBE/TZ2P methods are given in Table 2. The electron affinities were theoretically estimated from the energy differences of the frontier orbitals of LUMO (ε_1*) of the compounds under study (B) and fullerene C_{60} calculated by the PM3 method

$$EA = EA(C_{60}) - \varepsilon^*_1(B) + \varepsilon^*_1(C_{60})$$

and from the total energy differences of the anions ($E(B^-)$) and the starting molecules ($E(B)$) calculated by the DFT/PBE/TZ2P method,

$$EA = E(B) - E(B^-).$$

The electron affinities for C_{60}, **3**, **4** (*cis*-3), and **4** (*cis*-2) are 2.90, 2.72, 2.45, and 2.51 eV, respectively. In all cases, EAs in Table 2 are normalized to the experimental EA for fullerene C_{60} (2.65 eV) as the reference molecule.

Estimations of EAs of the compounds under study by both methods provide evidence that this characteristic in the gas phase also changes nonadditively. As in solution, the decrease in EA of the adduct upon introduction of the second pyrrolidinocarbazole group is 1.5 times larger than that observed upon introduction of the first group. The absolute values of the gas-phase shifts of EAs are larger than the corresponding changes in EA for the solvated molecules. This is evidence that a solvent slightly eliminates the influence of the addends on the electron transfer.[20] It should be emphasized that the nonadditivity of the influence of the pyrrolidinocarbazole groups is observed only for the *cis*-3 isomer and is absent for the *cis*-2 isomer, for which the effect of the first addend is similar to that of the second addend. Earlier, we have noted[21] that the atoms of the *cis*-3 bond in fullerenopyrrolidines are most pyramidalized and this may be one of the reasons why the influence of the addend in this position is more efficient.

To summarize, we synthesized for the first time mono- and bis-carbazolylfullerenopyrrolidines and studied their electrochemical properties and structures.

Experimental

The HPLC analysis was carried out on a Gilson chromatograph equipped with an UV detector (C18 reversed-phase column (Partisil-5 ODS-3); toluene—MeCN (1 : 1, v/v) as the eluent). The organic solvents were dried and distilled. Fullerene C_{60} of 99.9% purity (produced at the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences, Nizhnii Novgorod) was used. The starting aldehydes **1** and **2** were prepared according to known procedures.[22] All chemical operations were carried out under dry argon.

The UV spectra were recorded on a Specord M-40 spectrophotometer in CH_2Cl_2. The IR spectra were measured on a Bruker-Vector 22 Fourier-transform spectrometer (KBr pellets). The ^1H and ^{13}C NMR spectra were recorded on Bruker WM-250 (250 MHz for ^1H) and Bruker MSL 400 (100.57 MHz for ^{13}C and 400.00 MHz for ^1H) spectrometers in $CDCl_3$ and CS_2 with Me_4Si as the standard. The mass spectra were obtained on a MALDI-TOF MS instrument (DynamoThermo-BioANALYSIS, Germany) using trihydroxyanthracene as the matrix.

Cyclic voltammograms were recorded on a PI-50-1 potentiostat equipped with an H 307/2 X-Y recorder. A glassy-carbon disk (d = 2 mm) electrode pressed into Fluoroplast served as a working electrode. Before each measurement, the electrodes were subjected to mechanical polishing. The potentials were measured relative to the standard potential of the ferrocene—ferrocenium ion redox system (Fc/Fc^+) using an $Ag/AgNO_3$ silver reference electrode (0.01 mol L^{-1}) in MeCN. Dissolved oxygen was removed by bubbling nitrogen through the solution at 295 K. Quantum-chemical calculations were carried out with the use of the PRIRODA [23,24] (DFT) and GAMESS [25] (PM3) program packages. The density functional theory (DFT) with the PBE exchange-correlation potential was employed.[24] The calculations were carried out with the use of the triple-zeta basis set and two polarization functions (TZ2P).

***N*-Methyl-1-(9-isoamylcarbazol-3-yl)[60]fullereno[1,2-*c*]pyrrolidine (3) and *cis*-3-1,1′-bis(9-isoamylcarbazol-3-yl-*N*,*N*′-dimethyl)[60]fullereno[1,2-*c*:1′,2′-*c*′]dipyrrolidine (4).** 3-Formyl-9-isoamylcarbazole (**1**) (0.191 g, 0.72 mmol) in chlorobenzene (15 mL) and *N*-methylglycine (0.160 g, 1.8 mmol) were added to a solution of fullerene C_{60} (0.432 g, 0.6 mmol) in chlorobenzene (200 mL). The reaction mixture was refluxed under dry argon for 3.5 h, the composition being monitored by HPLC. After 3.5 h, the major portion of fullerene C_{60} was involved in the reaction. The reaction mixture was filtered, and then the filtrate was washed with distilled water (2×35 mL) and concentrated to ~50 mL. Column chromatography on SiO_2 (hexane—toluene, 1 : 1, as an eluent) afforded unconsumed fullerene C_{60} (100.6 mg), compound **3** (260.0 mg, 55.7% yield), and bis-adduct **4** (26.5 mg, 8% yield). Compound **3**. MALDI-TOF MS, found: m/z 1012.98 $[M]^+$. $C_{80}H_{24}N_2$. Calculated: M = 1013.08. UV (CH_2Cl_2), λ_{max}/nm: 258, 326, 432, 704. IR, ν/cm^{-1}: 526, 571, 598, 621, 726, 769, 814, 1034, 1180, 1246, 1332, 1463, 1489, 1599, 2852, 2922. ^1H NMR ($CDCl_3$), δ: 1.06 (d, 6 H,

J = 6.4 Hz); 1.26 (d, 1 H, J = 6.4 Hz); 1.76 (dd, 2 H, J = 6.3 Hz); 2.87 (s, 3 H); 4.35 (m, 2 H); 5.07 (s, 1 H); 5.12 (d, 2 H, J = 6.8 Hz); 7.13—8.03 (m, 7 H, H arom.). ^{13}C NMR (CS_2 + $CDCl_3$), δ: 22.55, 26.33, 37.56, 39.99, 41.39, 68.78, 68.82, 69.99, 64.31, 77.78, 84.05, 108.24, 108.42, 119.09, 120.50, 125.78, 126.62, 126.72, 126.98, 128.08, 128.83, 134.26, 135.62, 135.67, 136.54, 136.61, 139.42, 139.97, 140.03, 140.19, 140.30, 141.33, 141.36, 141.53, 141.63, 141.80, 141.81, 141.88, 141.93, 141.97, 141.99, 142.01, 142.14, 142.15, 142.34, 142.38, 142.39, 142.51, 142.83, 142.97, 144.23, 144.25, 144.45, 144.53, 144.96, 145.04, 145.08, 145.12, 145.22, 145.34, 145.39, 145.42, 145.63, 145.74, 145.91, 145.94, 145.97, 146.04, 146.15, 146.25, 146.39, 146.75, 147.08, 147.12, 153.62, 153.72, 154.03, 156.23. Compound **4**. MALDI-TOF MS, found: m/z 1305.94 $[M]^+$. $C_{100}H_{48}N_4$. Calculated: M = 1305.53. UV (CH_2Cl_2), λ_{max}/nm: 417, 461, 638, 699. IR, ν/cm^{-1}: 524, 562, 601, 627, 728, 769, 800, 1024, 1151, 1187, 1210, 1247, 1330, 1466, 1489, 1599, 2775, 2950. ^{1}H NMR ($CDCl_3$), δ: 1.05 and 1.19 (both d, 6 H each, J = 6.4 Hz); 1.22—1.27 (m, 2 H); 1.73 (t, 4 H); 2.88 and 2.90 (both s, 3 H each, Me); 4.25 (m, 4 H); 4.91 (s, 2 H); 5.30 (d, 4 H, J = 6.8 Hz); 7.12—8.47 (m, 14 H, H arom.). ^{13}C NMR (CS_2 + $CDCl_3$), δ: 22.55, 26.33, 37.59, 39.97, 41.29, 68.41, 68.61, 70.04, 72.45, 83.70, 84.03, 84.10, 108.27, 119.09, 120.36, 125.17, 125.63, 128.78, 135.57, 135.66, 136.31, 136.77, 136.81, 138.18, 138.63, 139.03, 139.33, 139.47, 139.54, 139.69, 139.76, 139.82, 139.89, 139.98, 140.07, 140.10, 140.14, 140.25, 140.29, 140.32, 140.82, 141.65, 142.18, 143.14, 144.56, 144.69, 144.91, 145.01, 155.61.

***N*-Methyl-1-(6-formyl-9-isoamylcarbazol-3-yl)[60]fullereno[1,2-*c*]pyrrolidine (5) and *trans*-3-1,1′-(9-isoamylcarbazole-3,6-diyl)-*N*,*N*′-dimethyl[60]fullereno[1,2-*c*:1′,2′-*c*′]dipyrrolidine (6).** A solution of 3,6-diformyl-9-isoamylcarbazole (**2**) (0.105 g, 0.36 mmol) in chlorobenzene (10 mL) and a suspension of *N*-methylglycine (0.080 g, 0.90 mmol) in chlorobenzene (10 mL) were added with boiling to a solution of fullerene C_{60} (0.216 g, 0.30 mmol) in chlorobenzene (200 mL) under dry argon. The reaction mixture was refluxed for 5 h, after which the major portion of fullerene C_{60} (HPLC data) was consumed. The reaction mixture was filtered, washed with distilled water (2×35 mL), and concentrated to ~15 mL. Column chromatography on SiO_2 afforded unconsumed fullerene C_{60} (0.021 g; hexane—toluene, 1 : 1), monoadduct **5** (0.039 g, ~14 % yield; toluene—MeCN, 3 : 1), and bis-adduct **6** (0.008 g, 2.8% yield; DCB). Compound **5**. MALDI-TOF MS, found: m/z 1041.14 $[M]^+$. $C_{81}H_{24}N_2O$. Calculated: M = 1041.09. UV (CH_2Cl_2), λ_{max}/nm: 326, 431, 704. IR, ν/cm^{-1}: 526, 575, 598, 623, 662, 742, 768, 802, 883, 1028, 1180, 1212, 1331, 1463, 1484, 1596, 1687 (C=O), 2777, 2950. ^{1}H NMR ($CDCl_3$), δ: 1.07 (d, 6 H, J = 6.3 Hz); 1.79 (t, 2 H); 2.88 (s, 3 H); 4.33 (t, 2 H); 5.04 and 5.08 (both m, 1 H each); 5.12 (d, 2 H, J = 6.8 Hz); 7.14—8.59 (m, H arom.); 10.07 (1 H). ^{13}C NMR (CS_2 + $CDCl_3$), δ: 22.48, 26.38, 37.57, 39.96, 41.84, 68.84, 70.06, 83.87, 108.73, 119.11, 123.02, 123.98, 125.21, 127.00, 128.15, 128.86, 129.05, 135.62, 136.72, 136.76, 139.88, 139.97, 140.09, 140.14, 140.78, 140.84, 140.99, 141.07, 141.33, 141.40, 141.48, 141.57, 141.60, 141.67, 141.79, 141.93, 142.01, 142.15, 142.18, 142.37, 142.42, 142.46, 142.58, 142.89, 143.36, 143.70, 143.86, 144.21, 144.44, 144.56, 144.60, 144.71, 144.78, 144.97, 145.02, 145.09, 145.18, 145.29, 145.35, 145.39, 145.79, 145.97, 146.04, 146.08, 146.53, 147.11, 147.15, 153.40, 153.61, 154.00, 155.97, 191.25. Compound **6**. MALDI-TOF MS, found: m/z 1068.91. $C_{83}H_{30}N_3$. Calculated: M = 1068.17. UV (CH_2Cl_2), λ_{max}/nm: 419, 459, 490. IR, ν/cm^{-1}: 526, 572, 596, 767, 881, 1024, 1149, 1179, 1211, 1276, 1330, 1423, 1459, 1477, 1598, 2776, 2945. ^{1}H NMR (CS_2 + $CDCl_3$), δ: 1.09 (d, 6 H, J = 6.4 Hz); 1.27 (s, 1 H); 1.79 (d, 2 H, J = 6.3 Hz); 2.91 (s, 6 H); 4.96 (s, 2 H); 5.29 (d, 4 H, J = 6.8 Hz); 7.18—8.63 (m, 6 H).

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