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Reaction of fullerene C_{60} with 2-azido-4,6-diphenylpyrimidine

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The first representative of the pyrimidine-substituted [60]fullereno[1,2-*b*]aziridines was synthesized by the reaction of fullerene C_{60} with 2-azido-4,6-diphenylpyrimidine. 2-(Azahomo[60]fullereno)-4,6-diphenylpyrimidine was found to be formed as a by-product. The electrochemical properties of the adducts were studied.

Key words: [60]fullerene, 2-azidopyrimidines, [60]fullereno[1,2-*b*]aziridine, azahomo[60]fullerene, electrochemistry.

Researchers are interested in reactions of fullerenes with 2-azidopyrimidines for several reasons.[1] First, these reactions make it possible to fix pharmacophobic pyrimidine fragments on the fullerene framework. Second, they afford adducts with different structures of the fullerene sphere and exocyclic organic fragment. Finally, covalent bonding in one molecule of the fullerene sphere and electron-withdrawing pyrimidine fragment increases the electron affinity (EA) of the sphere compared to the EA of non-modified fullerene C_{60}. For example, the reactions of C_{60} with 2-azidopyrimidine and 2-azido-5-nitropyrimidine afforded nitropyrimidine-substituted azahomofullerene and previously unknown [60]fullereno[1´,2´:4,5]imidazo[1,2-*b*]pyrimidines.[1] According to the data of cyclic voltammetry, all these adducts exhibit the stronger electron-acceptor properties than non-modified fullerene. However, no formation of [60]fullereno[1,2-*b*]aziridines, which are traditional for the reactions of fullerenes with organic azides,[2] was found in these reactions. The adduct of this structure, along with the formation of a new representative of pyrimidine-substituted azahomofullerenes, was obtained in the reaction of C_{60} with 2-azidopyrimidine with two phenyl substituents in positions 4 and 6 of the ring. This work is devoted to the study of this reaction, isolation of the adducts, and establishment of their structures and electron-withdrawing capability.

As known, azidopyrimidines can exist in solutions as two tautomers: azidic and tetrazolic.[3] The tetrazole—azide equilibrium depends on the structure and position of substituents in the pyrimidine cycle and the temperature and polarity of the solvent. According to the IR and ^{13}C, ^{1}H NMR spectra, 2-azido-4,6-diphenylpyrimidine (**1**) in the solid state and in solution exists only as the azidic tautomer. The IR spectrum of the solid sample of this compound in the KBr pellet contains three intense bands at 2153, 2125, and 2109 cm^{-1} characteristic of the N_3 azido group. They are retained in the IR spectrum of compound **1** in chloroform. The ^{13}C and ^{1}H NMR spectra of compound **1** exhibit signals of only one isomer.

The reactions of C_{60} with azide **1** were carried out in *o*-dichlorobenzene (*o*-DCB). The reactants in a ratio of 1 : 1 were first stirred at 100 °C. According to the TLC data, even after 40 h of heating, unreacted azide **1** remained in the reaction mixture. The separation of the components of the reaction mixture by column chromatography using toluene as the eluent gave fractions containing unreacted fullerene (70% of the starting amount of fullerene) and several fractions of the adduct. The adducts were not separated because of a small amount of the last fractions.

The temperature of the reaction of C_{60} with azide **1** was increased to 180 °C. According to the TLC data, compound **1** has completely reacted for 4 h of heating.

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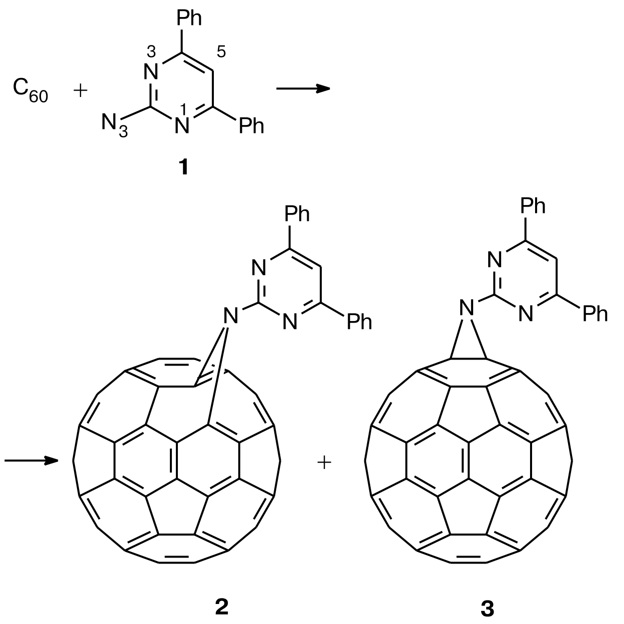

Reaction conditions: 180 °C, *o*-DCB, 4 h.

Column chromatography on silica gel using a toluene—petroleum ether (4 : 1) mixture as the eluent resulted in the separation of unreacted fullerene (15% of the starting amount of fullerene), a fraction containing monoadducts **2** and **3**, and several fractions of mixtures of polyadduct isomers. Cycloadducts **2** and **3** were isolated in the individual state, as followed from the TLC data, by the repeated column chromatography of the second fraction. The resulting yield of each adduct was 6 and 12%, respectively, of the starting amount of fullerene. The compositions of adducts **2** and **3** were established by elemental analysis. According to the results of this method, adducts **2** and **3** are monoadducts, *i.e.*, in each case, one azide molecule added to the fullerene framework accompanied by the elimination of the nitrogen molecule. The IR spectra of adducts **2** and **3** did not contain bands at 2100—2200 cm^{-1} corresponding to the azido group but contained intense bands at 526 cm^{-1} characteristic of all types of monoorgano[60]fullerenes. The pyrimidine and phenyl fragments of molecules of adducts **2** and **3** in the IR spectra were characterized by the same set of bands at the same wavelengths.

The ^1H NMR spectra of adducts **2** and **3** were also identical and did not substantially differ from the spectrum of the starting azide **1**. Thus, the combination of the elemental analysis and IR and ^1H NMR spectroscopic data indicates that monoadducts **2** and **3** differ only by the structure of the fullerene sphere.

An information on the fullerene sphere structure of monoorganofullerenes can be obtained from the UV and ^{13}C NMR spectra. The UV spectra of adducts **2** and **3** in the wavelength region of 200—400 nm contained two bands, whose λ_{max} did not substantially differ. At the same time, the spectrum of adduct **3** in a long-wave region exhibited a narrow band with λ_{max} 420 nm and two broad low-intense bands with λ_{max} 490 and 664 nm, respectively. In the UV spectrum of adduct **2**, the narrow band at 420—430 nm and the band with λ_{max} 660 nm were absent, whereas the broad band appeared at 520 nm. This shape of the UV spectra indicates[1,2] that adduct **2** is azahomo[60]fullerene (adduct at the 5,6-open bond of C_{60}), while adduct **3** has the [60]fullereno[1,2-*b*]aziridine structure (adduct at the 6,6-closed bond of C_{60}). The low yield of adduct **2** did not allow us to obtain a good ^{13}C NMR spectrum for this compound. Such a spectrum was obtained for adduct **3**.

In the proton decoupled ^{13}C NMR spectrum of adduct **3**, the fullerene sphere was characterized by 14 signals with δ 140—145 and one signal with δ 83.37. As known,[1,2] this region contains signals of the sp^2-hybridized carbon atoms of the fullerene sphere. The number of signals in the ^{13}C NMR spectrum of adduct **3** in this region and their relative intensities (three signals with intensity of 2 C, nine signals with intensity of 4 C, and two signals with 8 C intensity) correspond to the C_{2v} symmetry of the molecule. Theoretically,[4] 16 lines (3 with 2 C intensity and 13 with 4 C intensity) should correspond to this type of symmetry in the ^{13}C NMR spectrum of monoorganofullerenes. In the spectrum of adduct **3**, two lines with 4 C intensity each are probably overlapped.

In the ^{13}C NMR spectrum of adduct **3**, the positions of signals of the carbon atoms of the pyrimidine cycle and phenyl radicals did not substantially differ from those of signals of the same carbon atoms in the spectrum of the starting azide **1**. This indicates that the phenyl residues are equivalent and the nitrogen atoms of the pyrimidine cycle are not involved in ring closure on the fullerene surface. In other words, the data of the ^{13}C NMR spectrum in combination with the UV spectroscopic data indicate that adduct **3** is [60]fullereno[1,2-*b*]aziridinopyrimidine rather than [60]fullereno[1´,2´:4,5]imidazo[1,2-*b*]pyrimidine, whose formation has previously been observed in the reactions of fullerene with 2-azidopyrimidine and 2-azido-5-nitropyrimidine.[1]

As already mentioned above, the electrochemical reduction of fullerenoimidazolines and nitropyrimidine-substituted azahomofullerene occurred more easily than the reduction of non-modified fullerene.[1] Therefore, it was of interest to study the electron-acceptor capability of pyrimidine-substituted fullerenoaziridine **3** and azahomofullerene **2** and to estimate the influence of the fullerene sphere structure on the electrochemical reduction of the adducts with the same organic fragments. For this purpose, we studied the electrochemical behavior of adducts **2** and **3** by cyclic voltammetry (CV). The results obtained were compared to the CV data for non-modified fullerene and starting azide **1** and to the electron affinity values calculated by the PM3 method.

Table 1. Potentials (E_p^{red}/V) and currents (I_p^{red}/μA) at peaks in the CV curves of fullerene C_{60} and compounds **1**—**3**

Compound	E^1 (I_p^1)	E^2 (I_p^2)	E^3 (I_p^3)	E^4 (I_p^4)
C_{60}	−0.83 (4.2)	−1.24 (3.8)	−1.70 (3.9)	−2.16 (4.6)
1			−1.86 (11.8)	
2	−1.00 (1.5)	−1.44 (2.0)	−1.88 (1.4)	−2.35 (1.3)
3	−0.96 (3.4)	−1.28 (2.1)	−1.87 (4.9)	−2.34 (3.2)

Under the studied conditions, four reversible one-electron reduction peaks, whose potentials are presented in Table 1, are detected in the CV curve of the starting C_{60}. Azidopyrimidine **1** was reduced irreversibly. The single reduction peak was observed in the potential interval in which the second peak of non-modified fullerene was detected (Table 1). It is known that pyrimidines[5] with electron-withdrawing substituents at the C(2) atom are capable of accepting one electron during electrochemical reduction to form the radical monoanion. This is accompanied by the C(4)=N(3) bond opening followed by the protonation of the anionic center. It is most likely that this process occurs during the electrochemical reduction of azide **1**, because we have previously[6] shown that the azido group is not reduced in the potential interval from 0 to −2.5 V under the conditions studied. It is noteworthy that the reduction of azide **1** is more difficult than the reduction of nonsubstituted 2-azidopyrimidine[1] ($E^1{}_p{}^{red}$ = −1.81 V), which is probably related to the presence of the donating phenyl substituents in the pyrimidine cycle.

The cyclic voltammograms of adducts **2** and **3** exhibited four reversible reduction peaks. In both cases, the first peaks corresponded to the reduction of the fullerene spheres to form radical anions. Note that the withdrawing of the first electron by adduct **3** is by 40 mV easier than the reduction of adduct **2**, despite the isostructural character of azahomofullerenes and starting fullerene. Compared to non-modified C_{60}, both adducts **2** and **3** were reduced in the region of more cathodic potentials, which is characteristic of the most fullerene monoadducts and agrees with the donor character of the substituents in the pyrimidine cycle. The calculation showed that the electron affinity of adduct **2** did not substantially differ from that of adduct **3**, being 2.58 eV, which is lower than the electron affinity of non-modified fullerene (2.65 eV). The second peak in the CV curve of adduct **3** also corresponds to the transfer of one electron to the fullerene fragment to form the dianion. The current value of the third reduction peak of adduct **3** indicates that the fullerene sphere and pyrimidine fragment are simultaneously reduced. The sphere of adduct **3** reversibly withdraws the third electron, whereas the reduction of the pyrimidine fragment is accompanied by the protonation of the anionic center. The further reduction of adduct **3** forms the tetraanion.

Finally, the reduction of adduct **2** also forms the tetraanion. However, the potential of the second reduction peak is somewhat unusual. Relatively to the second peaks in the CV curves of C_{60} and adduct **3**, this peak in the CV curve of adduct **2** is considerably shifted toward the more cathodic region. This peak corresponds, most likely, to the simultaneous reduction of the fullerene and pyrimidine fragments of the molecule of adduct **2**, and the shift values indicate the partial conjugation of the fullerene sphere of azahomofullerene with the aromatic fragments of the molecules.

Thus, the use of 2-azidopyrimidine with the donating phenyl substituents in positions 4 and 6 of the pyrimidine cycle in the reaction with C_{60} results in the formation of two types of adducts with different structures of the fullerene sphere: azahomofullerene and previously unknown pyridine-substituted fullereno[1,2-*b*]aziridine. According to the calculation, the heats of formation of compounds **2** and **3** are close and equal to 911.5 and 914.5 kcal mol^{-1}, respectively. The energies of the highest occupied orbitals are −9.208 eV for adduct **2** and −9.213 eV for adduct **3**, and the energies of the lowest unoccupied orbitals coincide being −2.814 eV. The frontier orbitals of adducts **2** and **3** are predominantly localized on the fullerene shell. Note that the energies of the frontier orbitals of fullerene C_{60} calculated by the PM3 method are −9.208 and −2.887 eV. The dipole moments of adducts **2** (3.33 D) and **3** (3.95 D) do not either differ substantially. However, adducts **2** and **3** differ by the charges on the nitrogen atom of the aziridine cycle, being equal to 0.160 and 0.141 a.u., respectively, which indicates the more efficient conjugation and additional stabilization of the open structure **2**.

Experimental

IR spectra were obtained on a Bruker IFS-113V FTIR spectrometer in KBr pellets and $CHCl_3$ solutions. ^1H NMR spectra were recorded on a Bruker WM-250 instrument (250.13 MHz) in $CDCl_3$ using Me_4Si as the internal standard. ^{13}C NMR spectra were obtained on a Bruker MSL-400 instrument at ν_0 100.62 MHz. The δ values were calculated relatively to Me_4Si. UV spectra were recorded on a Specord UV-VIS instrument. In the CV studies, a stationary disk glassy-carbon electrode with a working surface area of 3.14 mm^2 was used as the working electrode. Voltammograms (CV curves) were recorded using a PI-50-1 potentiostat with a PR-8 programmer, and the electrochemical cell was connected according to the three-electrode scheme. CV curves were detected on a two-coordinate recorder with a linear potential scan rate of 50 mV s^{-1}. 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 cell, whose temperature was maintained at 25 °C, in an argon atmosphere. The concentration of C_{60} and azide **1** in solutions was $2 \cdot 10^{-3}$ mol L^{-1}, and that of the adducts was $1 \cdot 10^{-3}$ mol L^{-1}. The electronic structures, heats of formation, and electron affinities of compounds **2** and **3** were studied by the PM3 method using the GAMESS program.[7] The energies of the lowest unoccupied orbital (ε_l*) and experimental electron affinity of nonmodified fullerene C_{60} (2.65 eV) were used for the theoretical estimation of the electron affinities (EA) of adducts **2** and **3**: $\mathrm{EA(adduct)} = \mathrm{EA}(C_{60}) - \varepsilon^*_l(\mathrm{adduct}) + \varepsilon^*_l(C_{60})$. Anhydrous *o*-DCB and MeCN were obtained 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).[8] 2-Hydrazino-4,6-diphenylpyrimidine was synthesized according to a previously described procedure.[9]

2-Azido-4,6-diphenylpyrimidine (1). A solution of $NaNO_2$ (0.9 g, 13.0 mmol) in water (7 mL) was added by portions to a suspension of 2-hydrazino-4,6-diphenylpyrimidine (2.9 g, 11.4 mmol) in 18% hydrochloric acid (14 mL) cooled to 0 °C in such a way that the temperature of the reaction mixture did not exceed 0—3 °C. After 1 h, a precipitate formed was filtered off, washed with water, and recrystallized from aqueous EtOH. The yield of compound **1** was 2.3 g (74%), m.p. 150—151 °C. Found (%): C, 70.40; H, 4.12; N, 25.60. $C_{16}H_{11}N_5$. Calculated (%): C, 70.32; H, 4.06; N, 25.63. IR (KBr), ν/cm^{-1}: 2153, 2125, 2109 (N_3); 1569, 1526, 1441, 1338, 764, 688 (Ph, pyrimidine cycle). IR ($CHCl_3$), ν/cm^{-1}: 2154, 2133, 2115 (N_3); 1574, 1529, 1443, 1345 (Ph, pyrimidine cycle). UV (CH_2Cl_2), λ_{max}/nm: 257, 317. ^1H NMR, δ: 7.48—7.55 (m, 6 H, 2 Ph, *m*-H, *p*-H, C_6H_5); 7.87 (s, 1 H, H(5)); 8.17 (dd, 4 H, 2 Ph, 2 *o*-H, $^3J_{H,H}$ = 6.9 Hz, $^4J_{H,H}$ = 2.9 Hz). ^{13}C NMR, δ: 108.41 (d, C(5), $^1J_{C,H}$ = 165.1 Hz); 127.50 (ddd, *o*-C (Ph), $^1J_{C,H}$ = 161.6 Hz, $^3J_{C,H}$ = 8.0 Hz, $^4J_{C,H}$ = 7.0 Hz); 129.12 (dd, *m*-C (Ph), $^1J_{C,H}$ = 160.9 Hz, $^2J_{C,H}$ = 7.0 Hz); 131.50 (dt, *p*-C (Ph), $^1J_{C,H}$ = 161.6 Hz, $^3J_{C,H}$ = 7.0 Hz); 136.42 (m, C_i(Ph)); 162.77 (s, C(2)); 166.99 (s, C(4), C(6)).

Reaction of C_{60} with azide 1. Azide **1** (43 mg, 0.16 mmol) was added to a solution of C_{60} (95 mg, 0.132 mmol) in anhydrous *o*-DCB (25 mL), and the mixture was heated with stirring for 4 h at 180 °C. The solvent was evaporated *in vacuo*, and a residue was chromatographed on a column with silica gel. Using a toluene—petroleum ether (4 : 1) mixture as the eluent, C_{60} (14 mg, 15%) and fractions containing mono- and polyadducts were isolated. Compound **2** (8 mg, 6%) (R_f = 0.67, a toluene—petroleum ether (4 : 3) mixture as the eluent) and compound **3** (15 mg, 12%) (R_f = 0.42) were isolated by double chromatography of the fraction containing the monoadducts.

2-(Azahomo[60]fullereno)-4,6-diphenylpyrimidine (20). Found (%): C, 94.38; H, 0.77; N, 4.31. $C_{76}H_{11}N_3$. Calculated (%): C, 94.51; H, 1.14; N, 4.35. IR (KBr), ν/cm^{-1}: 1584, 1570, 1524, 1430, 1341, 763, 689 (Ph, pyrimidine cycle); 526 (fullerene cycle). UV (CH_2Cl_2), λ_{max}/nm: 258, 327, 443, 520. ^1H NMR, δ: 7.55—7.58 (m, 6 H, 2 Ph); 8.02 (s, 1 H, H(5)); 8.29 (dd, 4 H, 2 Ph, $^3J_{H,H}$ = 6.5 Hz, $^4J_{H,H}$ = 2.5 Hz).

2-{[60]Fullereno[1,2-*b*]aziridino}-4,6-diphenylpyrimidine (3). Found (%): C, 94.22; H, 0.67; N, 4.30. $C_{76}H_{11}N_3$. Calculated (%): C, 94.51; H, 1.14; N, 4.35. IR (KBr), ν/cm^{-1}: 1584, 1570, 1524, 1429, 1340, 763, 688 (Ph, pyrimidine cycle); 526 (fullerene fragment). UV (CH_2Cl_2), λ_{max}/nm: 256, 325, 420 (narrow), 490, 664. ^1H NMR, δ: 7.53—7.56 (m, 6 H, 2 Ph); 7.94 (s, 1 H, H(5)); 8.22 (dd, 4 H, 2 Ph, $^3J_{H,H}$ = 6.3 Hz, $^4J_{H,H}$ = 2.8 Hz). ^{13}C NMR, δ: 108.72 (C(5)); 126.91, 128.47, 130.07, 136.77 (Ph); 163.99 (C(2)); 166.53 (C(4), C(6)); $C_{60}N_2$: 83.37, 143.04, 144.35, 145.00 (2 C), 140.34, 141.25, 142.49, 142.60, 144.08, 144.71, 144.98, 145.21, 145.41 (4 C), 143.34, 145.34 (8 C).

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