Mendeleev Commun., 2006, **16(6)**, 309–311

Synthesis and unusual electrochemical properties of nitropyrimidine-substituted diazadihomo(C_{60}-I_h)[6,6]fullerene

Irina P. Romanova,* Gulshat G. Yusupova, Olga A. Larionova, Adilya A. Nafikova, Dmitry G. Yakhvarov, Vladislav V. Zverev, Yury Ya. Efremov and Oleg G. Sinyashin

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Centre of the Russian Academy of Sciences, 420088 Kazan, Russian Federation. Fax: +7 8432 75 2253; e-mail: romanova@iopc.knc.ru

DOI: 10.1070/MC2006v016n06ABEH002387

A bisadduct regioisomer with two open transannular [6,6]-bonds was synthesised by the cycloaddition reaction of C_{60} and 2-azido-5-nitropyrimidine.

The reactions of fullerenes with organic azides are of great interest since they result in the formation of adducts with various structures of a fullerene sphere, giving extensive opportunities for the search of organofullerenes with required properties. In addition to 6,6-closed, 5,6-closed and 5,6-open monoadducts,[1–4] these reactions result in the formation of 6,6-closed, 6,6- or 5,6-open isomers of the bisadducts.[2,5–8] The latest has attracted considerable interest because of the large size of molecules with a defined three-dimensional architecture, unique properties of fullerenes and additional properties due to organic fragments.[9] Saturation of several bonds of the fullerene sphere changes significantly its electron state. The electron affinity (EA) of the sphere decreases as a rule.[10] However, the addition of two strong electron-acceptor fragments to the fullerene sphere can compensate the decrease of EA and increase the EA of a fullerene C_{60} fragment. Thus, a bisadduct of C_{60} with 2,3-bis-{[(methoxycarbonyl)acetoxy]ethylthio}-6,7-bis(hexadecylthio)-tetrathiafulvalene is electrochemically reduced by 510 mV more easily than C_{60}.[11]

Earlier, we have demonstrated that the reaction of C_{60} with 2-azido-5-nitropyrimidine **1** resulted in the formation of three monoadducts (Scheme 1). This reaction affords 2-(azahomo-[60]fullereno)-5-nitropyrimidine **2** at 180 °C, while at 160 °C 1-(5-nitropyrimidin-2-yl)[60]fullereno[1,2-*b*]aziridine **3** and at 100 °C 4-nitro[60]fullereno[1′,2′:4,5]imidazo[1,2-*b*]pyrimidine **4** were formed.[3,12,13] These products were isolated from the reaction mixtures by column chromatography. In addition to the monoadducts, the fractions containing a mixture of polyadducts were also isolated.

We failed to separate the polyadduct mixtures resulted from the reaction of C_{60} with azide **1** at 100 and 160 °C. At the same time, compound **5** (R_f 0.08; Sorbfil; eluent, toluene) was isolated (15%) from the mixture formed at 180 °C. R_f of **5** differed substantially from R_f of adduct **2** (R_f 0.76; Sorbfil; eluent, toluene), adduct **3** (R_f 0.98; Sorbfil; eluent, toluene) and **4** (R_f 0.93; Sorbfil; eluent, toluene).[3,12,13] The elemental analysis indicated that compound **5** is the adduct of C_{60} with two azide **1** accompanied with the loss of two N_2 molecules.[†]

Bisadduct **5** was studied by electron impact mass spectrometry using direct injection. In the mode of the fast heating up to 450 °C, the peak with *m*/*z* 858 corresponding to the monoadduct of C_{60} and azide **1** with the elimination of N_2 was observed in the spectrum. In the course of visual examination of the oscillogram an extremely low-intensity peak, corresponding to the molecular ion of bisadduct **5** with *m*/*z* 996, appeared at 200 °C in addition to the intense peak with *m*/*z* 858. No peaks with *m*/*z* 858 and 996 were detected on slow heating of adduct **5** to 450 °C. At 260 °C, the peak with *m*/*z* 276 corresponding to 4,4′-dinitroazopyrimidine appeared because of the decomposition of bisadduct **5**. Thus, the mass-spectrometric data evidence the low thermal stability of bisadduct **5**.

The structure of bisadduct **5** was established by ^{13}C, ^{1}H NMR, UV and IR spectroscopy.[†] In the ^{13}C NMR spectrum, 31 signals of a fullerene sphere (26×2C, 1×4C and 4×1C) were recorded; 29 signals were recorded in the region δ 133–145 ppm and two signals were recorded at δ 115.44 and 130.84 ppm. The number of lines in the ^{13}C NMR spectrum and their relative intensities along with the absence of signals of sp^3-hybridized carbon atoms in the region 70–90[1–5] prove the diazadihomofullerene structure of adduct **5** having C_S symmetry of the molecule and correspond to a regioisomer with two open transannular [6,6]-bonds.[5]

A singlet at δ 9.17 was found in the ^{1}H NMR spectrum of bisadduct **5**. The signal indicates the equivalence of hydrogen atoms in the pyrimidine fragment. Note that this signal is high-field shifted relative to that of the corresponding hydrogen atoms in the ^{1}H NMR spectrum of azide **1** and monoadducts **2**, **3**.[12,13]

The toluene, *o*-DCB and CH_2Cl_2 solutions of bisadduct **5** are greenish. The UV-VIS spectrum of **5**, recorded in CH_2Cl_2, has a low-intensity wide band at 532 nm.[5]

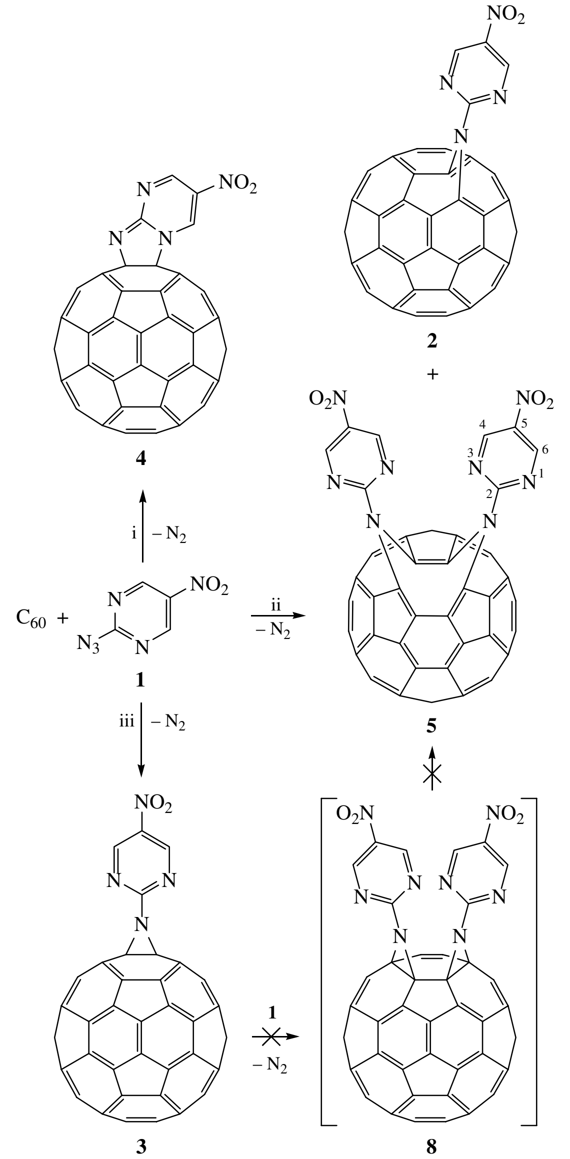
The IR spectrum of bisadduct **5** indicated the presence of a fullerene sphere and a nitropyrimidine fragment in the product. The intensity of a band at 526 cm^{-1} was much lower than that of nitropyrimidine fragment and was a half of the absorption observed in the spectra of monoadducts **2**–**4**. Such a correlation between the absorption bands intensities of exoedral and fullerene fragments in the IR spectra of phosphorylated and isocyanurate mono- and bisadducts was reported previously.[8,14]

It was shown[5] that the bisadducts with two open transannular [6,6]-bonds were formed as a result of azide addition to a 6,6-closed monoadduct.[5] All attempts to obtain bisadduct **5** by the reaction of fullerenoaziridine **3** with azide **1** were unsuccessful (Scheme 1). The mixtures of regioisomeres were formed. Moreover, the reaction of azahomofullerene **2** with azide **1** affords a product with physicochemical characteristics similar to those of **5**.[‡] Based on these data, we supposed that the bisadduct **5** was formed by other scheme. The reaction of fullerene C_{60} with azide **1** passes through the formation of monoazahomofullerene **2** (5,6-open monoadduct) (Scheme 2). Compound **2**

[†] IR spectra were obtained on a Bruker IFS-113V instrument. ^{1}H NMR spectra were recorded on a Bruker WM-250 spectrometer at 250 MHz and ^{13}C NMR spectra, on a Bruker MSL-400 spectrometer at 100 MHz. Chemical shifts were measured with reference to the signal of Me_4Si. UV spectra were recorded on a Specord UV-VIS spectrophotometer. The mass spectra were measured on a MAT 212 instrument (Finnigan) using the MASPEC II32 data processing system and the system of direct injection into the heated ion source with a voltage of 60 V and an electron emission current of 0.5 mA.

Azide **1** (19 mg, 0.14 mmol) was added to a solution of C_{60} (57 mg, 0.08 mmol) in anhydrous *o*-DCB (40 ml), the mixture was heated with stirring for 6 h at 180 °C. The solvent was eliminated *in vacuo*, the residue was chromatographed on a column with silica gel. C_{60} (17 mg, 30%), compound **2** (11 mg, 16%) and bisadducts mixture containing fraction were isolated by column chromatography using toluene as an eluent. The repeated chromatographing of the last fraction produced bisadduct **5** (12 mg, 15%).

Bisadduct **5**: ^{1}H NMR ($CDCl_3$) δ: 9.17 (s, 2H, H-4, H-6). ^{13}C NMR ($CDCl_3$) δ: 138.50 (d, C-5, $^{2}J_{CH}$ 2.9 Hz), 140.00 (d, C-2, $^{3}J_{CH}$ 7.2 Hz), 155.52 (d, C-4, C-6, $^{1}J_{CH}$ 194.7 Hz); $C_{60}N_2$: 137.12, 140.04, 144.89, 146.25 ($C_{60}N_2$, 1C), 115.44, 130.84, 135.92, 137.92, 139.23, 139.94, 141.51, 141.72, 141.85, 142.42, 142.53, 143.32, 143.35, 143.46, 143.49, 143.61, 143.65, 143.75, 143.94, 144.55, 144.95, 145.00, 145.05, 145.08, 145.99, 146.30 ($C_{60}N_2$, 2C), 140.94 ($C_{60}N_2$, 4C). UV-VIS (CH_2Cl_2, λ_{max}/nm): 258, 325, 532 (br.). IR (KBr, ν/cm^{-1}): 1571, 1333, 847 (NO_2), 1450 (pyrimidine cycle), 526 (fullerene fragment). Found (%): C, 81.22; H, 0.59; N, 10.6. Calc. for $C_{68}H_4N_8O_4$ (%): C, 81.72; H, 0.40; N, 11.2.



Scheme 1 *Reaction conditions*: i, *o*-DCB, 100 °C, 16 h; ii, *o*-DCB, 180 °C, 6 h; iii, *o*-DCB, 160 °C, 4.5 h.

reacts with one more molecule of azide **1**, resulting in the formation of thermally unstable bisadduct **6**. The decomposition of compound **6** affords bisadduct **5**. It is well known that compounds similar to bisadduct **6** can form regioisomers similar to bisadduct **7**.[15]

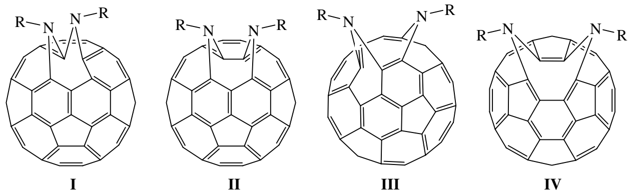
The total energy and the energy difference between compounds **5**, **7** and **8** (*cis*-1 6,6-closed bisadduct) were calculated by the DFT method. The gradient-correlated density functional theory with Perdew–Burke–Ernzerhof nonempirical nonlocal exchange-correlation functional (DFT/PBE) was used.[16] Calculations were executed with a three-exponential basis set and two polarization functions (TZ2P) using the PRIRODA program.[17]

Table 1 The total energy (*E*) and the energy difference (Δ*E*) for compounds **5**, **7** and **8** calculated by the DFT method.

Compound	*E* (a.e.)	Δ*E*/kcal mol^{-1}
5	–3329.51443	0.00
7	–3329.51007	2.73
8	–3329.50787	4.12

[‡] Azide **1** (5 mg, 0.034 mmol) was added to a solution of azahomofullerene **2** (20 mg, 0.023 mmol) in anhydrous *o*-DCB (5 ml), the mixture was heated with stirring for 5 h at 180 °C. The solvent was eliminated *in vacuo*, and the residue was chromatographed on a column with silica gel using toluene as an eluent. A minor amount of C_{60}, compound **2** (10 mg, 50%) and bisadduct **5** (7 mg, 30%) were isolated.

Table 2 The total energy (*E*) and the energy difference (Δ*E*) between regioisomeres **I**–**IV** calculated by the DFT method.



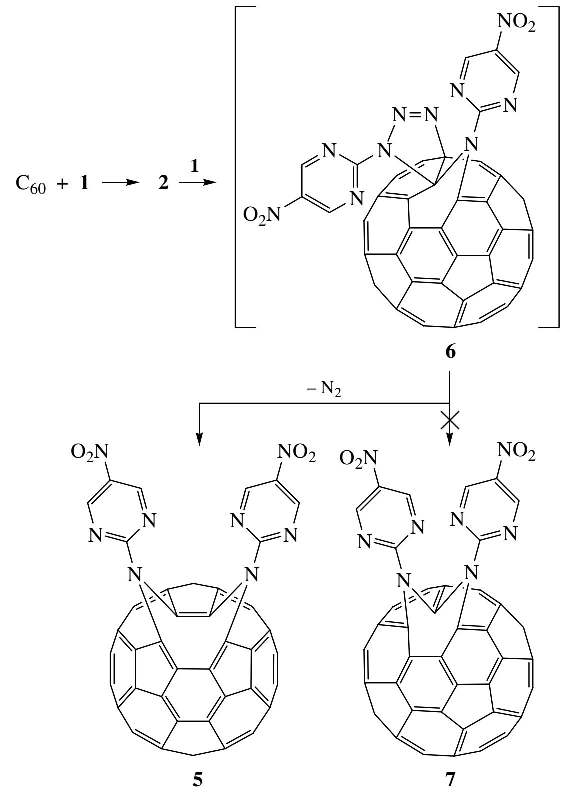
Isomer	R = H		R = Me	
	E (e.a.)	Δ*E*/kcal mol^{-1}	*E* (e.a.)	Δ*E*/kcal mol^{-1}
I	–2394.86898	17.70	–2473.38630	17.45
II	–2394.89719	0.00	–2473.41412	0.00
III	–2394.88480	7.77	–2473.40508	5.67
IV	–2394.86062	22.95	–2473.38567	17.85

It was shown (Table 1) that compound **5** was the most stable and compound **7** was the least stable. It turned out that the formation of compound **5** was more favourable than that of bisadduct **8**.

Most likely, the stability of compound **5** is due to the electron acceptor nature of nitropyrimidine fragments because in case of regioisomers **I**–**IV** with R = H or Me the same order of regioisomer stability was observed (Table 2). In these cases, regioisomer **IV** was least stable.

As far as we know, there is no data on the electrochemical reduction of diazahomofullerenes. We studied the reduction of bisadduct **5** by cyclic voltammetry (CV); the results, as well as comparative data for C_{60}, azide **1**, monoadducts **2**–**4**, are given in Table 3.

Four classical reversible one-electron peaks of reduction are observed in the voltammetric curve of fullerene C_{60} (Table 3).[1,2] The reduction of azide **1** is observed in the same potential range as for C_{60}. Four irreversible reduction peaks appear in the voltammetric curve of **1**. The first peak is attributed to the reduction of the nitro group. The subsequent peaks can also be related to the nitro group reduction, as well as to electron transfer to the pyrimidine fragment of the molecule.



Scheme 2 Formation of bisadduct **5**.

Table 3 Potentials (E_p^{red}) in cyclic voltammograms for C_{60} and compounds **1**–**5**.[a]

Compound	E_p^{red}/V (I_p^{red}/µA)									
C_{60}	−0.83	−1.24	−1.70	−2.16						
1	−1.11[b]	−1.51[b]	−2.02[b]	−2.20[b]						
2	−0.75[c]	−1.11	−1.22	−1.68	−1.88	−2.18				
3	−0.79[c]	−1.15[b]	−1.75	−2.23						
4	−0.73[c]	−1.07	−1.20	−1.68	−1.82	−2.21				
5	−0.60[c] **(I)**	−0.88 **(II)**	−1.03[c] **(III)**	−1.33 **(IV)**	−1.45[c] **(V)**	−1.73	−1.86	−2.12	−2.31	2.42

[a] Solution concentration, 1×10^{-3} mol dm^{-3}; supporting electrolyte, 0.1 M Bu_4NBF_4; cathode, carbon glass (CG) ($S_{work} = 3.14$ mm^2; reference electrode, 0.01 M $Ag/AgNO_3$ in MeCN; $V_{pot} = 50$ m s^{-1}). [b] The irreversible wave. [c] The quasi-reversible wave.

The irreversibility of the reduction peaks for nitro groups, as in the case of nitrobenzene, is probably the result of the nitrogen-containing group protonation in the course of reduction under heavy dilution.[18]

As for pyrimidine fragments reduction, its irreversibility can arise from C(4)=N(3) bond opening in the heterocyclic fragment.[19] The azido group is not electrochemically active in the studied potential region.[3,4] Note that in *o*-DCB solution, in which the electrochemical experiment was performed, compound **1** presents as the azide form, according to the ^{1}H and ^{13}C NMR data, but not in tetrazole form, which is possible for azidopyrimidines.[12]

The voltammetric curve of adduct **5** exhibited five one-electron reduction peaks [Figure 1(*a*)] at potential scan from 0 to –1.5 V; three of them (**I**, **III** and **V**) are reversible. That gives grounds to attribute them to the reduction of the fullerene fragment of the molecule, while peaks **II** and **IV** can be ascribed to the reduction of two nitro groups with formation of a polyanionic bisadduct. Some more peaks appeared in the cyclic voltammogram [Figure 1(*b*)] at further potential scanning up to –2.5 V.

These peaks could correspond to both the subsequent reduction of the fullerene sphere and the pyrimidine fragment reduction. The reduction of the products of isomerization of trianion with 5,6-open bonds to trianion with 6,6-closed bonds is quite similar to that noted previously for some homofullerenes.[20]

The comparison of the reduction potentials demonstrates that the first reduction peak of the fullerene sphere of bisadduct **5** is shifted by 230 mV to the anode region as compared with that of the C_{60}. It could be the result of the electron acceptor ability of two nitropyrimidine fragments. Note that bisadduct **5** is reduced easier than monoadducts **2**–**4**,[3,12,13] which were reduced easier than the pristine C_{60}.

Thus, the reaction of C_{60} with azide **1** at 180 °C affords both monoadduct **2** and bisadduct **5**, in which two 6,6-transannular bonds being open. First electron transfer to bisadduct **5** is performed easier compared to the pristine fullerene, due to the presence of two electron-withdrawing nitropyrimidine fragments on the fullerene sphere. Moreover, it is probable that the conjugation exists between the fullerene sphere and nitropyrimidines fragments. This conjugation assists at monoadducts **2**–**4**.

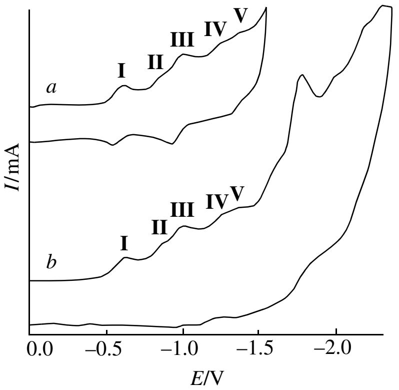


Figure 1 Cyclic voltammogram for bisadduct **5**.

This study was supported by the Russian Foundation for Basic Research (grant no. 05-03-32418) and OCCM Programme no. 7.

References

1 A. Hirsch and B. Nuber, *Acc. Chem. Res.*, 1999, **32**, 795.
2 U. Reuther and A. Hirsch, *Carbon*, 2000, **38**, 1539.
3 I. P. Romanova, V. V. Kalinin, A. A. Nafikova, D. G. Yakhvarov, V. V. Zverev, V. I. Kovalenko, G. L. Rusinov, P. V. Plekhanov, V. N. Charushin, and O. G. Sinyashin, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 163 (*Russ. Chem. Bull., Int. Ed.*, 2003, **52**, 173).
4 O. G. Sinyashin, I. P. Romanova, G. G. Yusupova, V. I. Kovalenko, V. V. Yanilkin and N. M. Azancheev, *Mendeleev Commun.*, 2000, 96.
5 G. Schick, A. Hirsch, H. Mauser and T. Clark, *Chem. Eur. J.*, 1996, **2**, 935.
6 C. K.-F. Shen, H.-H. Yu, C.-G. Juo, K.-M. Chien, G.-R. Her and T.-Y. Luh, *Chem. Eur. J.*, 1997, **3**, 744.
7 M. Iglesias, B. Gomez-Lor and A. Santos, *J. Organomet. Chem.*, 2000, **599**, 8.
8 I. P. Romanova, G. G. Yusupova, A. A. Nafikova, V. I. Kovalenko and O. G. Sinyashin, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 1376 (*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 1491).
9 T. Da Ros and M. Prato, *Chem. Commun.*, 1999, 663.
10 C. Boudon, J.-P. Gisselbrecht, M. Gross, L. Isaacs, H. L. Anderson, R. Faust and F. Diederich, *Helv. Chim. Acta*, 1995, **78**, 1334.
11 P. Zeng, Y. Liu, D. Zhang, C. Yang, Y. Li and D. Zhu, *J. Phys. Chem. Solids*, 2000, **61**, 1111.
12 I. P. Romanova, G. G. Yusupova, O. A. Larionova, A. A. Balandina, Sh. K. Latupov, V. V. Zverev, D. G. Yakhvarov, G. L. Rusinov and O. G. Sinyashin, *Izv. Akad. Nauk, Ser. Khim.*, 2006, 484 (*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 502).
13 I. P. Romanova, V. V. Kalinin, D. G. Yakhvarov, A. A. Nafikova, V. I. Kovalenko, P. V. Plekhanov, G. L. Rusinov and O. G. Sinyashin, *Mendeleev Commun.*, 2002, 51.
14 O. G. Sinyashin, I. P. Romanova, F. R. Sagitova, V. A. Pavlov, V. I. Kovalenko, Yu. V. Badeev, N. M. Azancheev, A. V. Ilyasov, A. V. Chernova and I. I. Vandyukova, *Mendeleev Commun.*, 1998, 79.
15 T. Grosser, M. Prato, V. Lucchini, A. Hirsch and F. Wudl, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1343.
16 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.
17 D. N. Laikov, *Chem. Phys. Lett.*, 1997, **281**, 151.
18 *Organic Electrochemistry*, eds. M. Baser and H. Lund, Marcel Dekker, New York, Basel, 1983.
19 P. A. S. Smith, J. H. Hall and R. O. Kan, *J. Am. Chem. Soc.*, 1962, **84**, 485.
20 M. Eiermann, F. Wudl, M. Prato and M. Maggini, *J. Am. Chem. Soc.*, 1994, **116**, 8364.

Received: 19th May 2006; Com. 06/2732