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Synthesis and electrochemical properties of 2-(azahomo[60]fullereno)-5-nitropyrimidine

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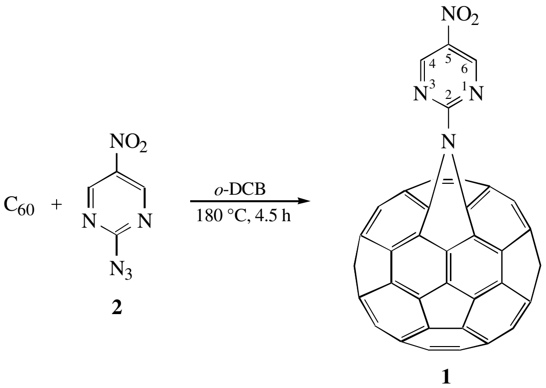
2-(Azahomo[60]fullereno)-5-nitropyrimidine was synthesised by the cycloaddition reaction of C_{60} and 2-azido-5-nitropyrimidine.

The practical applications of fullerenes are determined by their solubility and electron affinity. These properties can be modified by the addition of electron-withdrawing organic fragments to fullerenes. However, the number of fullerene derivatives with electron affinities higher than that of parent fullerenes is limited.[1–4] In most cases, the opening of fullerene π-bonds leads to a decrease in the electron affinity. For [60]fullerene, the lowest decrease in the electron affinity was observed in homofullerenes; however, the synthesis and identification of such C_{60} derivatives are difficult to perform. Earlier, we prepared isocyanurato-substituted azahomo[60]fullerene.[5] Its electrochemical reduction was 80 mV easier than that of C_{60}. Two N-aryl-substituted azahomofullerenes,[3] which are reduced easier than C_{60}, are known. However, the structure of N-aryl-substituted azahomofullerenes was not reliably determined by UV spectroscopy.

We described here the synthesis and electrochemical properties of nitropyrimidino-substituted azahomo[60]fullerene. Pyrimidinofullerenes were earlier obtained in a reaction of [60]fullerene with pyrimidine *o*-chinodimethanes and presented 6,6-closed adducts of C_{60}.[6] To introduce an electron-withdrawing nitropyrimidinic fragment to a fullerene molecule, we used the cycloaddition of organic azides to the fullerene, which led to the formation of azahomofullerenes.[7] We were the first to use a pyrimidino-substituted azide in this reaction.

Azide **2**[†] (0.14 mmol) reacted with [60]fullerene (0.08 mmol) in boiling *o*-dichlorobenzene. The reaction was monitored by mass spectrometry. After heating for 4.5 h, two peaks (720 and 858) were detected in the mass spectrum of the reaction mixture. The former peak corresponded to C_{60}, and the latter peak corresponded to monoadduct **1**. The unreacted fullerene (30%) and monoadduct **1** (18%) were separated by column chromatography (toluene as an eluent). After drying in a vacuum, monoadduct **1** was obtained as brown powder readily soluble in toluene, chloroform and methylene chloride. Its structure was studied by ^{13}C NMR, ^{1}H NMR, UV and IR spectroscopy.



In the ^{13}C NMR spectrum[‡] of monoadduct **1**, signals due to the carbons of a fulleroid sphere and nitropyrimidinic fragment were observed. The positions of signals of fulleroid sphere carbons (δ 133–147 ppm), their number (32 signals) and relative intensities (24 signals had intensity 2C, 2 signals had intensity 4C, due to the signals overlapping, and 4 signals had intensity 1C) pointed at azahomo[60]fullerene structure of the molecule with C_s symmetry. This conclusion was proved by the UV spectrum.[‡] The bands of a pyrimidine ring, nitro group and a band characteristic of a monoadduct [60]fullerene were observed in the IR spectrum[‡] of monoadduct **1**. The structure of the nitropirimidine fragment was also confirmed by the ^{1}H NMR spectrum of monoadduct **1**.[‡]

We studied the thermal stability of azahomo[60]fullerene **1** and found that, contrarily to isocyanurate-substituted azahomo[60]fullerenes, which thermally isomerised to [60]fullereno-[1,2-*b*]aziridines,[5,8] nitropyrimidine-substituted azahomo[60]fullerene **1** was unusually stable on boiling in a solution of *o*-dichlorobenzene for 10 h. Only after 20 h heating azahomo[60]fullerene **1** decomposed to the parent fullerene.

The redox-properties of azahomofullerene **1** were studied by cyclic voltammetry. The cyclic voltammogram of C_{60} exhibited four classically reversible waves of reduction with peak potentials, summarised in Table 1 (Figure 1). At these potentials the reduction of azide **2** also occured (Table 1). Thus, the cyclic voltammogram of azide **2** exhibited four waves of reduction, two of them having the greatest currents were irreversible. All the reduction waves of azide **2** correspond to the reduction of the nitropyrimidine fragment since the azide group was not reduced in the studied range of potentials.[5] The relative irreversibility of the reduction waves of the nitro group is explained by carrying out the reduction process at the potential development from –0.7 to –2.5 V, accompanied by the transfer of four electrons to the molecule and its decomposition. The cyclic voltammogram of azahomo[60]fullerene **1** is presented in Figure 1. At the development of potential up to –0.9 V, the first one-electron wave (I) is reversible. Note that the potential of the peak of this reduction wave is 80 mV less negative than the potential of the first peak of reduction of parent C_{60}.

Based on the values of potential and reversibility of the wave of reduction, we consider that the first peak in the cyclic volt-

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[†] IR spectra were obtained on a Bruker IFS-113V instrument. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker MSL-400 spectrometer at 250 and 100 MHz, respectively. Chemical shifts were measured with reference to the signals of $CDCl_3$, which was used as a solvent. The mass spectra were measured on a MALDI TOF MS instrument (Dynamo).

Compound **2** was obtained by the published method.[9] ^{1}H NMR (250 MHz, $CDCl_3$) δ: 9.35 [s, 2H, CH(4,6)]. $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$) δ: 139.06 [C(5)], 155.30 [CH(4,6)], 166.15 [C(2)]. UV-VIS (CH_2Cl_2, λ_{max}/nm): 290. IR (KBr, ν/cm^{-1}): 1571, 1331, 873, 833 (NO_2), 1417, 639 (pyrimidine cycle), 2138 (N_3).

[‡] Compound **1**: R_f 0.76 (Silufol; eluent, toluene). ^{1}H NMR (250 MHz, $CDCl_3$) δ: 9.38 [s, 2H, CH(4,6)]. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.17 [d, C(5), $^{2}J_{CH}$ 1.2 Hz], 155.30 [d, CH(4,6), $^{1}J_{CH}$ 188.6 Hz], 141.77 [d, C(2), $^{3}J_{CH}$ 6.7 Hz], 138.06, 138.90, 139.02, 143.71 ($C_{60}N$, 1C), 134.35, 135.30, 135.87, 137.45, 138.06, 138.75, 140.10, 141.76, 141.82, 142.87, 143.03, 143.10, 143.21, 143.41, 143.66, 143.83, 144.17, 144.35, 144.37, 144.41, 144.52, 145.04, 146.30, 147.34 ($C_{60}N$, 2C), 144.15, 144.59 ($C_{60}N$, 4C). UV-VIS (CH_2Cl_2, λ_{max}/nm): 259, 325, 431 (br.), 539 (br.). IR (KBr, ν/cm^{-1}): 526 (C_{60}), 1575, 1332, 849 (NO_2), 1456, 645 (pyrimidine cycle).

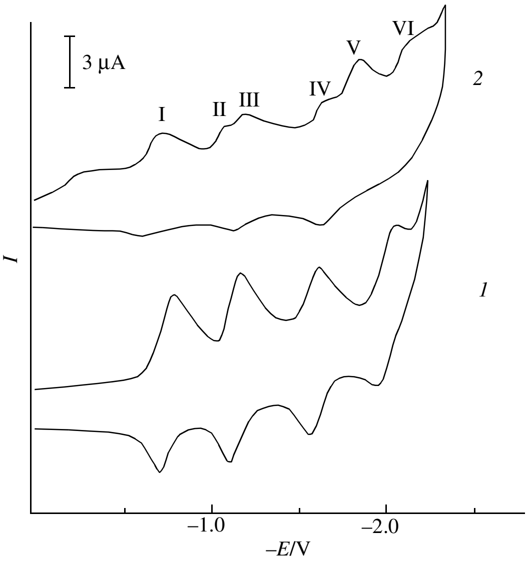

Figure 1 Cyclic voltammograms of (*1*) C_{60} and (*2*) azahomo[60]fullerene **1**.

Table 1 Peak potentials and currents of waves in the cyclic voltammograms of C_{60}, adduct **1** and azide **2** [in a mixture of *o*-dichlorobenzene and MeCN (3:1) at 25 °C].[a]

Compound	E_p^{red} / V (I_p/µa)					
	K_1^b	K_2	K_3	K_4	K_5	K_6
C_{60}	–0.83 (4.2)	–1.24 (3.8)	–1.70 (3.9)	–2.16 (4.6)		
2	–1.11 (24.5)[c]	–1.51 (2.5)	–2.02 (25)[c]	–2.20 (4.0)		
1	–0.75 (3.5)	–1.11 (2.3)[c]	–1.22 (1.3)	–1.68 (3.3)	–1.88 (3.5)[c]	–2.18 (3.6)
	I	II	III	IV	V	VI

[a] Solution concentrations, 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; $V_{pot} = 50$ mV s^{-1}). [b] The reduction waves of substrates observed in cyclic voltammograms. [c] The irreversible wave.

ammogram of azahomofullerene **1** corresponds to the transposition of one electron on the fullerene sphere. At a further development of the potential up to –2.5 V, five waves of reduction were observed in the cyclic voltammogram of azahomofullerene **1**. In the potential range from –1.00 to –1.50 V, the reduction of both fullerene and pyrimidine fragments takes place, as can be seen in two overlapped reduction waves II and III. Wave II is irreversible, and its potential is in the range of potentials of reduction of azide **2**. In this connection, we consider that wave II corresponds to the reduction of the nitropyrimidine fragment in the molecule of azahomofullerene **1**. The reversibility of waves III points at the reduction of a fullerene sphere of azahomofullerene **1**, and this process occurs easier ($\Delta E_p = 20$ mV) than the addition of the second electron to initial C_{60}. A comparison of the peak potentials of reduction waves IV, V and VI with the potentials of the reduction waves of C_{60} and azide **2** allowed us to conclude that reversible waves IV and VI correspond to the reduction of the fullerene sphere and irreversible wave V, to the reduction of the nitropyrimidinic fragment.

Thus, we found that 2-(azahomo[60]fullereno)-5-nitropyrimidine **1** is reduced easier than parent C_{60}. The reduction of fullerene and nitropyrimidine fragments occurs in the same interval of potentials, but the first electron is transfered to the homofullerene fragment of the molecule. The compounds of this type are interesting for the synthesis of complexes with organic donors, which can exhibit ferromagnetic properties.

References

1 B. M. Illesca and N. Martin, *J. Org. Chem.*, 2000, **65**, 5986.
2 P. Zeng, Y. Liu, D. Zhang, C. Yang, Y. Li and D. Zhu, *J. Phys. Chem. Solids*, 2000, **61**, 1111.
3 J. Zhou, A. Rieker, T. Grösser, A. Skiebe and A. Hirsch, *J. Chem. Soc., Perkin Trans. 2*, 1997, 1.
4 H. Irngartinger and T. Escher, *Tetrahedron*, 1999, **55**, 10753.
5 O. G. Sinyashin, I. P. Romanova, G. G. Yusupova, A. A. Nafikova, N. M. Azancheev, V. V. Yanilkin, V. I. Kovalenko and Y. G. Budnikova, *Mendeleev Commun.*, 2000, 61.
6 A. C. Tome, R. F. Enes, J. A. S. Cavalero and J. Elguero, *Tetrahedron Lett.*, 1997, **38**, 2557.
7 M. Casses, M. Duran, J. Mestres, N. Martin and M. Sola, *J. Org. Chem.*, 2001, **66**, 433.
8 O. G. Sinyashin, I. P. Romanova, G. G. Yusupova, A. A. Nafikova, V. I. Kovalenko, N. M. Azancheev, S. G. Fattakhov and V. S. Reznik, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 2064 (*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 2162).
9 V. L. Rusinov and O. G. Chupakhin, *Nitroazines*, Nauka, Novosibirsk, 1991, p. 133 (in Russian).

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