Synthesis and electrochemical properties of the *N*-isocyanurate derivative of azahomo[60]fullerene

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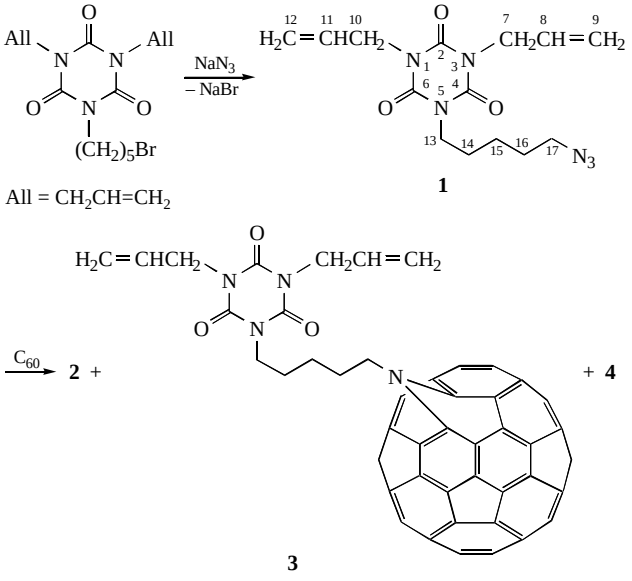
The cyclic voltammogram of the title compound exhibits three reversible reduction peaks which are less negative than that of [60]fullerene.

The development of new fullerene materials such as semiconductors, superconductors, ferromagnetics, optoelectronic materials and artificial photosynthesis systems are based on the electron-accepting properties of fullerenes.[1] In general, functionalization of [60]fullerene with a large number of substituents leads to a decrease in the electron affinity of the fullerene moiety. As a result, [60]fullerene derivatives are reduced electrochemically at more negative potentials than the parent C_{60}.[2] This problem has been successfully solved by attaching electron-withdrawing groups or 'periconjugation' fragments.[3–7] To increase the electron affinity of the fullerene derivatives, we proposed to add an isocyanuric acid moiety, which contains three electron-withdrawing carbonyl groups, to C_{60}.

We describe here the synthesis and electrochemical properties of the first example of isocyanurate-containing fullerene, 5-[5′-(azahomofullereno)pentyl]-1,3-diallyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione **3**, obtained by the [3 + 2]-cycloaddition of 5-[5′-(azidopentyl)]-1,3-diallyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione **1** to C_{60}.

Compound **1** was prepared by the reaction of 5-(5′-bromopentyl)-1,3-diallyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione with sodium azide in boiling dry acetone (8 h). The product was isolated as light yellow viscous liquid by column chromatography (75% yield). The structure of azide **1** was studied by ^{1}H NMR, ^{13}C NMR and IR spectroscopy, and the composition was determined by elemental analysis.† The identification of ^{1}H and ^{13}C NMR signals of methylene groups of the pentyl fragment in azide **1** was performed by comparing the experimental and calculated chemical shifts, taking into account the influence of substituents in alkanes. The chemical shifts of the ^{13}C signals were evaluated by the empirical Grant–Pole equation,[8] and the δ values of CH_2(13) and CH_2(17) proton signals were calculated according to the Shuleri equation.[9] The CH_2(14) and CH_2(16) proton signals were identified by an analysis of the selective double resonance of CH_2(14)-{CH_2(13)}, CH_2(13)-{CH_2(14)}, CH_2(16)-{CH_2(17)} and CH_2(17)-{CH_2(16)}.

The reaction of [60]fullerene (0.1 mmol) with azide **1** (0.3 mmol) was carried out in boiling dry *o*-dichlorobenzene under a nitrogen atmosphere. After 4 h, the solvent was removed by distillation, and the reaction mixture was separated by column chromatography on silica gel using toluene as an eluent. Unreacted fullerene (8% in terms of the initial amount) and products **2** (1–2%), **3** (20%) and **4** (5%) were obtained. The removal of the eluent in a vacuum resulted in compounds **2**–**4** as dark brown viscous liquids. To obtain the products as powders, they were dissolved in diethyl ether and then dried in a vacuum for 5 h.



The structure of compound **3** was examined by ^{1}H NMR, ^{13}C NMR, IR and UV spectroscopy, and the composition was determined by elemental analysis. According to the elemental analysis data, **3** is a monoadduct of C_{60} and azide **1**.‡

The ^{13}C NMR spectrum of compound **3** shows that the addition of azide **1** to C_{60} takes place at the 6,5-bond. This spectrum contains 32 signals in the region between δ 133 and 148 ppm, which is typical of the sp^2 carbon signals of fullerene derivatives. The intensities of four signals correspond to one carbon atom, and the intensities of 28 signals correspond to two carbon atoms. In accordance with the proposed structure, no sp^3 carbon signals of the fullerene fragment were observed.[10] This ^{13}C NMR

† **1**: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.48 [m, 2H, CH_2(15)], 1.68 [m, 2H, CH_2(14)], 1.90 [m, 2H, CH_2(16)], 3.43 [m, 2H, CH_2(17), AA′XX′ system, $^3J_{HH}$ 7.4 Hz], 3.91 [m, 2H, CH_2(13), AA′XX′ system, $^3J_{HH}$ 7.4 Hz], 4.46 [d, 4H, CH_2(7), CH_2(10), $^3J_{HH}$ 6.0 Hz], 5.23 [d, 2H, =CH_{cis}(9), =CH_{cis}(12)], 5.26 [d, 2H, =CH_{cis}(9), =CH_{cis}(12)], 5.85 [ddt, 2H, CH(8), CH(11), $^3J_{HH}^{cis}$ 9.0 Hz, $^3J_{HH}^{trans}$ 18.0 Hz]. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 24.78 [tm, C(15), $^1J_{CH}$ 125.6 Hz], 26.48 [tm, C(14), $^1J_{CH}$ 124.5 Hz], 31.73 [tm, C(16), $^1J_{CH}$ 130.4 Hz], 42.28 [tm, C(13), $^1J_{CH}$ 142.3 Hz, $^2J_{CH}$ 4.6 Hz, $^3J_{CH}$ 8.5 Hz], 44.46 [tm, C(7), C(10), $^1J_{CH}$ 143.6 Hz, $^2J_{CH}$ 5.2 Hz, $^3J_{CH}^{cis}$ 7.9 Hz, $^3J_{CH}^{trans}$ 13.3 Hz], 50.80 [tm, C(17), $^1J_{CH}$ 141.7 Hz], 118.41 [tm, C(9), C(12), $^1J_{CH}$ 157.5 Hz], 130.71 [dm, C(8), C(11), $^1J_{CH}$ 159.60 Hz], 148.04 [m, C(4), $^3J_{CH}$ 3.6 Hz], 148.28 [m, C(2), C(6), $^3J_{CH}$ 3.6 Hz]. IR (KBr, ν/cm^{-1}): 1691, 766 (C=O), 1645 (C=C), 933, 993 (=CH), 2943, 2852, 1460 (CH), 2098 (N_3). Found (%): C, 52.38; H, 6.72; N, 26.20. Calc. for $C_{14}H_{20}N_6O_3$ (%): C, 52.50; H, 6.25; N, 26.25.

‡ **3**: ^{1}H NMR (250 MHz, $CDCl_3$) δ: 1.47 [m, 2H, CH_2(15)], 1.67 [m, 2H, CH_2(14)], 1.89 [m, 2H, CH_2(16)], 3.40 [m, 2H, CH_2(17), AA′XX′ system, $^3J_{HH}$ 7.4 Hz], 3.88 [m, 2H, CH_2(13), AA′XX′ system, $^3J_{HH}$ 7.4 Hz], 4.46 [d, 4H, CH_2(7), CH_2(10), $^3J_{HH}$ 6.0 Hz], 5.23 [d, 2H, =CH_{cis}(9), =CH_{cis}(12)], 5.27 [d, 2H, =CH_{cis}(9), =CH_{cis}(12)], 5.82 [ddt, 2H, CH(8), CH(11), $^3J_{HH}^{cis}$ 9.0 Hz, $^3J_{HH}^{trans}$ 18.0 Hz]. ^{13}C NMR (100 MHz, $CDCl_3$) δ: 21.35 (*Me*Ph), 22.60 [C(15)], 24.42 [C(14)], 28.90 [C(16)], 42.31 [C(13)], 44.90 [C(7), C(10)], 51.30 [C(17)], 119.00 [C(9), C(12)], 125.21, 128.13 and 128.94 (Me*Ph*), 130.91 [C(8), C(11)], 133.69, 135.78, 136.18 (1C), 137.11, 137.29 (1C), 137.76, 137.79, 138.00, 138.45, 139.17, 140.70, 141.37, 142.57, 142.65, 142.74, 142.84, 143.05, 143.33, 143.48 (1C), 143.59, 143.78, 144.05, 144.09, 144.22, 144.26, 144.39, 144.49, 144.67, 144.97, 145.09 (1C), 146.89, 147.74 (1C), 148.41 [C(4)], 148.67 [C(2), C(6)]. UV–VIS [CH_2Cl_2, λ_{max}/nm (lg ε/dm^3 mol^{-1} cm^{-1})]: 261 (5.62), 330 (5.04), 403 (4.23), 430 (4.02), 546 (3.63). IR (KBr, ν/cm^{-1}): 1691, 763 (C=O), 1645 (C=C), 937, 990 (=CH), 2920, 2852, 1453 (CH). 526, 570, 1176 (C_{60}). Found (%): C, 87.30; H, 2.10; N, 5.48. Calc. for $C_{74}H_{20}N_4O_3\cdot(C_6H_5Me)_{0.2}$ (%): C, 87.81; H, 2.09; N, 5.43.

Table 1 Reduction of C_{60} and compound **3** [$E_{1/2}$ in a mixture of *o*-dichlorobenzene and MeCN (3:1) at 25 °C].[a]

Compound	E^1_{red} / V	E^2_{red} / V	E^3_{red} / V
C_{60}	–0.90	–1.25	–1.77
3	–0.82	–1.14	–1.68

[a]Solution concentrations, 1×10^{-3} mol dm^{-3}; supporting electrolyte, 0.1 M Bu_4NBF_4; scanning rate, 50 mV s^{-1}, working electrode, Pt; reference electrode, $Ag/AgNO_3$ in 0.01 M MeCN.

spectrum is consistent with the C_S symmetry of the molecule with an open annulene structure (the structure of azahomo[60]-fullerene).[10,11] In addition, the ^{13}C NMR spectrum of **3** showed signals of two equivalent allyl groups, five methylene and three carbonyl groups, two of which are equivalent.

The UV–VIS spectroscopy data also confirm the azahomofullerene structure of **3**.‡ The low-intensity broad absorption bands in the region 350–700 nm are assigned to the open annulene structure.[10] Parent azide **1** does not exhibit absorption bands in this region.

The signals of protons of two equivalent allyl substituents at the isocyanurate ring and of five methylene groups were observed in the ^1H NMR spectrum of **3**. Note that the chemical shifts of the signals due to methylene protons at the nitrogen atom of **3** do not differ from the chemical shifts of protons of this group in the parent azide, although it is well know that [60]fullerene shifts the signals of protons of neighbouring groups to the weak field region.[12]

The IR spectrum of compound **3** exhibits bands of both isocyanurate and fullerene fragments and no absorption bands in the azide region at 2100 cm^{-1}.‡

Thus, all structure data indicate that the [3 + 2]-cycloaddition of 5-[5′-(azidopentyl)]-1,3-diallyl-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione **1** to [60]fullerene results in the formation of a derivative having an open annulene structure.

Elemental analysis§ indicates that compound **4** is a diadduct of azide **1** and [60]fullerene.

Cyclic voltammograms of azahomo[60]fullerene **3** exhibited three reversible reduction peaks regardless of the scanning rate (20–250 mV). Each of these peaks corresponds to the transfer of one electron onto the fullerene. Note that azide **1** was not reduced under analogous conditions, and C_{60} exhibited three reversible reduction peaks (Table 1, Figure 1). It is of importance that all of the reduction potentials of compound **3** are less negative than the corresponding potential of [60]fullerene.

This unusual behaviour of azahomo[60]fullerene **3** arises from the strong electron-withdrawing influence of isocyanurate on the fullerene moiety through the methylene chain or though the intramolecular interaction of isocyanurate carbonyl groups and the fullerene moiety. Thus, compound **3** is the first example of a [60]fullerene monoadduct which is reversibly reduced at less negative potentials than C_{60}.[5–7]

§ **4**: IR (KBr, ν/cm^{-1}): 1691, 766 (C=O), 1645 (C=C), 933, 993 (=CH), 2941, 2861, 1460 (CH). Found (%): C, 80.49; H, 3.42; N, 7.30. Calc. for $C_{88}H_{40}N_8O_6$ (%): C, 80.98; H, 3.07; N, 7.36.

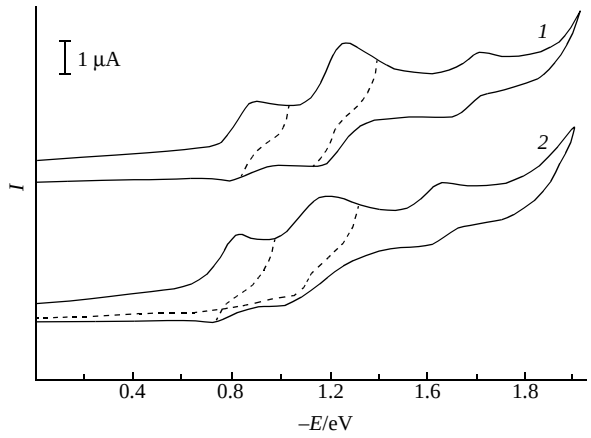


Figure 1 Cyclic voltammograms of (*1*) C_{60} and (*2*) azahomo[60]fullerene **3**.

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