Synthesis and electrochemical properties of *N*-isocyanurate-substituted aziridino[1,6][60]fullerene, an unusual product of cycloaddition to the 5,6-junction of fullerene

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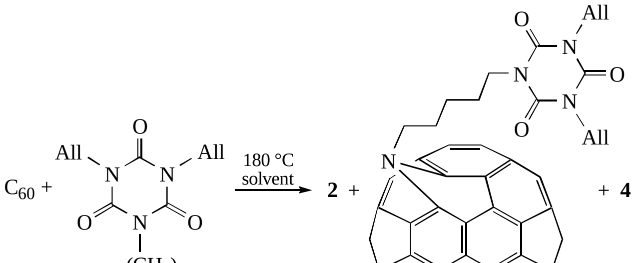
The main product of the cycloaddition of 1,3-diallyl-5-(5′-azidopentyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione to C_{60} at 100 °C is an *N*-isocyanurate-substituted aziridino[1,6][60]fullerene.

The reactions of fullerenes with organic azides result in various products. It is well known[1,2] that *N*-substituted triazolino[1,2]-[60]fullerenes are formed at the first stage of the reactions of azides with C_{60}. The subsequent thermal elimination of N_2 from triazolinofullerenes led to azahomo[60]fullerenes (the structures with an open 5,6-junction of fullerene) as major products and to aziridino[1,2][60]fullerenes (the product of addition to a closed 6,6-junction of fullerene) as minor products. Moreover, it was suggested[1] that aziridino[1,6][60]fullerenes at the 5,6-junction of C_{60} are intermediate products of dissociation without opening the fullerene framework. This formation of monoadducts was proved by the isolation of triazolino[1,2]- and aziridino[1,2][60]fullerenes, as well as azahomo[60]fullerenes, from reaction mixtures. The formation of aziridino[1,6][60]fullerenes is still an open question. Theoretically, these structures can exist and even be stable. Banks *et al.*[3] have reported on the isolation of aziridino[1,6][60]fullerene. However, Smith *et al.*[4] and Schick *et al.*[5] have cast doubt on these results. In this study, we examined the reaction of an *N*-isocyanurate-substituted azide with [60]fullerene and isolated a product, which was characterized as the 5,6-closed product of cycloaddition of the azide to C_{60} using spectral methods.

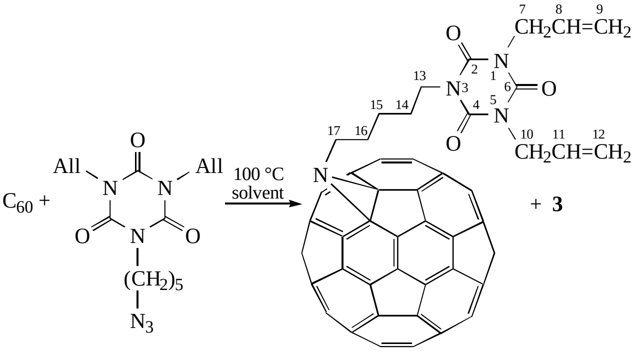
Earlier,[6] we found that the main product of the cycloaddition reactions of 1,3-diallyl-5-(5′-azidopentyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione **1** to C_{60} in *o*-dichlorobenzene at 180 °C was 1,3-diallyl-5-[5′-(azahomo[60]fullereno)pentyl]-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione **3**, which exhibited $R_f = 0.59$ (eluent: toluene–diethyl ether, 10:1). In addition to **3**, products **2** and **4** were also isolated from the reaction mixture by column chromatography in low yields.



1 All = $CH_2CH{=}CH_2$ **3**

We supposed[6] that compound **4** ($R_f = 0.1$) was the diadduct of azide **1** and [60]fullerene. The spectral characteristics of product **2** ($R_f = 0.75$) were not reported previously[6] because of a very low yield. According to the value of R_f, we suppose this product to be a low-polarity monoadduct of [60]fullerene and azide **1**.

To obtain compound **2** in amounts sufficient for a structural study by spectral methods, the conditions of the reaction of azide **1** with C_{60} were changed (*o*-dichlorobenzene as a solvent, 100 °C). The reaction mixture was heated for 4 h and chromatographed on silica gel. The unreacted fullerene (13% of the initial amount) and products **2** (23% yield) and **3** (1–2% yield) were isolated. After the removal of the eluent in a vacuum, product **2** was stirred in diethyl ether and dried in a vacuum at 50 °C for 2 h.



1 All = $CH_2CH{=}CH_2$ **2**

The elemental analysis of compound **2**[†] showed that it is a monoadduct of C_{60} and azide **1**. The ^{13}C NMR spectrum[†] of this monoadduct exhibited 31 signals in the region typical of *sp*^{2} carbon atoms of fullerene derivatives (δ between 130 and 150 ppm). The intensities of 4 signals corresponded to one carbon atom, and the intensities of 27 signals corresponded to two carbon atoms. An additional signal at δ 120.21 ppm was observed in the spectrum, the intensity of which corresponded to two carbon atoms. Earlier,[6] the signal at δ 120 ppm was not observed in the ^{13}C NMR spectra of compound **3** and azahomo[60]fullerenes.[4] If this signal is due to the *sp*^{3} carbon of fullerene, such a set of signals corresponds to a monoadduct at the 6,6-junction or closed 5,6-junction of fullerene.[7] Note that for known aziridino[1,2][60]fullerenes the *sp*^{3} carbon signals were usually detected at δ 75 and 85 ppm.[4] Banks *et al.*[3] observed a signal at 104.2 ppm in the ^{13}C NMR spectrum of aziridino[1,6][60]fullerene. This signal was ascribed to *sp*^{3} carbons of fullerene.

[†] Compound **2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.50 (d, 4H, $CH_2^{7,10}$, $^3J_{HH}$ 6.5 Hz), 5.88 (ddt, 2H, $CH_2^{8,11}$, $^3J_{HH}^{9cis}$ 10.9 Hz, $^3J_{HH}^{9trans}$ 18.0 Hz), 5.24 (d, 2H, $CH_{trans}^{9,12}$), 5.32 (d, 2H, $CH_{cis}^{9,12}$), 4.00 (m, AA′XX′, 2H, CH_2^{13}, $^3J_{HH}$ 7.4 Hz), 1.84 (m, 2H, CH_2^{14}), 1.79 (m, 2H, CH_2^{15}), 2.07 (m, 2H, CH_2^{16}), 3.81 (m, 2H, CH_2^{17}, $^3J_{HH}$ 7.0 Hz). ^{13}C NMR (100.62 MHz, $CDCl_3$) δ: 148.69 (s, 2C, $C^{2,4}$), 148.42 (s, 1C, C^6), 44.9 ($C^{7,10}$), 130.89 (dm, $C^{8,11}$, $^1J_{CH}$ 156.6 Hz), 118.99 (tm, $C^{9,12}$, $^1J_{CH}$ 158.2 Hz), 42.9 (C^{13}), 27.6 (C^{14}), 24.4 (C^{15}), 28.9 (C^{16}), 51.3 (C^{17}); $C_{60}N$: 120.21 (2C), 133.67 (2C), 135.77 (2C), 136.16 (2C), 137.10 (2C), 137.27 (1C), 137.78 (1C), 137.99 (2C), 139.15 (2C), 139.45 (2C), 140.68 (2C), 140.70 (2C), 141.36 (2C), 142.57 (2C), 142.67 (2C), 142.73 (2C), 142.84 (2C), 143.04 (2C), 143.32 (2C), 143.47 (1C), 143.57 (2C), 143.77 (2C), 144.04 (2C), 144.08 (2C), 144.25 (2C), 144.27 (2C), 144.36 (2C), 144.49 (2C), 144.65 (2C), 144.96 (2C), 146.68 (1C), 147.73 (2C). UV–VIS [CH_2Cl_2, λ_{max}/nm (lg ε)]: 261 (5.15), 330 (4.54), 403 (3.71), 430 (3.48), 555 (3.15). IR (KBr, ν/cm^{-1}): 1690 (C=O), 1645 (C=C), 928.991 (=C–H), 2921, 2851, 1455 (CH), 526 (C_{60}). Found (%): C, 87.30; H, 2.10; N. 5.48. Calc. for $C_{74}H_{20}N_4O_3 \cdot (C_6H_5CH_3)_{0.2}$ (%): C, 87.81; H, 2.09; N, 5.43.

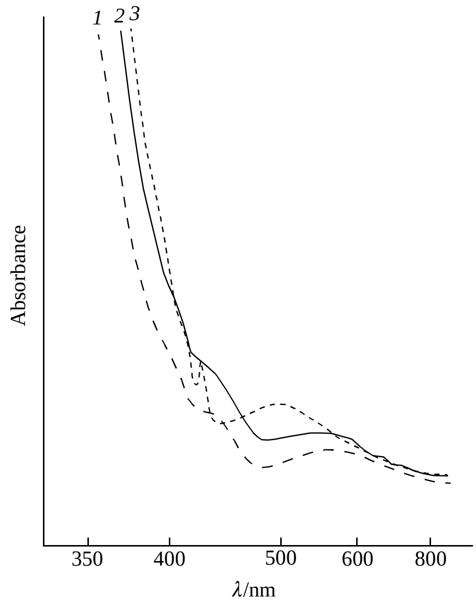


Figure 1 UV–VIS spectra of (*1*) *N*-isocyanurate-substituted aziridino[1,6]-[60]fullerene **2**, (*2*) azahomo[60]fullerene **3** and (*3*) aziridino[1,2][60]fullerene **5** in CH_2Cl_2.

The UV–VIS spectrum of compound **2**[†] (Figure 1) is similar to the spectrum of azahomo[60]fullerene **3**; the difference is in the position of a weak broad band at 500–600 nm (λ_{max} = 555 or 546 nm in the spectrum of compound **2** or **3**, respectively). Moreover, a weak and sharp peak at λ_{max} = 420–430 nm, which is typical of monoadducts at the closed 6,6-junction of fullerene,[4] is absent from the spectrum of compound **2**.

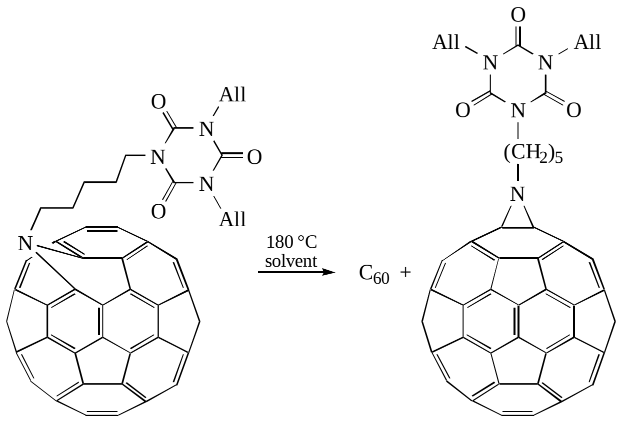
Thus, according to the UV–VIS and ^{13}C NMR spectra, compound **2** is a monoadduct of azide **1** at the 5,6-junction of fullerene (aziridino[1,6][60]fullerene). In the ^{13}C NMR spectrum, the signal at δ 120.21 ppm should be assigned to *sp*^{3} carbon of the fullerene fragment. This position of the signal of *sp*^{3} carbons of the fullerene fragment can be explained by either the electron-withdrawing influence of the isocyanurate heterocycle or the structure of aziridino[1,6][60]fullerene, in which the fullerene sphere was retained. The *sp*^{3} carbon signals at δ 120.62 and 94.19 ppm were observed in the spectrum of the product of reaction between C_{60} and diazomethane.[8] The *sp*^{3} carbon signals of the fullerene fragment of a phosphorylated isoxazoline derivative of fullerene were also detected in the same field (δ 124.7 and 104.1 ppm).[9] The assignment of the signal at δ 120.21 ppm to the *sp*^{3} carbon of the fullerene fragment in the ^{13}C NMR spectrum of compound **2** excludes the azahomofullerene structure of this compound, which might be an isomer of **3** with a different orientation of the substituent at nitrogen of the fullerene fragment. Note that the probability of separating such isomers is low because of the fast inversion at N at ambient temperature.[10]

The ^{1}H NMR spectrum of compound **2**[†] shows the signals of two equivalent allyl groups in the isocyanurate heterocycle and of five methylene groups, which bind the isocyanurate heterocycle to fullerene. Moreover, the signals of the methylene groups are 0.2–0.4 ppm downfield shifted in comparison with the position of these signals in the ^{1}H NMR spectrum of azide **1**.[6] The protons of the methylene group closest to the nitrogen atom of aziridinofullerene are more strongly shifted. Note that a downfield shift of the signals of protons is characteristic of fullerene derivatives at the 5,6-junction.[11]

The IR spectrum of compound **2** exhibits bands of both isocyanurate and fullerene fragments, and no absorption is detected in the azide region at 2100 cm^{-1}.[†]

Thus, the spectral data show that the main product of the cycloaddition of azide **1** to C_{60} at 100 °C is an aziridinofullerene at the 5,6-junction of C_{60} without opening the fullerene framework.

In connection with the isolation of aziridino[1,6][60]fullerene **2** and azahomo[60]fullerene **3** from the reaction mixture of **1** and C_{60}, the question arises of whether an *N*-isocyanurate-containing aziridino[1,2][60]fullerene (an aziridinofullerene at the closed 6,6-junction of C_{60}) can be formed. The latter was obtained by the thermal isomerization of azahomo[60]fullerene **3**.[6]



3 All = $CH_2CH{=}CH_2$ **5**

As a result of 20 h heating of azahomo[60]fullerene **3** (10 mg) in boiling *o*-dichlorobenzene (5 ml), the partial decomposition of azahomo[60]fullerene **3** to parent C_{60} (4 mg, 57% yield) and the formation of compound **5** (3 mg, 30% yield) were observed. The fullerene and compound **5** were separated by column chromatography on silica gel using toluene–diethyl ether (10:1) as an eluent (R_f 0.62 for **5**). The UV–VIS spectrum[‡] of **5** shows an absorption band at λ_{max} = 424 nm (Figure 1), which is typical of closed 6,6-bridged fullerene monoadducts.[4] The IR spectrum of compound **5** indicates the retention of fullerene and isocyanurate fragments. Note that compound **5** cannot be synthesised by the reaction of azide **1** and C_{60} in boiling *o*-dichlorobenzene because of a subsequent reaction of obtained azahomo[60]fullerene **3** with parent azide **1**. A viscous dark-brown liquid was formed by heating a mixture of azide **1** and C_{60} at 100 °C for 10 h. The isolation of individual products from this mass was unsuccessful.

Earlier,[6] we showed by cyclic voltammetry that azahomo[60]fullerene **3** is electrochemically reduced at less negative potentials than the reduction potentials of C_{60}. Here, we examined the electrochemical reduction of compound **2**. Similarly to azahomo[60]fullerene **3**,[6] compound **2** shows three reversible peaks of reduction ($E^1_{\text{red}} = -0.97$, $E^2_{\text{red}} = -1.40$ and $E^3_{\text{red}} = -1.86$ V),[§] each of them corresponds to the transfer of one electron to the aziridinofullerene molecule. However, these peaks are in the region of more negative potentials relative to the peaks of the reduction potential of C_{60} ($E^1_{\text{red}} = -0.92$, $E^2_{\text{red}} = -1.34$ and $E^3_{\text{red}} = -1.80$ V).[§] Such an electrochemical behaviour is typical of aziridino[1,2][60]fullerenes.[12]

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[‡] Compound **5**: UV–VIS [CH_2Cl_2, λ_{max}/nm (lg ε)]: 261 (5.15), 331 (4.48), 411 (4.38), 424 (4.37), 498 (4.30), 598 (4.22), 681 (4.16). IR (KBr, ν/cm^{-1}): 1696 (C=O), 1645 (C=C), 932.990 (=C–H), 2924, 2852, 1457 (CH), 526 (C_{60}).

[§] The conditions of the experiment: solution, a mixture of *o*-dichlorobenzene and MeCN (2:1); temperature, 25 °C; solution concentration, 1×10^{-3} mol dm^{-3}; working electrode, Pt; reference electrode, Ag/AgNO$_3$ 0.01 mol dm^{-3} in MeCN; supporting electrolyte, 0.05 mol dm^{-3} $Et_4N{\cdot}BF_4$; scan rate, 50 mV s^{-1}.

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