# First example of the interaction of fullerene $C_{60}$ with hydrazoic acid

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The one-pot synthesis of unsubstituted aziridinofullerene and triazolinofullerene was performed for the first time *via* the cycloaddition of fullerene $C_{60}$ with hydrazoic acid, which was generated *in situ* by the reaction of $NaN_3$ with $H_2SO_4$.

**Key words:** fullerene $C_{60}$, hydrazoic acid, cycloaddition, triazolinofullerene, aziridinofullerene.

The reactions of fullerenes with azides have attracted considerable interest due primarily to the possibility of preparing compounds containing azacyclopropane moieties,[1—7] which exhibit biological activity[8,9] and have electron-withdrawing properties.[10] The experience of the synthesis of N-unsubstituted aziridinofullerene[11—13] and azahomofullerene[14] is one of the simplest examples of the reactions of $C_{60}$ with azides. These syntheses were performed in several steps. The above-mentioned compounds are promising precursors in the synthesis of water-soluble aziridinofullerenes and azahomofullerenes with different structures.[11,15] By the moment of the beginning of our research, data on the direct interaction of fullerene $C_{60}$ with hydrazoic acid were absent in the literature. Only methods for the synthesis of *N*-(*tert*-butoxycarbonyl)-aziridino[2´,3´:1,9]fullerene,[11,12] *N*-(*tert*-butoxycarbonyl)-azahomofullerene,[14] and *N*-(diphenylphosphoryl)aziridino[2´,3´:1,9]fullerene[16] were described. The elimination of the *tert*-butoxycarbonyl[11,12,14] or diphenylphosphoryl[13] groups from these compounds resulted in the formation of the target N-unsubstituted aziridino- and azahomofullerenes, respectively.

The known methods for the synthesis of N-unsubstituted aziridinofullerene have drawbacks, such as the involvement of many steps, high energy consumption due to high temperatures, and long reaction times.

## Results and Discussion

Taking into account the aforesaid and with the aim of developing an efficient method for the synthesis of aziridinofullerenes, in the present study we performed for the first time the one-pot synthesis of N-unsubstituted aziridinofullerene (**1**) by the reaction of fullerene $C_{60}$ with hydrazoic acid ($C_{60} : HN_3 = 1 : 108$), which was generated *in situ* by the reaction of $NaN_3$ with $H_2SO_4$. The reaction of fullerene $C_{60}$ with $HN_3$ was performed in a sealed tube (60 °C, 3 h, chlorobenzene), which led to the formation of a mixture of mono- and bis-addition adducts (**1** and **2**, respectively) in a total yield of ~50% and a ratio of 11 : 1 (Scheme 1). We found that N-unsubstituted triazolinofullerene (**3**) can be synthesized as the only product in ~15% yield by performing the reaction at lower temperature (40 °C, 3 h, chlorobenzene, sealed tube). Compound **3** was shown to be unstable even at room temperature, and it undergoes gradual decomposition accompanied by elimination of $N_2$ to give unsubstituted aziridinofullerene **1**. The same result can be obtained by performing the reaction at 60 °C.

An increase in the duration of the reaction of $C_{60}$ with $HN_3$ to 6 h leads to a substantial increase in the yield of compound **2** and the formation of polyaddition cycloadducts as a poorly soluble black solid precipitate. The analysis of the solid precipitate by MALDI TOF mass spectrometry showed that the number of addends bound to the fullerene cage is 18, as evidence by the molecular ion at *m*/*z* 994.703.

The photochemical reaction (300 nm, 500 W, 25 min, toluene) of fullerene $C_{60}$ with $HN_3$ at room temperature produces exclusively aziridinofullerene **1** in ~15% yield. The photolysis was carried out in a sealed tube containing a toluene solution of fullerene $C_{60}$ saturated with hydrazoic acid. Under these conditions, we did not found adducts **3** of $C_{60}$ and $HN_3$, which could be formed *via* 1,3-dipolar cycloaddition, because the intermediate nitrene apparently underwent very rapid decomposition in the course of the photochemical reaction.[17]

We also synthesized aziridinofullerene **1** by bubbling gaseous $HN_3$ through a toluene solution of $C_{60}$ under dry argon flow at 80 °C for 1 h. The yield of the target cycloadduct **1** was 20%.

Compounds **1** and **3** were isolated by semipreparative HPLC and characterized. The $^{13}$C NMR spectrum of cy-

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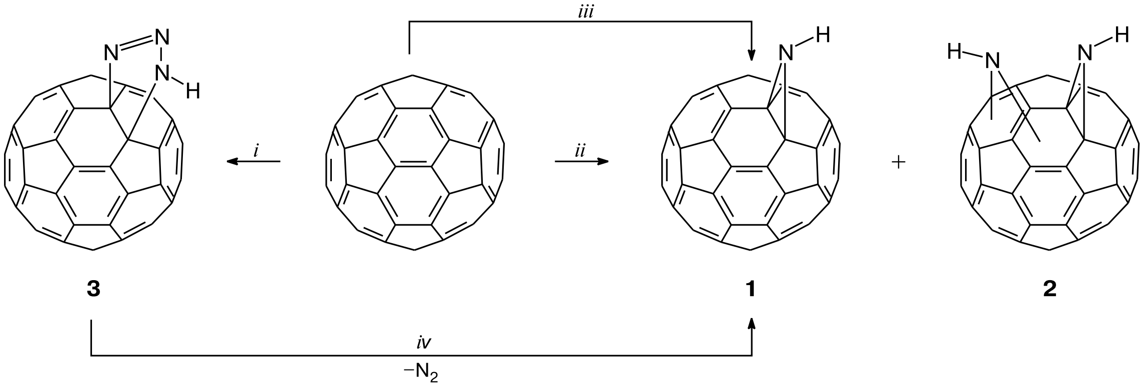
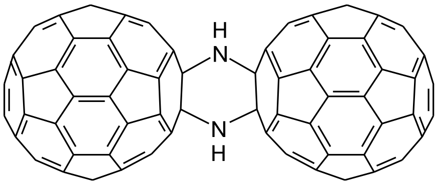
**Scheme 1**



*i.* $HN_3$, 40 °C, 3 h, chlorobenzene; *ii.* $HN_3$, 60 °C, 3 h, chlorobenzene; *iii.* $HN_3$, *h*ν (l = 300 nm), 25 °C, 25 min, toluene; *iv.* 60 °C, 30 min, chlorobenzene.

cloadduct **1** shows 16 signals in the region of $sp^2$-hybridized carbon atoms and one signal at δ 79.27 assigned to $sp^3$-hybridized carbon atoms, which is in good agreement with the literature data.[11,12] However, the chemical shift of the hydrogen atom of the aziridine ring in the $^1H$ NMR spectrum in $CDCl_3$ substantially differs from that reported in the literature[11] (δ 4.61 *versus* 5.9). The fact that the signal at δ 4.61 belongs to the hydrogen atom of the N—H bond in compound **1** is unambiguously established by the presence of the cross-peak with the carbon atom of the fullerene cage in the HMBC experiment and the absence of the corresponding signal in the $^1H$ NMR spectrum of the product obtained in the analogous reaction with $DN_3$.

The mass spectrum of compound **1** shows a molecular ion peak at *m/z* 735.656 (calculated 735.657) consistent with the molecular formula $C_{60}HN$ and a low-intensity peak at *m/z* 1471.316 (calculated 1471.313), which apparently belongs to the corresponding dimer (**D**).

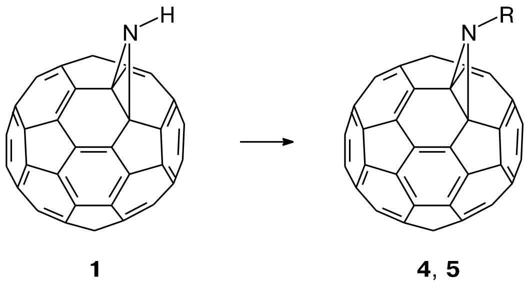


**D**

We failed to perform $^1H$ and $^{13}C$ NMR experiments with compound **3** because of low stability of this compound under ambient conditions. Based on the data from HPLC, MALDI TOF mass sepctrometry, and IR and UV spectroscopy, compound **3** was identified as triazolino[4´,5´:1,9]fullerene. Thus, the UV spectrum of **3** is characterized by an absorption maximum at λ = 425 nm. The IR spectrum of triazolinofullerene **3** shows absorption bands at 3431 (NH), 1601, 1501, 1459, 1380, 1080, 1040, 820, and 520 $cm^{-1}$. The mass spectrum of cycloadduct **3** corresponds to the molecular formula $C_{60}HN_3$ (*m/z* 762.598 $[M - H]^+$, 735.656 $[M - N_2]^+$, and 720.642 $[M - HN_3]^+$), which also confirms the fact that we obtained triazolinofullerene.

To more reliably establish the structure of aziridinofullerene **1**, we performed transformations characteristic of secondary amines, such as the *N*-acetylation and *N*-benzoylation of compound **1** by the corresponding carboxylic acid chlorides according to a procedure described earlier[15] (Scheme 2). The $^1H$ and $^{13}C$ NMR, IR, and UV spectroscopic characteristics and mass-spectrometric data for the resulting individual *N*-acetylaziridino[2´,3´:1,9]fullerene (**4**) and *N*-benzoylaziridino[2´,3´:1,9]fullerene (**5**) are in complete agreement with the data published in the literature.[14,15]

**Scheme 2**



**4:** R = Ac ($CH_3COCl$, Py, chlorobenzene, 70 °C, 1 h, 95%);
**5:** R = PhCO (PhCOCl, Py, chlorobenzene, 70 °C, 1 h, 92%)

In summary, we performed for the first time the one-pot synthesis of N-unsubstituted aziridino[2´,3´:1,9]fullerene and triazolino[4´,5´:1,9]fullerene by the reaction of hydrazoic acid with fullerene $C_{60}$ under the conditions of thermal and photochemical reactions.

## Experimental

Commercially available fullerene $C_{60}$ with 99.5% purity (G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhnii Novgorod) was used in experiments. The reaction products were analyzed by HPLC on an Altex 330 chromatograph (USA) equipped with an UV detector at a wavelength of 313 nm. Components of the mixture were separated on a 250×10 mm Cosmosil Buckyprep Waters semipreparative column at room temperature; toluene was used as the mobile phase; the flow rate was 2.0 mL $\text{min}^{-1}$. The IR spectra were recorded on a Vertex 70V (Bruker) spectrometer in KBr pellets. The UV spectra were measured on a LAMBDA 750 (Perkin—Elmer) spectrophotometer. The $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker Avance-400 spectrometer (400.13 and 100.62 MHz, respectively) with the use of a $CDCl_3$—$CS_2$ mixture (1 : 5) as the solvent. The positive- and negative-ion mass spectra were obtained on a MALDI TOF/TOF Autoflex-III Bruker instrument with $S_8$ as the matrix and in the absence of the matrix in the reflection mode. For deposition on a metal target, the samples were dissolved in toluene.

**Cycloaddition of hydrazoic acid to fullerene $C_{60}$ (general procedure).** Sodium azide (0.1 g) and distilled water (0.1 mL) were placed in a 7 mL glass tube. Then a solution of $C_{60}$ (0.0139 mmol) in chlorobenzene (2 mL) was added, and the tube was plunged into a vessel with liquid nitrogen until the reaction mixture was completely frozen, after which $H_2SO_4$ (0.15 g) was added to the mixture. The tube was sealed, placed in a miniature autoclave, and heated to 40 or 60 °C for 3 h, after which the reaction mixture was cooled to ~20 °C, twice washed with distilled water, and treated with an aqueous $NaHCO_3$ solution to the neutral point. Then toluene (7 mL) was added, and the organic layer was passed through a column with a small amount of silica gel. Reaction products **1**—**3** and fullerene $C_{60}$ were separated by semipreparative HPLC using toluene as the eluent. Compound **1** was identified by comparing its spectral characteristics with those published in the literature.[11,12] All experiments were carried out in dry argon flow.

**Triazolino[4´,5´:1,9]($C_{60}$-$I_h$)[5,6]fullerene (3).** IR, ν/$\text{cm}^{-1}$: 3431 (NH), 1601, 1501, 1459, 1380, 1080, 1040, 820, 520. UV ($CHCl_3$), $\lambda_{\text{max}}$/nm: 260, 328, 425. MALDI-TOF MS, found: $m/z$ 762.598 $[M - H]^+$. $C_{60}N_3$. Calculated: $M = 762.662$.

**Photochemical reaction of hydrazoic acid with fullerene $C_{60}$.** A solution of fullerene $C_{60}$ (0.0139 mmol) in dry degassed toluene (10 mL) was placed in a 15 mL quartz tube, and gaseous $HN_3$ was bubbled through the solution in dry argon flow for 10 min. The tube was plunged in a vessel with liquid nitrogen until the reaction mixture was completely frozen. Then the tube was sealed, heated to ~20 °C, and irradiated at $\lambda = 300$ nm using a 500 W bulb for 25 min. The reaction mixture was twice washed with distilled water and treated with an aqueous $NaHCO_3$ solution to the neutral point. The organic layer was passed through a column with a small amount of silica gel. Reaction product **1** and fullerene $C_{60}$ were separated by semipreparative HPLC using toluene as the eluent. Compound **1** was identified by comparing the spectral characteristics with those published in the literature.[11,12]

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