First example of the interaction of fullerene C\textsubscript{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\textsubscript{60} with hydrazoic acid, which was generated in situ by the reaction of NaN\textsubscript{3} with H\textsubscript{2}SO\textsubscript{4}.

**Key words:** fullerene C\textsubscript{60}, hydrazoic acid, cycloaddition, triazolinofullerene, aziridino-fullerene.

The reactions of fullerenes with azides have attracted considerable interest due to the possibility of preparing compounds containing azacyclopropane moieties,\textsuperscript{1–7} which exhibit biological activity\textsuperscript{8,9} and have electron-withdrawing properties.\textsuperscript{10} The experience of the synthesis of N-unsubstituted aziridinofullerene\textsuperscript{11–13} and azahomofullerene\textsuperscript{14} is one of the simplest examples of the reactions of C\textsubscript{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.\textsuperscript{11,15} By the moment of the beginning of our research, data on the direct interaction of fullerene C\textsubscript{60} with hydrazoic acid were absent in the literature. Only methods for the synthesis of N-(tert-butoxycarbonyl)-aziridino[2',3':1,9]fullerene,\textsuperscript{11,12} N-(tert-butoxycarbonyl)-azahomofulleren,\textsuperscript{14} and N-(diphenylphosphoryl)aziridino[2',3':1,9]fullerene\textsuperscript{16} were described. The elimination of the tert-butoxycarbonyl\textsuperscript{11,12,14} or diphenylphosphoryl\textsuperscript{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 aziridinofulleren 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\textsubscript{60} with hydrazoic acid (C\textsubscript{60}: HN\textsubscript{3} = 1:108), which was generated in situ by the reaction of NaN\textsubscript{3} with H\textsubscript{2}SO\textsubscript{4}. The reaction of fullerene C\textsubscript{60} with HN\textsubscript{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\textsubscript{3} 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\textsubscript{60} with HN\textsubscript{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\textsubscript{60} with HN\textsubscript{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\textsubscript{60} saturated with hydrazoic acid. Under these conditions, we did not found adducts 3 of C\textsubscript{60} and HN\textsubscript{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.\textsuperscript{17}

We also synthesized aziridinofullerene 1 by bubbling gaseous HN\textsubscript{3} through a toluene solution of C\textsubscript{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 \textsuperscript{13}C NMR spectrum of cy
cloadduct 1 shows 16 signals in the region of sp²-hybridized carbon atoms and one signal at δ 79.27 assigned to sp³-hybridized carbon atoms, which is in good agreement with the literature data.\textsuperscript{11,12} However, the chemical shift of the hydrogen atom of the aziridine ring in the \(^1\)H NMR spectrum in CDCl\(_3\) substantially differs from that reported in the literature\textsuperscript{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 \(^1\)H 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).

We failed to perform \(^1\)H 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 spectrometry, and IR and UV spectroscopy, compound 3 was identified as triazolinofullerene. Thus, the UV spectrum of 3 is characterized by an absorption maximum at \(\lambda = 425\) 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 aziridino fullerene 1, we performed transformations characteristic of secondary amines, such as the \(N\)-acetylation and \(N\)-benzylation of compound 1 by the corresponding carboxylic acid chlorides according to a procedure described earlier\textsuperscript{15} (Scheme 2). The \(^1\)H and \(^13\)C NMR, IR, and UV spectroscopic characteristics and mass-spectrometric data for the resulting individual \(N\)-acetylaaziridino[2\(^{\prime}\),3\(^{\prime}\):1,9]fullerene (4) and \(N\)-benzyllaaziridino[2\(^{\prime}\),3\(^{\prime}\):1,9]fullerene (5) are in complete agreement with the data published in the literature.\textsuperscript{14,15}

\begin{scheme}
\begin{align*}
i. & \text{HN}_3, 40^\circ\text{C, 3 h, chlorobenzene;} \\
ii. & \text{HN}_3, 60^\circ\text{C, 3 h, chlorobenzene;} \\
iii. & \text{HN}_3, h\nu (l = 300 \text{ nm}), 25^\circ\text{C, 25 min, toluene;} \\
iv. & 60^\circ\text{C, 30 min, chlorobenzene.}
\end{align*}
\end{scheme}

In summary, we performed for the first time the one-pot synthesis of \(N\)-unsubstituted aziridino[2\(^{\prime}\),3\(^{\prime}\):1,9]fullerene and triazolinofullerene 3 by the reaction of hydrazoic acid with fullerene C\(_{60}\) under the conditions of thermal and photochemical reactions.