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The synthesis of *N*-isocyanurato-substituted aziridino[1,2][60]fullerenes

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N-Isocyanurato-substituted aziridino[1,2][60]fullerenes were synthesized for the first time as the main products by the reaction of isocyanurato-substituted azides with C_{60}. The thermal stability and the electrochemical behavior of the compounds synthesized were studied.

Key words: [60]fullerene, azidoalkylisocyanurates, aziridino[1,2][60]-fullerenes, electrochemistry.

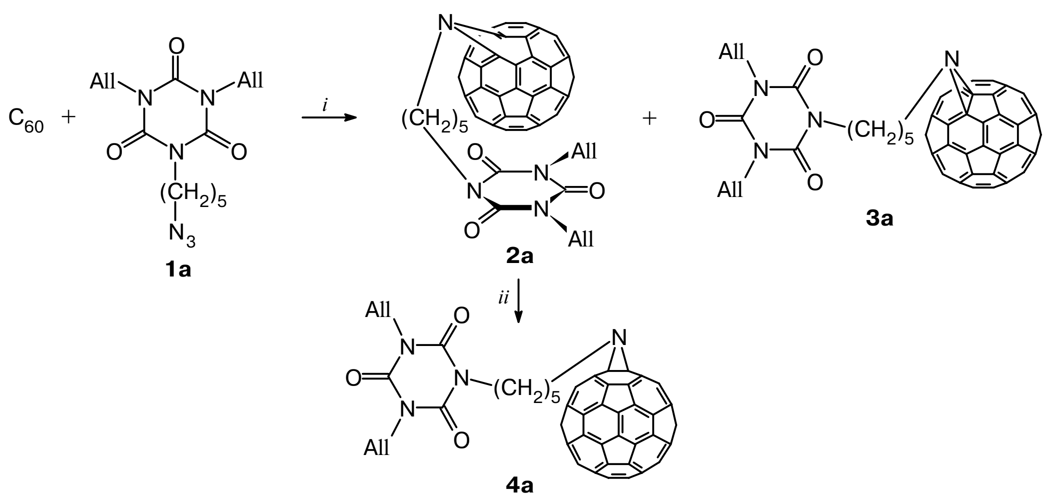
The introduction of electron-withdrawing substituents into a fullerene molecule is known[1] to increase in some cases the electron affinity of the fullerene spheroid. To study the mutual influence of the electron-withdrawing isocyanurate fragment and the fullerene cage, we developed methods of synthesis and studied the structures and properties of the fullerene monoadducts resulting from cycloaddition of isocyanuratoalkyl azides to C_{60}. The length of the polymethylene chain between the fullerene fragment and the isocyanurate heterocycle and the nature of the substituents in the latter were varied.

Previously,[2,3] we demonstrated that the main product formed in the reaction of 1,3-diallyl-5-(5-azidopentyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**1a**) with [60]fullerene in a *o*-dichlorobenzene solution at 180 °C is 1,3-diallyl-5-{5-(azahomo[60]fullereno)pentyl}-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**2a**), which undergoes electrochemical reduction at more negative potentials than the initial C_{60}. As a minor product, this reaction yields a stable adduct at the fullerene 5,6-bond formed without opening of the fullerene sphere, namely, 1,3-diallyl-5-{5-(aziridino[1,6][60]fullereno)pentyl}-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**3a**), whose redox properties did not differ from those of most fullerene monoadducts (Scheme 1).

In this study, we show that the reaction of C_{60} with other isocyanuratoalkyl azides **1b—e** under similar conditions (180 °C, *o*-dichlorobenzene) gives aziridino[1,2][60]fullerenes **4** resulting from cycloaddition at the 6,6-bond without opening of the fullerene sphere rather than the expected adducts with an azafulleroid structure, azahomo[60]fullerenes.[2—5]

Azides **1b—e** were synthesized by refluxing the corresponding 1,3-disubstituted-5-(ω-haloalkyl) isocyanurates **5b—e** with sodium azide in anhydrous acetone for 6—8 h (Scheme 2). The target compounds were isolated in a pure state by column chromatography. The initial compounds **5c—e** were prepared similarly to 1,3-diallyl-5-

Scheme 1



Reagents and conditions: *i*. *o*-DCB, 180 °C, 4 h; *ii*. *o*-DCB, 180 °C, 20 h.

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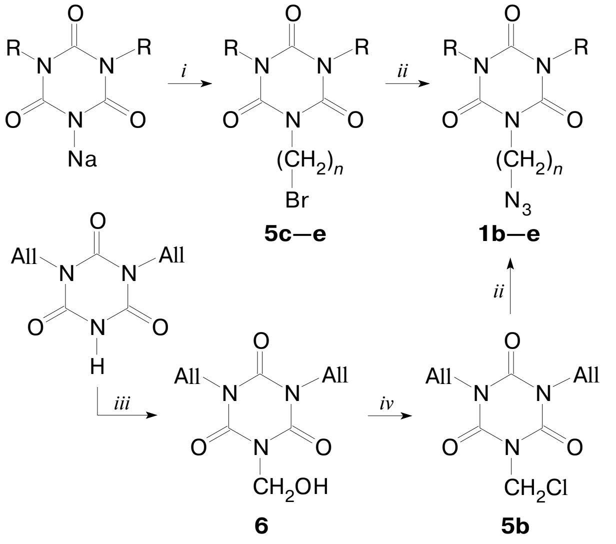
alkyl isocyanurates, known from the literature,[6,7] by the reaction of monosodium 1,3-diallyl- and 1,3-di-(2-cyanoethylisocyanurates with an excess of the corresponding dihalide. Compound **5b** is formed on treatment of 1,3-diallyl-5-hydroxymethyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**6**) with thionyl chloride. Compound **6** was formed in a good yield by oxymethylation of 1,3-diallylisocuanuric acid with formaldehyde. Azides **1b,c** are thick colorless liquids, while azides **1d,e** are white crystalline solids stable against atmospheric moisture. Over a period of several days at ~20 °C, azide **1b** was converted into a solid. The structures of compounds **1**, **5**, and **6** were determined by ^{1}H and ^{13}C NMR and IR spectroscopy; the compositions were confirmed by elemental analysis data (Table 1—4).

Scheme 2



1, 5	b	c	d	e
R	All	All	CH_2CH_2CN	CH_2CH_2CN
n	1	3	3	5

Reagents and conditions: (*i*) $Br(CH_2)_nBr$, $n = 3, 5$; DMF, 50—60 °C, 3 h;
(*ii*) NaN_3, Me_2CO, 6 h;
(*iii*) a 27% solution of CH_2O in H_2O, Py, MeCN, ~25 °C, 2 h;
(*iv*) $SOCl_2$, CH_3Cl, ~25 °C, 1 h and 61 °C, 2 h.

The reactions of C_{60} with azides **1b—e** were performed, like that with **1a**,[2] in a refluxed solution in *o*-dichlorobenzene. The final products and the unreacted fullerene (10—15% of the initial amount) were separated by column chromatography. The major reaction products thus isolated were compounds **4b—e** (in 20—25% yield relative to the fullerene taken in the reaction), which were monoadducts, as indicated by elemental analysis data.

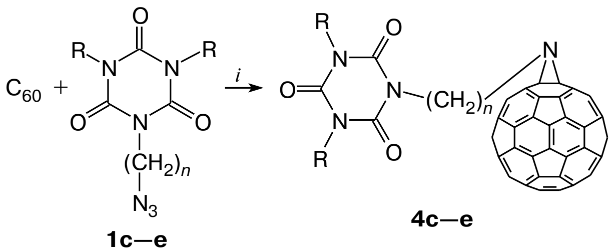
Spectroscopic investigation of the structures of monoadducts **4c—e** showed that each of them is an individual product of cycloaddition of the corresponding azide at the 6,6-bond of C_{60} (Scheme 3).

The UV spectra of compounds **4c—e** (Table 5) exhibit sharp narrow absorption bands at about 420 nm, typical of adducts at the [60]fullerene 6,6-bond.[5] In the region characteristic of the sp^2-hybridized carbon atoms of the fullerene fragment of the ^{13}C NMR spectra of these compounds (δ 133 to 147) (Table 6), 31 signals

Table 1. Yields and elemental analysis data of compounds **1b—e**, **4b—e**, **5b—e**, **6**, **7b—d**, and **9d,e**

Compound	Yield (%)	M.p. /°C	Found / Calculated (%) C	H	N	Hal	Molecular formula
1b	70		45.56 45.45	4.50 4.54	31.53 31.82		$C_{10}H_{12}N_6O_3$
1c	76		49.25 49.31	5.41 5.48	28.80 28.76		$C_{12}H_{16}N_6O_3$
1d	82	105	45.06 45.28	4.34 4.40	35.53 35.22		$C_{12}H_{14}N_8O_3$
1e	80	67	48.32 48.55	5.17 5.20	32.49 32.37		$C_{14}H_{18}N_8O_3$
4b	19		87.46 87.87	1.50 1.25	5.53 5.86		$C_{70}H_{12}N_4O_3$
4c	20		87.35 87.80	1.71 1.63	5.43 5.69		$C_{72}H_{16}N_4O_3$
4d	21		85.51 85.54	1.41 1.39	8.37 8.32		$C_{72}H_{14}N_6O_3$
4e	23		85.43 85.85	1.84 1.73	8.32 8.09		$C_{74}H_{18}N_6O_3$
5b	53	47	46.55 46.60	4.56 4.66	16.46 16.31	13.75 13.78	$C_{10}H_{12}ClN_3O_3$
5c	75		43.51 43.63	4.88 4.84	12.31 12.72	24.53 24.24	$C_{12}H_{16}BrN_3O_3$
5d	49	115	40.26 40.46	3.92 3.93	19.59 19.67	22.27 22.45	$C_{12}H_{14}BrN_5O_3$
5e	48	79—81	44.51 43.75	4.90 4.68	18.31 18.23	20.53 20.83	$C_{14}H_{18}BrN_5O_3$
6	70	148	53.21 53.81	6.12 5.83	18.51 18.83		$C_{10}H_{13}N_3O_3$
7b	5		80.31 80.53	1.70 2.01	9.52 9.39		$C_{80}H_{24}N_8O_6$
7c	4		80.43 80.76	2.90 2.56	8.79 8.97		$C_{84}H_{32}N_8O_6$
7d	5		77.31 77.53	2.58 2.15	7.29 7.38		$C_{84}H_{28}N_{12}O_6$
8	3		87.32 87.80	1.17 1.63	5.49 5.69		$C_{72}H_{16}N_4O_3$
9d	51	118	49.61 49.65	4.70 4.85	28.63 28.96		$C_{24}H_{28}N_{12}O_6$
9e	54	80	52.60 52.83	5.42 5.66	26.06 26.41		$C_{28}H_{36}N_{12}O_6$

Scheme 3



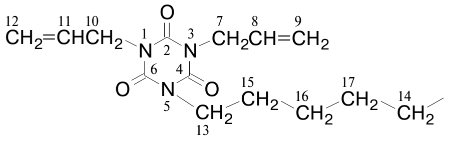
i. *o*-DCB, 180 °C, 4 h.

Table 2. ^{1}H NMR spectra (CDCl$_3$) of compounds **1b—e**, **4b—e**, **5b—e**, and **6**

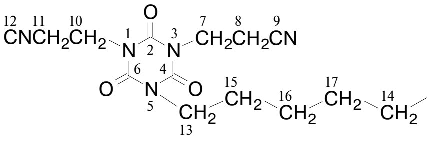
Compound	δ ($^3J_{HH}$/Hz)								
	NC(7,10)H$_2$ (4 H)	NC(13)H$_2$ (2 H)	NC(14)H$_2$ (2 H)	C(15)H$_2$ (2 H)	C(16)H$_2$ (2 H)	C(17)H$_2$ (2 H)	C(8,11)H	C(9,12)H$_{trans}$ (2 H)	C(9,12)H$_{cis}$ (2 H)
1b	4.43 d (J = 5.0)	5.22 s				5.81 ddt	5.27 d (2 H)	5.19 d (J = 17.1)	(J = 10.2)
1c	4.45 d (J = 8.0)	4.32 m	3.35 m	2.17 m			5.84 ddt (2 H)	5.27 d (J = 20.0)	5.19 d (J = 12.0)
1d	4.07 m* (J = 6.5)	3.92 m	3.47 m	2.12 m			2.71 (m, 4 H, J = 6.0)*		
1e	4.10 m (J = 6.5)	3.83 m	3.47 m	2.12 m	1.50 m		2.73 (t, 4 H, J = 6.0)		
4b	4.58 d, 4.62 d (J = 6.0)	5.85 s, 5.93 s					5.98 m	5.41 d, 5.42 d (J = 17.3)	5.30 d, 5.31 d (J = 9.9)
4c	4.52 d (J = 6.0)	4.02 m	3.39 m	2.21 m			5.92 ddt	5.35 d (J = 18.4)	5.27 d (J = 10.2)
4d	4.25 t (J = 4.2)	4.23 m	3.98 m	2.51 m			2.80 (m, 4 H, J = 6.8)		
4e	4.25 m (J = 4.3)	4.05 m	3.93 m	1.88 m	1.77 m	2.09 m	2.92 (m, 4 H, J = 6.8)		
5b	4.49 d (J = 4.49)	5.67 s					5.87 ddt	5.32 d (J = 18.0)	5.26 d (J = 10.0)
5c	4.42 d (J = 6.0)	3.97 m	3.33 m	2.15 m			5.81 ddt	5.24 d (J = 17.0)	5.10 d (J = 12.0)
5d	4.20 m (J = 6.5)	4.13 m	3.47 m	2.27 m			2.71 (m, 4 H, J = 6.5)		
5e	4.25 m (J = 6.5)	3.92 m	3.42 m		1.70 m		2.76 (m, 4 H, J = 6.5)		
6	4.49 d (J = 5.8)	5.45 d (J = 10.0) 3.78 (OH)					5.97 ddt	5.31 d (J = 18.5)	5.26 d (J = 10.0)
9d	4.24 m (J = 6.5)	4.05 m	3.46 m	2.27 m			2.79 (m, 4 H, J = 6.8)		
9e	4.22 m (J = 6.5)	3.91 m	3.41 m	1.90 m	1.49 m	1.68 m	2.79 (m, 4 H, J = 6.8)		

* For the protons of all methylene groups, $^3J_{HH} = 1/2(^3J_{AX} + {}^3J_{AX'})$ for the AA′XX′-system spectrum.

Table 3. ^{13}C NMR (CDCl$_3$) spectra of compounds **1b—e** and **5b**



b, c



d, e

Atom	δ ($^1J_{CH}$/Hz)				
	1b	**1c**	**1d**	**1e**	**5b**
C(2)	147.70 m	148.00 m	148.15 m	148.17 m	147.38 m
C(4), C(6)	148.07 m	148.60 m	148.15 m	148.06 m	146.85 m
C(7), C(10)	44.29 tm (142.2)	44.82 tm (140.0)	38.30 tm (145.0)	38.25 tm (147.6)	44.73 tm (143.4)
C(8), C(11)	130.22 dm (159.1)	130.68 dm (159.6)	16.31 dm (140.8)	16.38 dm (137.5)	130.21 dm (158.9)
C(9), C(12)	119.07 tm (157.35)	118.77 tm (156.8)	116.45 tm (5.2)*	116.28 tm (5.5)*	118.85 tm (157.5)
C(13)	57.07 tm (161.0)	41.79 tm (142.9)	42.25 tm (143.3)	43.06 tm (148.9)	49.77 tm (171.13)
C(14)		29.48 tm (151.7)	29.63 tm (152.3)	33.12 tm (147.2)	
C(15)		30.50 tm (127.3)	30.28 tm (128.2)	26.58 tm (130.5)	
C(16)				24.94 tm (127.5)	
C(17)				31.87 tm (125.3)	

* $^2J_{CH}$.

Table 4. IR spectra (cm^{-1}) of compounds **1b—e**, **4b—e**, **5b—e**, **6**, **7b,c,** and **9d,e**

Compound	ν(C=O)	ν(C=C)	δ(CH)	ν(CN)	ν(CHal) or ν(OH)	ν(N$_3$)	ν(C$_{60}$)
1b	1700	1645	940, 1000			2117	
1c	1685	1648	940, 1000			2105	
1d	1700			2255		2100	
1e	1690			2255		2105	
4b	1694	1647	930, 989				527
4c	1691	1646	930, 989				527
4d	1693			2250			526
4e	1693			2252			527
5b	1700		942, 1000		703 (ν(CCl))		
5c	1700	1646	934, 1000		500 (ν(CBr))		
5d	1690			2260	500 (ν(CBr))		
5e	1688			2258	500 (ν(CBr))		
6	1690		935, 1010		3480 (ν(OH))		
7b	1691	1645	931, 990				527
7c	1690	1645	931, 990				527
9d	1691			2252			
9e	1690			2253			

were found. Four of them corresponded in intensity to one carbon, and 27 signals corresponded to two carbons. In addition, the ^{13}C NMR spectrum of this compound exhibited signals with δ ~120, which belonged, in our opinion, to the sp^3-hybridized carbon atoms of fullerene incorporated in the aziridine heterocycle. It should be noted that the in ^{13}C NMR spectra of known aziridino[1,2][60]fullerenes, the signals due to the sp^3 carbon atoms usually occur at about 70—85 ppm.[5] The downfield shift of the signals for the sp^3 carbon atoms of the fullerene fragment in the spectra of **4c—e** appears to be due to the electron-withdrawing influence of the isocyanurate fragment. For example, signals for sp^3 carbon atoms at δ 120.62 and 94.19 have been observed previously in the ^{13}C NMR spectrum of the [60]fullerene adduct with diazomethane.[8] The same region of the spectrum was found to contain signals for the sp^3 carbon atoms in the phosphorylated isoxazoline derivative of [60]fullerene (δ 124.7 and 104.1).[9]

The isocyanurate fragment is responsible for two singlets due to the carbonyl groups and signals of the carbon atoms of the two equivalent substituents (either allylic or cyanoethyl) in the ^{13}C NMR spectra of compounds **4c—e** (see Table 6). The equivalence of substituents in the isocyanurate rings is also indicated by the data of ^{1}H NMR spectra of compounds **4c—e**. It should be noted that the signals of protons of the methylene group attached directly to nitrogen of the aziridinofullerene fragment did not shift significantly relative to the positions of the signals for these protons in the spectra of the initial azides (see Table 2); this is typical of monoadducts at the fullerene 6,6-bond.[10] The IR spectra (see Table 4) of compounds **4c—e** fully corresponded to the structures of monoisocyanurato-substituted fullerenes.

Table 5. UV spectra of compounds **4b—e**, **7b,c**, and **9d,e** in CH$_2$Cl$_2$

Compound	λ$_{max}$/nm (log ε/dm^3 mol^{-1} cm^{-1})
4b	261 (5.07), 329 (4.57), *421* (3.48), 539 (3.15)
4c	261 (5.10), 328 (4.58), *428* (3.47), 538 (3.14)
4d	259 (5.13), 327 (4.55), *423* (3.33), 507 (3.05), 543 (3.03)
4e	259 (5.08), 326 (4.52), *422* (3.35), 508 (3.03), 536 (3.02)
7b	259 (4.36), 322 (3.82)
7c	259 (5.06), 323 (4.63)
9d	258 (4.85), 323 (4.46)
9e	256 (4.85), 321 (4.46)

The result of the reaction of C_{60} with azide **1b** was of interest by itself. The UV spectrum of the major product **4b** (see Table 5) displayed an absorption band at about 421 nm, typical of 6,6-bond adducts; however, it was somewhat broader than the analogous bands in the spectra of monoadducts **4c—e**. The ^{13}C NMR spectrum of product **4b** contained 45 signals in the region of δ 133—147, three signals with equal intensities in the region of carbonyl groups with δ 149—147, and three signals with δ 120.18, 83.0, and 58.43 (see Table 6), of which the first was assigned to the fullerene sp^3 carbon atoms incorporated in the aziridine heterocycle, while the last one was attributed to the carbon atom of the methylene group attached directly to aziridine nitrogen. In addition, the allyl groups of the isocyanurate fragment were responsible for two groups of signals. Two groups of signals due to the protons of the allyl groups were also detected in the ^{1}H NMR spectrum of product **4b** (see Table 2). Instead of the one expected singlet for the protons of the methyl group between the isocyanurate and aziridine fragments, two singlets with δ 5.85 and 5.93 were observed. It should also be noted that the signals of all protons in the spectrum of compound **4b** undergo a substantial downfield shift from their positions in the spectrum of the initial azide.

The abnormal spectral characteristics of the product of reaction of C_{60} with azide **1b** might be due, among

Table 6. ^{13}C NMR spectra of compounds **4b—e** and **9e** ($CDCl_3$)

Atom	δ ($^1J_{CH}$/Hz)				
	4b	**4c**	**4d**	**4e**	**9e**
C(2)	148.71, 148.61, 148.26	148.47	148.70	148.19	148.19 m
C(4), C(6)	149.08	148.57	148.12	148.16 m	
C(7), C(10)	45.20, 45.26	45.09	38.48	38.36	38.35 tm (147.6)
C(8), C(11)	130.65, 130.85	130.97	16.58	16.48	16.43 tm (137.4)
C(9), C(12)	119.52, 119.48	119.31	116.40	116.29	115.98 tm (5.2)*
C(13)	58.43, 83.0	42.07	42.48	43.40	43.19 tm (142.6)
C(14)		49.98	50.25	51.20	33.81 tm (151.0)
C(15)		26.82	30.30	28.87	26.69 tm (121.3)
C(16)				27.24	25.04 tm (121.65)
C(17)				27.61	31.99 tm (132.7)
$C_{60}N$	120.21 133.79, 136.10, 136.32, 136.40, 137.75, 138.45, 138.51, 138.68, 139.40, 139.93, 140.05, 140.85, 140.96, 141.82, 142.08, 142.12, 142.63, 142.69, 142.77, 142.85, 143.03, 143.04, 143.05, 143.11, 143.12, 143.38, 143.51, 143.55, 143.75, 143.76, 143.84, 143.85, 144.10, 144.21, 144.25, 144.36, 144.47, 144.51, 144.76, 144.80, 144.83, 144.85, 145.11, 145.15, 147.79	**2C:** ** 120.28, 133.87, 135.78, 136.36, 136.58, 138.24, 138.57, 139.34, 140.84, 141.37, 142.70, 142.72, 142.76, 142.94, 143.10, 143.41, 143.61, 143.84, 143.93, 144.16, 144.28, 144.30, 144.43, 144.52, 144.66, 144.68, 144.92, 147.66 **1C:** ** 137.73, 137.94, 140.21, 144.56	**2C:** ** 120.30, 133.84, 135.74, 136.19, 136.43, 138.26, 138.59, 139.45, 140.92, 140.93, 141.31, 142.72, 142.77, 142.78, 143.02, 143.41, 143.61, 143.84, 143.93, 144.16, 144.28, 144.30, 144.43, 144.52, 144.66, 144.68, 144.92, 147.66 **1C:** ** 137.73, 137.94, 140.21, 144.56	**2C:** ** 120.21, 133.64, 135.73, 136.13, 137.06, 137.96, 138.42, 139.14, 141.32, 142.20, 142.55, 142.62, 142.71, 142.83, 143.08, 143.32, 143.58, 143.76, 144.02, 144.08, 144.22, 144.24, 144.37, 144.47, 144.64, 144.94, 145.06, 147.69 **1C:** ** 137.13, 137.77, 140.71, 144.57	

* $^2J_{CH}$.

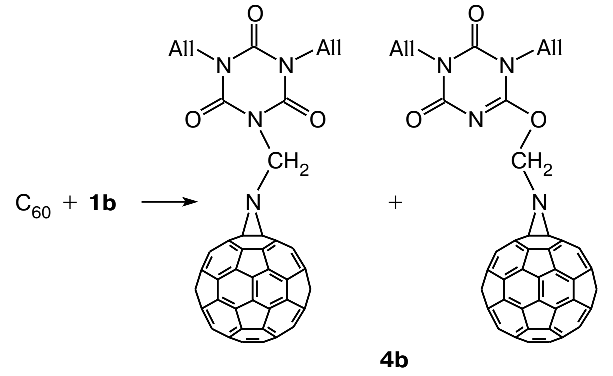
** The signals whose intensity corresponds to one (1C) and two (2C) carbon atoms are given.

other reasons, to the fact that this reaction affords a mixture of two isomers of azahomo[60]fullerene **2b**, differing in the arrangement of the substituent at the nitrogen atom of the aziridine fragment with respect to the fullerene spheroid. However, all the azahomo[60]fullerenes known from the literature[4,5] are characterized by fast inversion of nitrogen of the $C_{60}N$ fragment, which precludes detection of the isomers even at low temperatures.[4] Meanwhile, the azahomo[60]fullerene structure does not comply with the presence of signals with δ 120.18 and 83.0 in the ^{13}C NMR spectrum of product **4b**, or with the number and relative intensities of signals of the carbonyl carbon atoms, or with the number of signals in the region of the sp^2-hybridized carbon atoms of the fullerene fragments. The same spectral parameters make it possible to reject the presence of the azahomo[60]fullerene **2b** in the aziridino[1,2][60]fullerene **4b** sample isolated.

We are more disposed to attribute the specific spectral pattern of the reaction product formed from C_{60} and azide **1b** to the formation of a mixture of two isomers differing in the structure of the isocyanurate fragment. It is known that isocyanuric acid derivatives can exist as either N- or O-isomers.[11,12] Therefore, based on the published data and the data of NMR and IR spectra of product **4b**, we cannot rule out the possibility that the cycloaddition of azide **1b** with C_{60} has given a mixture of N- and O-isomers. The N- to O-isomer ratio in the mixture varied from 1 : 1 to 2 : 1, depending on the process duration (Scheme 4).

This assumption is supported by the presence of a signal with δ 83.0 in the ^{13}C NMR spectrum and two singlets with δ 5.85 and 5.93 in the ^1H NMR spectrum. In the IR spectrum of a solid sample, the absorption band at 1027 cm^{-1} corresponds to vibrations of the C—O bond. The IR spectrum of solid **4b** does not differ from that of its solution in $CDCl_3$ in the regions free from the absorption bands of the solvent. In addition, no changes are observed in the ^1H NMR spectrum of **4b** upon either

Scheme 4



4b

keeping the sample for 15 days at room temperature or upon heating it to 50 °C in an NMR spectrometer.

Thus, study of the cycloaddition of isocyanurato-substituted azides **1a—e** to C_{60} at 180 °C showed that both azahomo[60]fullerenes[2] and aziridino[1,2][60]fullerenes can be produced as the major products. Previously,[3] we showed that azahomo[60]fullerene **2a** isomerizes into aziridino[1,2][60]fullerene **4a** on prolonged (~20 h) refluxing in an *o*-dichlorobenzene solution. When aziridino[1,2][60]fullerenes **4b—e** were heated under similar conditions with monitoring by UV spectroscopy and TLC, aziridino[1,2][60]fullerenes **4d** and **4e** remained unchanged, while their structural analogs **4b** and **4c** decomposed to give C_{60}. This experiment demonstrates that isocyanurato-substituted aziridino[1,2][60]fullerenes are thermally more stable than the corresponding azahomo[60]fullerenes.

It should be noted that, apart from monoadducts **4b—e**, these reactions give compounds **7b—d**, which are fullerene bis-adducts with the corresponding azide, in yields not more than 5%. The formation of low-polarity monoadduct **8**, whose yield did not exceed 2—3%, was observed in the reaction of C_{60} with azide **1c**. Due to the low yields, the structures of bis-adducts **7b—d** and monoadduct **8** were not studied by NMR spectroscopy methods.

In addition to the above-mentioned compounds, products **9d** and **9e**, containing no fullerene fragment in the molecule, were isolated upon the reaction of C_{60} with azides **1d** and **1e**, containing cyanoethyl substituents in the isocyanurate ring. The yield of these products depends on the amount of the azide used in the reaction. When the reaction of C_{60} was carried out with an excess of azide **1e**, compound **9e** was isolated and characterized by ^{1}H and ^{13}C NMR, IR, and UV spectroscopy. The absence of an absorption band for the azido group in the IR spectrum, the equivalence of two cyanoethyl substituents in the isocyanurate ring, and the absence of additional signals in the ^{13}C NMR spectrum of this compound allowed us to conclude that product **9e** is an azo compound. Azo compounds are known to result upon dimerization of nitrenes generated either thermally or photochemically from the corresponding azides.[13]

Now we will consider the reasons for the formation of products with different structures in the reactions of isocyanurato-substituted azides with C_{60} under the same conditions (temperature, solvent, and reaction duration) using the experimental results we obtained and the published data concerning the mechanisms of cycloaddition of organic azides to C_{60}. Presumably,[14] azahomofullerenes result from [3+2]-cycloaddition of the organic azide to fullerene, whose first step gives rise to triazolino[1,2][60]fullerene **10**. This product, being thermally unstable, eliminates a nitrogen molecule, being thus converted into aziridino[1,6][60]fullerene **3**, which subsequently isomerizes into azahomo[60]fullerene **2**. The formation of aziridino[1,2][60]fullerene **4** is attributed to a different reaction mechanism, according to which the organic azide first decomposes to give the corresponding nitrene,[15] which then reacts with a C_{60} molecule according to [2+1]-cycloaddition pattern. This mechanism was proved only for azidoformates.[15]

The formation of aziridino[1,2][60]fullerenes **4d—e** in the reaction of C_{60} with azides **1d** or **1e** proceeds apparently according to the [2+1]-cycloaddition route that includes generation of the corresponding nitrenes under the reaction conditions (Scheme 5). Note that refluxing of individual azides in a *o*-dichlorobenzene solution in the absence of fullerene gives polymeric products rather than compounds **9d** and **9e**. In our opinion, decomposition of azides containing cyanoethyl substituents in the isocyanurate ring to give nitrenes is promoted by the fullerene.

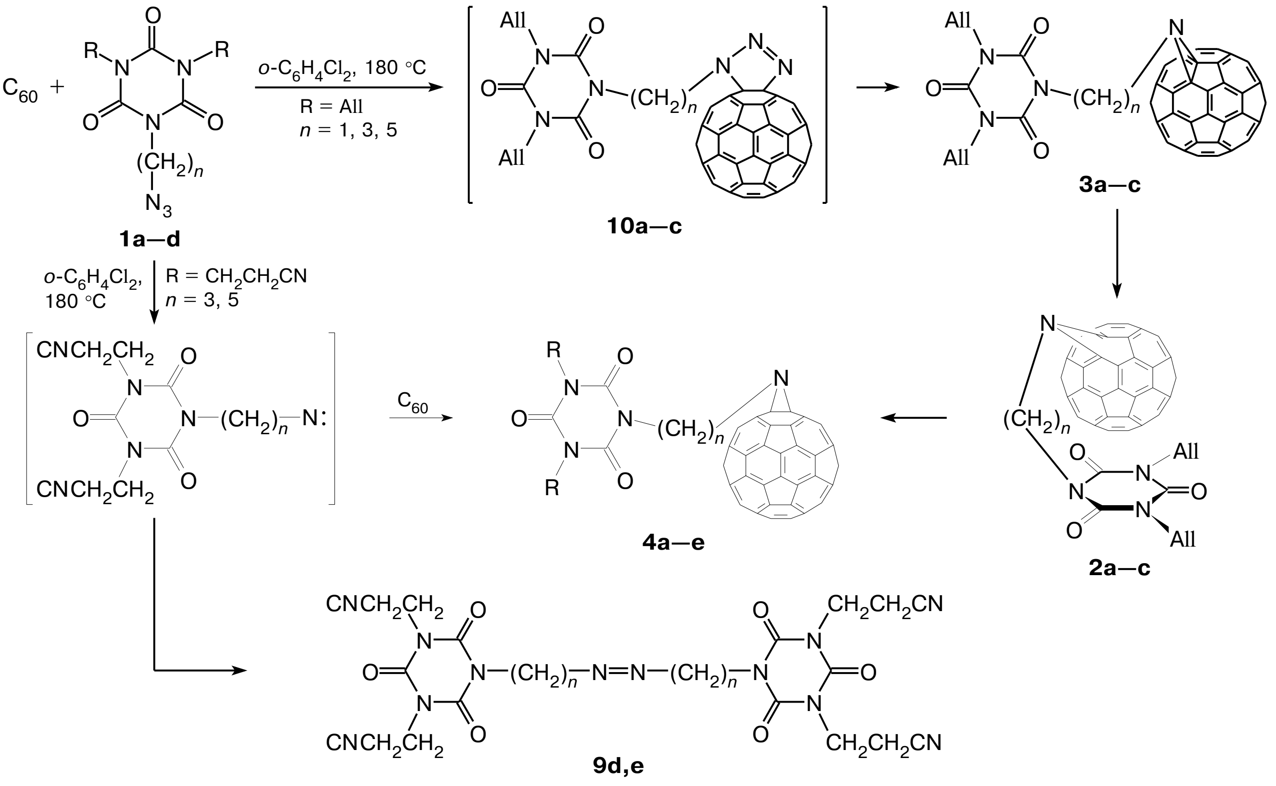
In the reactions of azides **1a—c** with C_{60}, we were unable to isolate or detect azo compounds. Based on the data obtained, we believe that azides **1a—c** add to fullerene according to the [3+2]-cycloaddition pattern to give initially triazolino[1,2][60]fullerenes **10a—c**, which decompose under the reaction conditions to aziridino[1,6][60]fullerenes **3a—c**, which, in turn, isomerize into the corresponding azahomo[60]fullerenes **2a—c**. The latter products are converted into aziridino[1,2][60]fullerenes **4a—c**, this transition being apparently facilitated by the close positions of the electron-withdrawing isocyanurate ring and the fulleroid fragment, which decreases the strength of the double bond, whose strain is widely discussed in the literature.[16] Note that for azide **1a**, the formation of aziridino[1,6][60]fullerene[2,3] **3a** and azahomo[60]fullerene[2,3] **2a** and the subsequent thermal transformations of monoadduct **3a** into compound **2a** and of **2a** into aziridino[1,2][60]fullerene[3] **4a** were proved experimentally.

Previously,[2] we found that azahomo[60]fullerene **2a** undergoes stepwise and reversible reduction at less negative potentials than the initial C_{60}. We studied the electrochemical behavior of aziridino[1,2][60]fullerenes **4c—e** prepared in this work by cyclic voltammetry. Like azafulleroid **2a**, compounds **4c—e** undergo reversible and stepwise electrochemical reduction in which one electron is transferred to the fullerene fragment in each step (Table 7); however, this occurs at more negative potentials than with C_{60}, which is typical of C_{60} monoadducts with dipolarophilic reagents.[10] This is due to the disruption of conjugation in the π-electronic system of fullerene upon the appearance of sp^3-hybridized carbon atoms. The initial azides were not reduced under these conditions.

Table 7. Reduction peak potentials ($E_{\text{p,red}}$/V) of C_{60} and compounds **4c,d,e**

Compound	$E^1_{\text{p,red}}$	$E^2_{\text{p,red}}$	$E^3_{\text{p,red}}$
C_{60}	−0.93	−1.34	−1.79
4c	−0.95	−1.38	—
4d	−0.94	−1.35	−1.83
4e	−0.95	−1.37	−1.80

Scheme 5



The data we obtained on the electrochemical reduction suggest that the main factor determining the redox potentials of compound **2a** is most likely the through-space intramolecular interaction between the fullerene fragment and the highly polar carbonyl groups of the isocyanurate heterocycle,[11] resulting in a decrease in the electron density on fullerene. This assumption is supported by the data of the UV spectrum of compound **2a**, which exhibits a charge transfer band with λ_{max} = 945 nm, missing from the spectra of other isocyanurato-substituted fullerenes.

Experimental

IR spectra were recorded on a Bruker IFS-113V FT IR spectrometer for fullerene derivatives, azides **1d** and **1c**, and azo compounds **9d,e** in KBr pellets; for azides **1b,c** and haloalkylisocyanurates **5b—e**, in thin films for liquid samples and in mineral oil for solid samples. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WSL-400 spectrometer (400.13 MHz and 100.62 MHz, respectively). The δ values were referred to the signal of $CHCl_3$ (for ^{1}H) and the $CDCl_3$ solvent (for ^{13}C). UV spectra were recorded on a Specord UV VIS spectrophotometer. The electrochemical reduction of C_{60} and its derivatives were studied by cyclic voltammetry in a mixture of *o*-DCB and MeCN (3 : 1) at 25 °C; the solution concentration was $1 \cdot 10^{-3}$ mol L^{-1}, the scanning velocity was 50 mV s^{-1}; a Pt working electrode and an $Ag/AgNO_3$ (0.01 *M* in MeCN) reference electrode were used; a 0.1 *M* solution of Et_4NClO_4 was used as the supporting electrolyte.

Acetone and chloroform used in the syntheses were dried over $CaCl_2$, and Py was dried over KOH; this was followed by distillation of all solvents over P_2O_5. Commercial MeCN was used. 1,3-Diallyl- and 1,3-di(2-cyanoethyl)isocyanuric acids were prepared by known procedures.[17,18] The C_{60} fullerene was prepared at the G. A. Razuvaev Institute of Organometallic Chemistry of the RAS.

1,3-Disubstituted 5-(ω-azidoalkyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-triones (1b—e) (general procedure). A solution of the corresponding 1,3-disubstituted 5-(ω-haloalkyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)trione (**5b—e**) (0.015 mol) in 10 mL of acetone was added dropwise to a refluxed suspension of NaN_3 (0.025 mol) in 20 mL of anhydrous acetone. After 6 h of stirring, NaHal was filtered off, the filtrate was concentrated *in vacuo* and chromatographed on a column with silica gel; azides **1b,c** were eluted by a mixture of hexane with Et_2O (5 : 1); azides **1d** and **1e** were isolated using a 1 : 1 and a 5 : 1 hexane—acetone mixtures, respectively. The yields, the data of elemental analysis, and the spectral characteristics of compounds **1b—e** are listed in Tables 1—4.

1,3-Diallyl-5-chloromethyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (5b). Thionyl chloride (2.06 g, 0.017 mol) was added dropwise with stirring to a solution of compound **6** (4 g, 0.016 mol) in 50 mL of dry chloroform. The reaction mixture was stirred for 1 h at ~20 °C, refluxed for 2 h, and left for 12 h. Volatile components were evaporated *in vacuo* and the residue solidified on standing. The unreacted compound **6** was separated by recrystallization from a mixture of benzene with petroleum ether (1 : 3). After separation of compound **6**, the product **5b** remained in the filtrate. The solvent from the filtrate was evaporated *in vacuo*, and the remaining thick brown liquid was twice chromatographed on a column with silica gel (using a mixture of petroleum ether and Et_2O (1 : 1) as the eluent, R_f 0.50). On standing, product **5b** solidified. The yield, the data of elemental analysis, and the spectral characteristics of compound **5b** are given in Tables 1—4.

1,3-Diallyl-5-(3-bromopropyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (5c). 1,3-Diallylisocuanuric acid (20.9 g, 0.1 mol) was added to a solution of NaOH (4 g, 0.1 mol) in 200 mL of water. The mixture was stirred for 1 h at 60—70 °C. Water was evaporated *in vacuo* and the residue was diluted with toluene, which was evaporated first under atmospheric pressure and then *in vacuo.* 1,3-Dibromopropane (80.8 g, 0.4 mol) was added to the resulting dry monosodium 1,3-diallylisocuanurate. The mixture was stirred for 3 h at 50—60 °C to a neutral medium. DMF was evaporated *in vacuo*, the residue was diluted with 50 mL of C_6H_6, the precipitate was filtered off, and the residue was dried *in vacuo* and chromatographed on a column with silica gel (a mixture of petroleum ether and Et_2O, 2 : 1, as the eluent) to give compound **5c** as an oil (R_f 0.36). The yields, the elemental analysis data, and the spectral characteristics of compound **5c** are listed in Tables 1, 2, and 4.

1,3-Bis(2-cyanoethyl)-5-(3-bromopropyl)- and 1,3-bis(2-cyanoethyl)-5-(5-bromopentyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-triones (5d and 5e). 1,3-Bis(2-cyanoethyl)isocuanuric acid was added to a butanol solution of Bu^nONa prepared from Na (35 mmol) and 120 mL of Bu^nOH and the mixture was refluxed with stirring for 8 h. The solvent was evaporated *in vacuo* and the residue was dried by azeotropic distillation of butanol with toluene. Toluene was evaporated *in vacuo* and 100 mL of dry DMF and a fivefold molar excess of the corresponding dibromoalkane were added to the residue. The temperature raised spontaneously to 30—35 °C. The reaction mixture was heated for 45 min at 50 °C until a neutral medium was attained. DMF and excess dibromoalkanes were removed *in vacuo.* The residue was chromatographed on a column with silica gel (a mixture of benzene and acetone (4 : 1) was used as the eluent, R_f 0.43 (**5d**) and R_f 0.38 (**5e**)). The products **5d** and **5e**, formed as oils, solidified on standing and were twice recrystallized from a mixture of Pr^iOH with dioxane (20 : 1) for compound **5d** and from MeOH for compound **5e**. The yields, the data of elemental analysis, and the spectral characteristics of compounds **5d** and **5e** are listed in Tables 1, 2, and 4.

1,3-Diallyl-5-hydroxymethyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (6). A 27% aqueous solution (4 g) of formaldehyde (0.036 mol) was gradually added to a suspension of diallylisocyanuric acid (5 g, 0.02 mol) in 20 mL of Py and 13 mL of MeCN. The reaction mixture was stirred for 2 h at ~20 °C and left for 12 h. The solvents were evaporated *in vacuo*, petroleum ether was added to the remaining thick colorless liquid, and the mixture was triturated to give a powder. Recrystallization from a mixture of benzene with petroleum ether (1 : 3) gave compound **6** as a while powder. The yields, the data of elemental analysis, and the spectral characteristics of compound **6** are listed in Tables 1, 2, and 4.

Reactions of C_{60} with 1,3-disubstituted 5-(ω-azidoalkyl)-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-triones (5b—e) (general procedure). A mixture of C_{60} (0.1 mmol) and the corresponding azide **1b—e** (0.3 mmol) in 25 mL of dry degassed *o*-DCB was heated with reflux for 4 h and the solvent was distilled off from the reaction mixture at ambient pressure. The residue was chromatographed on a column with silica gel. In the reaction of fullerene with azide **1b**, products **4b** (elution with toluene) and **7b** (a mixture of toluene with Et_2O, 20 : 1) were isolated (for Silufol plates, R_f 0.64 (**4b**) and R_f 0.13 (**7b**) (elution with a mixture of toluene with Et_2O, 10 : 2)); in the reaction with azide **1c**, three products were obtained: **8**, **4c** (toluene), and **7c** (a mixture of toluene with Et_2O, 10 : 1) (R_f 0.83 (**8**), R_f 0.66 (**4c**) and R_f 0.15 (**7c**) (elution with a mixture of toluene with Et_2O, 10 : 2)); the reaction with azide **1d** gave three products: **4d** (a mixture of toluene with Et_2O, 6 : 1), **7d** (a mixture of toluene with acetone, 1 : 1), and **9d** (acetone) (R_f 0.61 (**4d**) and R_f 0.10 (**7d**) (elution with a mixture of toluene, Et_2O, and acetone, 10 : 2 : 2)); the reaction with azide **1e** gave products **4e** (a mixture of toluene with Et_2O, 6 : 1) and **9e** (a mixture of toluene with Et_2O, 5 : 1) (R_f 0.48 (**4e**) and R_f 0.39 (**9e**) (elution with a mixture of toluene with acetone, 10 : 1)). The yields, the data of elemental analysis, and the spectral characteristics of the products are listed in Tables 1, 2, and 4—6.

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