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Study of the factors determining the outcome of cycloaddition of isocyanurato-substituted azides to [60]fullerene

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The final outcome of cycloaddition of isocyanuratoalkyl azides to C_{60} depends on the temperature, the thermal stability of azides, the substituents in the isocyanurate ring, and the number of methylene groups in the alkyl radical. The thermal transformations of the monoadducts obtained were studied.

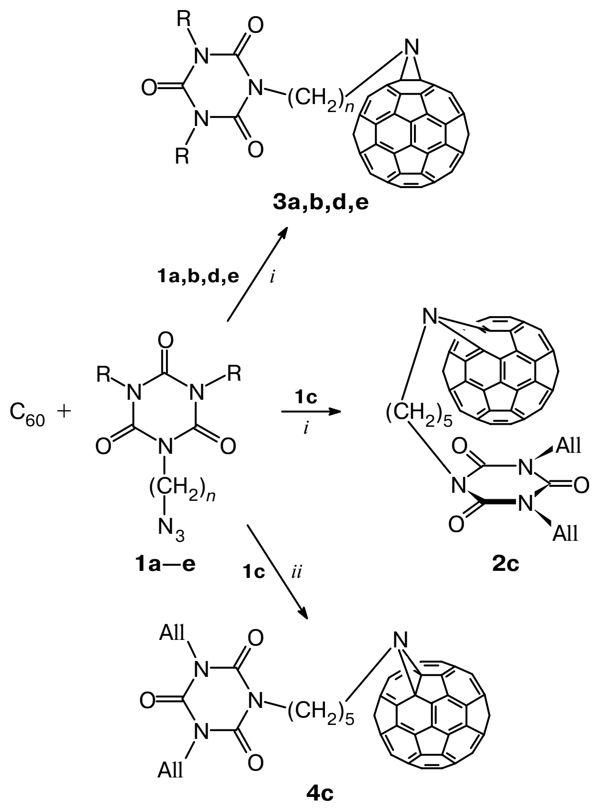
Key words: [60]fullerene, azidoalkyl isocyanurates, [60]fullereno[1,2-*b*]aziridines, azahomo[60]fullerenes, [60]fullereno[1,6-*b*]aziridines.

Previously,[1—3] we showed that cycloaddition of isocyanuratoalkyl azides **1a—e** to C_{60} gives rise to molecules possessing new properties and still retaining the properties inherent in fullerenes. Unlike fullerene, its isocyanurato-containing monoadducts are readily soluble in organic solvents. As in the case of fullerenes, the spherical fragment in the molecules of these compounds can undergo stepwise reversible reduction;[1] for azahomo[60]fullerene **2c**, this takes place at less negative potentials than C_{60} reduction.[2] Study of azide cycloaddition to fullerenes resulted in the first synthesis of stable [60]fullereno[1,6-*b*]aziridine,[3] which is the product of addition to a C—C bond between five- and six-membered rings of fullerene without opening of the cage.

Our study of the reactions of azides **1a—e** with [60]fullerene showed[1—3] that the type of monoadducts thus formed is determined by not only the reaction temperature but also the number of methylene units in the alkyl groups in the azide and the electron-withdrawing capacity of substituents in the isocyanurate ring. Depending on the nature of the substituents in positions 1 and 3 of the isocyanurate ring (either allyl or 2-cyanoethyl) and the length of the methylene chain (n = 1, 3, 5), refluxing the reactants in *o*-dichlorobenzene (*o*-DCB) yielded either azahomo[60]fullerene **2c** or [60]fullereno[1,2-*b*]aziridines **3a,b,d,e** (Scheme 1). A decrease in the temperature of the reaction of azide **1c** with C_{60} to 100 °C resulted in the formation of diallylisocyanuratoalkyl-substituted [60]fullereno[1,6-*b*]aziridines **4c**.[3]

To continue the investigation of factors determining the synthetic outcome of the reactions of fullerene with isocyanurate-substituted azides, in this work, we have changed the number of methylene units in diallyl-substituted azides and varied the process temperature.

Scheme 1



	a	**b**	**c**	**d**	**e**
R	All	All	All	CH_2CH_2CN	CH_2CH_2CN
n	1	3	5	3	5

Reagents and conditions: *i*. *o*-DCB, 180 °C, 4 h; *ii*. *o*-DCB, 100 °C, 4 h.

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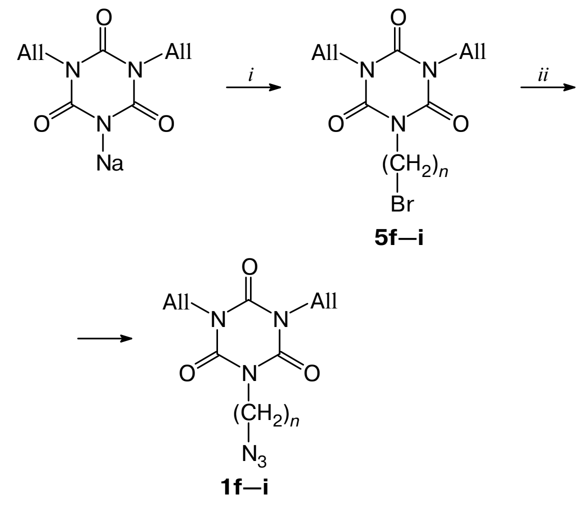
Scheme 2



n = 2 (**f**), 4 (**g**), 6 (**h**), 10 (**i**)

Reagents and conditions: *i.* $Br(CH_2)_nBr$, n = 2, 4, 6, 10; DMF, 50—60 °C, 3 h; *ii.* NaN_3, Me_2CO, 6 h.

Azides **1f—i** were synthesized by refluxing solutions of the corresponding 1,3-diallyl-5-(ω-bromoalkyl)isocyanurates **5f—i** with sodium azide in dry acetone for 6—8 h. The initial compounds **5f—i** were prepared by the reaction of monosodium 1,3-diallylisocyanurate with an excess of the corresponding dihaloalkane (Scheme 2). The target products were isolated by column chromatography as transparent colorless thick liquids. The compositions of compounds **5f—i** and **1f—i** were confirmed by elemental analysis and the structures were determined by physicochemical methods (Tables 1—3).

Table 1. Yields and data of elemental analysis for compounds **1f—i**, **5f—i**

Compound	Yield (%)	Found / Calculated (%) C	H	N	Hal	Molecular formula
1f	68	47.42	4.97	30.15	—	$C_{11}H_{14}N_6O_3$
		47.48	5.03	30.21		
1g	79	50.64	5.72	27.21	—	$C_{13}H_{18}N_6O_3$
		50.98	5.88	27.45		
1h	68	53.68	6.43	24.93	—	$C_{15}H_{22}N_6O_3$
		53.89	6.58	25.15		
1i	72	58.29	7.51	21.38	—	$C_{19}H_{30}N_6O_3$
		58.46	7.69	21.53		
5f	72	41.98	4.41	13.23	25.17	$C_{11}H_{14}BrN_3O_3$
		41.77	4.43	13.29	25.31	
5g*	73	45.15	5.03	12.09	23.02	$C_{13}H_{18}BrN_3O_3$
		45.34	5.23	12.20	23.25	
5h	71	48.19	5.73	11.09	21.27	$C_{15}H_{22}BrN_3O_3$
		48.38	5.91	11.29	21.50	
5i	70	53.07	6.83	9.64	18.45	$C_{19}H_{30}BrN_3O_3$
		53.27	7.01	9.81	18.69	

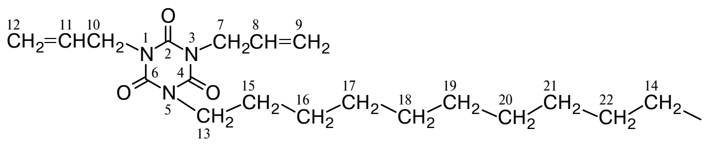
* M.p. 50 °C.

The reactions of azides **1f—i** with C_{60} were carried out in a solution in boiling *o*-DCB; the products and the unreacted fullerene were separated by column chromatography. As a result, individual monoadducts were isolated from the reactions of C_{60} with azides **1f,g,i** and a mixture of two monoadducts was formed in the case of azide **1h** (Scheme 3). The compositions of the monoadducts were established using data of elemental analysis (Table 4). The structures of individual monoadducts were determined by ^1H and ^{13}C NMR, IR, and UV

Table 2. ^1H NMR spectra ($CDCl_3$, δ, $^3J_{HH}$/Hz) of compounds **1f—i** and **5f—h**

Compound	NC(7,10)H (4 H)	NC(13)H (2 H)	NC(14)H (2 H)	C(15)H (2 H)	C(16)H (2 H)	C(17)H (2 H)	C(18)H (2 H)	C(8,11)H (2 H)	$C(9,12)H_{trans}$ (2 H)	$C(9,12)H_{cis}$ (2 H)
1f	4.28	4.08[a]	3.39	—	—	—	—	5.67	5.09	5.03
	(d, J = 5.8)	(m, J = 6.8)	(m, J = 6.8)					(ddt)	(d, J = 17.1)	(d, J = 10.2)
1g	4.47	3.92	3.42	1.82	1.88	—	—	5.87	5.22	5.25
	(d, J = 6.0)	(m, J = 6.9)	(m, J = 6.6)	(m)	(m)			(ddt)	(d, J = 17.1)	(d, J = 10.2)
1h	4.42	3.81	3.33	1.32, 1.39, 1.57, 1.79 (all m)				5.81	5.23	5.17
	(d, J = 5.8)	(m, J = 7.0)	(m, J = 7.0)					(ddt)	(d, J = 17.9)	(d, J = 10.9)
1i	4.44	3.82	3.35 (m)	1.32—1.80				5.84	5.25	5.19
	(d, J = 5.9)	(m, J = 7.6)		(m, C(15)H—C(22)H, 16 H)				(ddt)	(d, J = 17.1)	(d, J = 10.9)
5f	4.65	4.25	3.53	—	—	—	—	5.86	5.36	5.25
	(d, J = 6.0)	(m, J = 7.0)	(m, J = 7.0)					(ddt)	(d, J = 18.0)	(d, J = 10.0)
5g	4.54	3.96	3.46	1.09 (m)		—	—	5.80	5.29	5.24
	(d, J = 6.0)	(m, J = 7.0)	(m, J = 7.0)					(ddt)	(d, J = 17.0)	(d, J = 12.0)
5h	4.41	3.83	3.37	1.50 (m)				5.80	5.24	5.10
	(d, J = 6.0)	(m, J = 7.0)	(m, J = 7.0)					(ddt)	(d, J = 17.0)	(d, J = 12.0)

[a] For the protons of all methylene groups, $^3J_{HH} = 1/2(^3J_{AX} + {}^3J_{AX'})$ in the spectrum of an AA′XX′system.



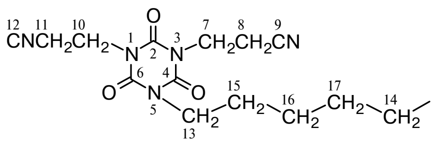


Table 3. ^{13}C NMR spectra of compounds **1f,g,i** ($CDCl_3$)

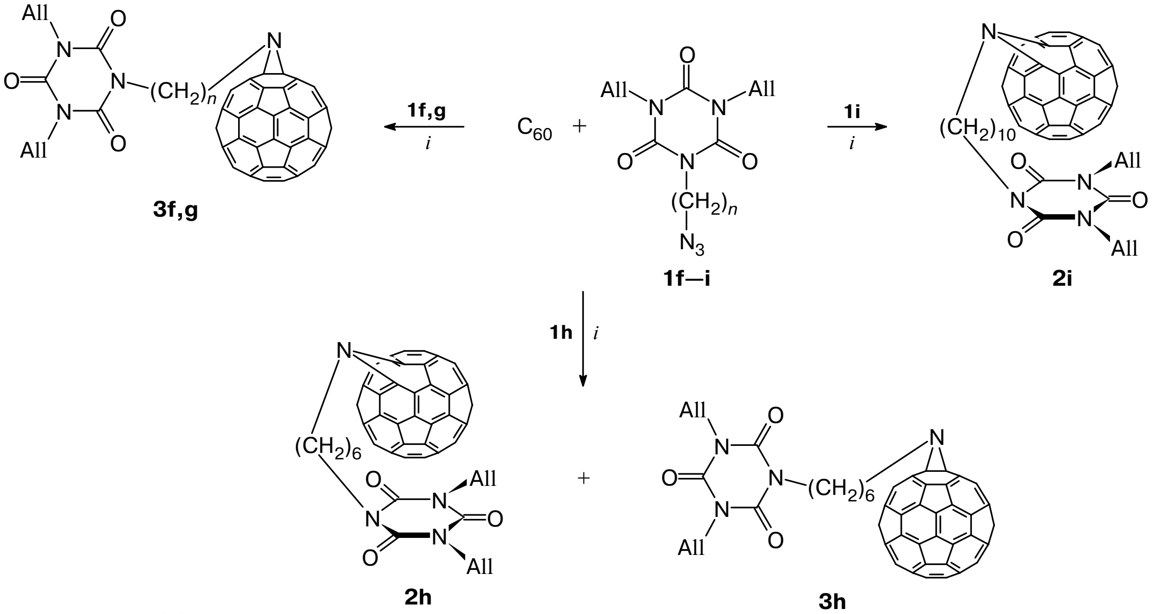
Atom	δ ($^1J_{CH}$/Hz)		
	1f	**1g**	**1i**
C(2)	147.96 (s)	148.31 (s)	148.23 (s)
C(4), C(6)	148.23 (s)	148.59 (s)	148.41 (s)
C(7), C(10)	44.67 (tm, *J* = 143.9)	44.82 (tm, *J* = 141.1)	44.52 (tm, *J* = 148.9)
C(8), C(11)	130.65 (dm, *J* = 159.9)	130.84 (dm, *J* = 158.9)	130.91 (dm, *J* = 158.9)
C(9), C(12)	118.82 (tm, *J* = 158.9)	118.94(tm, *J* = 157.4)	118.45 (tm, *J* = 155.9)
C(13)	43.27 (tm, *J* = 145.6)	43.02 (tm, *J* = 143.3)	42.81 (tm, *J* = 142.3)
C(14)	27.09 (tm, *J* = 153.9)	32.44 (tm, *J* = 151.9)	33.40 (tm, *J* = 151.2)
C(15)		29.71 (tm, *J* = 134.8)	32.55 (tm, *J* = 125.4)
C(16)		26.49 (tm, *J* = 132.84)	29.02 (tm, *J* = 122.5)
C(17)			28.97 (tm, *J* = 134.5)
C(18)			28.76 (tm, *J* = 126.8)
C(19)			28.37 (tm, *J* = 126.8)
C(20)			27.84 (tm, *J* = 122.6)
C(21)			28.46 (tm, *J* = 126.8)
C(22)			26.43(tm, *J* = 128.8)

spectroscopy. In all cases, diadducts were also isolated in 3 to 5% yields. According to TLC and ^{1}H NMR spectra, they were mixtures of isomers whose structures have not been studied.

The spectroscopic characteristics of the product formed in the reaction between azide **1i** and C_{60} were indicative of an azahomo[60]fullerene structure. For example, in the ^{13}C NMR spectrum of compound **2i**, the fullerene cage was represented only by signals of sp^2-carbon atoms with δ of 133 to 147 (Table 5), whose number and relative intensity corresponded to C_s symmetry of the molecule. In addition, compound **2i** was responsible for an UV spectrum typical of azahomo[60]fullerenes [3,4] (Table 6) with no band at 420—430 nm and the long-wavelength absorption band occurring at 534 nm. The ^{1}H NMR spectrum of product **2i** exhibited signals for the protons of the methylene groups separating the fullerene cage from the isocyanurate ring and signals for the protons of the two equivalent allyl groups in the isocyanurate ring.

The spectroscopic parameters of the monoadducts of azides **1f,g** with C_{60} attested in favor of [60]fullereno[1,2-*b*]aziridine structures **3f,g**. In addition to the 31 signals of the sp^2-hybridized carbon atoms of the fullerene cage, the ^{13}C NMR spectrum of compound **3g** (see Table 5) exhibited a signal with δ 120 due to the fullerene-cage sp^3 carbon atoms incorporated in the aziridine ring.[1] The number and the relative intensity

Scheme 3



i. *o*-DCB, 100 °C, 4 h.

Table 4. Yields and data of elemental analysis for compounds **2h+3h**, **2e,i**, **3f,g**, **4b,g,h**, and **6b,g,h**

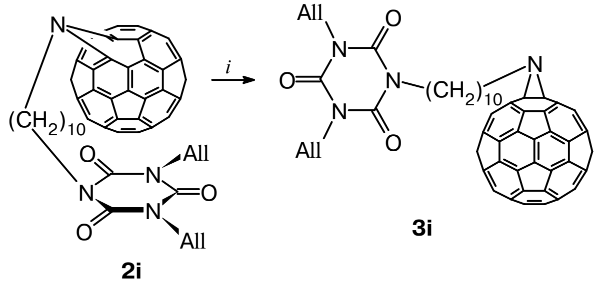
Compound	Yield (%)	Found / Calculated (%)			Molecular formula
		C	H	N	
2e	19	85.32 85.55	1.54 1.73	7.87 8.09	$C_{74}H_{18}N_6O_3$
2h+3h	5	87.53 87.72	2.08 2.14	5.19 5.36	$C_{75}H_{22}N_4O_3$
2i	18	87.25 87.61	2.68 2.77	5.05 5.17	$C_{79}H_{30}N_4O_3$
3f	21	87.50 87.83	1.32 1.44	5.59 5.77	$C_{71}H_{14}N_4O_3$
3g	25	87.44 87.77	1.66 1.80	5.58 5.61	$C_{73}H_{18}N_4O_3$
4b	22	87.32 87.80	1.17 1.63	5.49 5.69	$C_{72}H_{16}N_4O_3$
4g	3	87.58 87.77	1.76 1.80	5.60 5.61	$C_{73}H_{18}N_4O_3$
4h	4	87.60 87.72	2.10 2.14	5.20 5.36	$C_{75}H_{22}N_4O_3$
6b	5	85.19 85.37	1.35 1.58	8.21 8.30	$C_{72}H_{16}N_6O_3$
6g	6	85.16 85.38	1.53 1.75	8.02 8.18	$C_{73}H_{18}N_6O_3$
6h	11	85.16 85.38	1.92 2.07	7.87 7.96	$C_{75}H_{22}N_6O_3$

of ^{13}C NMR signals implied C_s symmetry of the molecules. The ^{13}C NMR spectrum of compound **3f** (see Table 5) was found to show 13 signals in the region of sp^2 carbon atoms and one signal with δ 97.24, indicating C_{2v} symmetry of the molecule. In addition, the UV spectra of both compounds **3f,g** (see Table 6) exhibited weak narrow bands at about 420—430 nm, typical of adducts at a 6,6-bond of fullerene. The ^1H NMR spectra (Table 7) and the IR spectra of adducts **3f,g,i** indicated that the diallylisocyanurate and alkyl fragments have been retained in the molecule and that the fullerene cage is present.

Upon the reaction of azide **1h** with C_{60}, a mixture of two monoadducts was isolated by column chromatography, as indicated by the data of elemental analysis, thin layer chromatography, and the ^1H NMR spectrum (see Table 7). The UV spectrum of the mixture (see Table 6) resembled the spectra of the corresponding azahomo[60]fullerenes;[3,4] however, it had a rather weak band at 420 nm, which implied that the mixture contained an adduct at a fullerene 6,6-bond. In view of the foregoing, we believe that this mixture consists of azahomo[60]fullerene **2h** and an impurity of [60]fullereno[1,2-*b*]aziridine **3h**.

We have also studied the thermal stability of individual compounds **2i** and **3f,g**. [60]Fullereno[1,2-*b*]aziridines **3f,g**, like compounds **3c—e** described previously,[1] proved to be thermally stable on heating for 20 h in *o*-DCB at 180 °C. Heating azahomo[60]fullerene **2i** for 10 h under the same conditions gave rise to [60]fullereno[1,2-*b*]aziridine **3i** (Scheme 4); this was confirmed by TLC and UV spectroscopy (see Table 6). The R_f value for product **3i** differed from this value for the starting azahomo[60]fullerene **2i**, and a band with λ_{max} 422 nm typical of adducts at a 6,6-bond appeared in the UV spectrum.

Scheme 4



i. *o*-DCB, 180 °C, 10 h.

The results obtained here, together with the data published previously[1,2] lead to the conclusion that the structure of cycloaddition products obtained from diallylisocyanuratoalkyl azides and C_{60} at 180 °C depends on the length of the alkyl group. When $n = 5$ or more, the reaction yields *N*-diallylisocyanurato-substituted azahomo[60]fullerenes **2**, whereas for smaller *n* values, the corresponding [60]fullereno[1,2-*b*]aziridines **3** are produced. In addition, data on the thermal behavior of monoadducts demonstrate that [60]fullereno[1,2-*b*]aziridines **3** are thermally more stable than azahomo[60]fullerenes **2** and are formed upon isomerization of the latter. It is known from the literature that methoxyethoxymethyl-substituted azahomo[60]fullerene is converted into ketolactam,[5] while isomerization of *N*-aryl-[6] and *N*-sulfonyl-substituted azahomo[60]fullerenes[7] into the corresponding [60]fullereno[1,2-*b*]aziridines takes place only on exposure to UV radiation. Thus, the transformations we discovered represent the first example of thermal isomerization of azahomo[60]fullerenes into [60]fullereno[1,2-*b*]aziridines. Therefore, there are grounds to believe that [60]fullereno[1,2-*b*]aziridines **3a,b,d,e—g**, isolated as the final products in the reactions of azides **1a,b,d,e—g** with C_{60}, are formed in the thermal transformations of the corresponding azahomo[60]fullerenes taking place during the reactions. The closer the isocyanurate ring to the fullerene sphere and the higher the electron-withdrawing capacity of the substituents in the ring, the higher the reaction rate.

Previously,[3] we showed in relation to the reaction of [60]fullerene with azide **1c** that the monoadduct structure depends on the reaction temperature. At 100 °C, the main reaction product is [60]fullereno[1,6-*b*]aziridine **4c** rather than azahomo[60]fullerene **2c**, which is formed at 180 °C.[2] In this connection, it was of interest to study fullerene cycloaddition reactions with other isocyanurato-

Table 5. ^{13}C NMR spectra of compounds **2e,i**, **3f,g**, **4b**, **6c,h** ($CDCl_3$, δ)

Atom	**2e**	**2i**	**3f**	**3g**	**4b**	**6c**	**6h**
C(2)	147.71	148.51	148.96	148.40	148.41	148.70	148.42
C(4), C(6)	148.13	148.68	148.10	148.74	149.03	148.74	148.63
C(7), C(10)	38.32	44.79	45.07	44.93	45.00	44.89	44.86
C(8), C(11)	16.48	131.08	119.19	130.91	130.83	130.97	130.93
C(9), C(12)	116.23	118.79	130.88	119.02	119.23	118.94	118.93
C(13)	43.41	43.15	42.05	42.84	30.81	42.77	42.90
C(14)	51.27	33.61	47.92	51.13	41.96	48.21	48.43
C(15)	27.43	32.79		26.68	26.67	29.01	27.65
C (16)	24.26	29.23		25.61		24.08	26.48
C(17)	28.89	29.19				27.33	26.24
C(18)		29.08					29.31
C(19)		28.61					
C(20)		28.06					
C(21)		27.72					
C(22)		26.58					
$C_{60}N$	**2C:** 133.70, 135.79, 136.19, 137.07, 138.01, 138.46, 139.18, 140.70, 141.36, 142.57, 142.64, 142.65, 142.73, 142.88, 143.06, 143.34, 143.59, 143.79, 144.03, 144.10, 144.24, 144.28, 144.39, 144.49, 144.66, 144.95, 146.62, 147.71 **1C:** 137.34, 137.79, 143.16, 143.50	**2C:** 133.77, 135.67, 136.23, 137.27, 137.31, 138.02, 138.49, 139.19, 140.73, 141.45, 142.60, 142.71, 142.79, 142.91, 143.09, 143.38, 143.63, 143.83, 144.10, 144.13, 144.26, 144.31, 144.44, 144.53, 144.72, 145.03, 147.09, 147.82, **1C:** 143.53, 143.19, 140.88, 137.81	**2C:** 97.24, 142.88, 145.10 **4C:** 140.85, 142.13, 142.24, 143.09, 143.81, 144.58, 144.64, 145.23 **6C:** 143.11 **8C:** 145.18, 144.71	**2C:** 120.99, 133.71, 135.81, 136.23, 137.04, 137.43, 138.06, 138.46, 139.21, 140.73, 141.39, 142.61, 142.66, 142.74, 142.86, 143.07, 143.17, 143.34, 143.59, 143.79, 144.02, 144.09, 144.24, 144.26, 144.40, 144.50, 144.66, 144.96, 147.72 **1C:** 137.79, 140.69, 143.17, 143.49	**2C:** 120.22, 133.78, 135.67, 136.27, 136.48, 138.17, 138.51, 139.27, 140.77, 141.29, 142.64, 142.65, 142.70, 142.87, 143.09, 143.34, 143.59, 143.77, 143.87, 144.09, 144.22, 144.23, 144.37, 144.46, 144.62, 144.86, 145.80, 147.59 **1C:** 137.64, 140.13, 143.16, 143.52	**2C:** 82.5, 136.00, 136.56, 140.22, 140.70, 141.84, 142.04, 142.07, 142.17, 142.45, 142.59, 142.69, 142.82, 142.96, 143.86, 144.38, 144.50, 144.67, 145.12, 145.16, 145.42, 145.70, 145.90, 145.92, 145.98, 145.99, 146.20, 146.22 **1C:** 147.42 **3C:** 143.05	**2C:** 82.10, 135.99, 136.55, 140.18, 140.68, 141.82, 142.01, 142.05, 142.16, 142.42, 142.56, 142.67, 142.78, 142.93, 143.84, 143.36, 144.47, 144.68, 145.10, 145.13, 145.40, 145.87, 145.88, 145.90, 145.93, 145.97, 146.17, 146.19 **1C:** 147.59 **3C:** 143.03

Table 6. UV spectra of compounds **2b,e,i**, **2h+3h**, **3f,g,i**, **4b,g,h**, and **6b,c,g,h**

Compound	λ_{max}/nm
2b	262, 331, 432, 547
2e	262, 332, 435, 550
2h+3h	258, 329, 430, 548
2i	261, 329, 430, 543
3f	263, 326, 426, 488
3g	260, 330, 428, 546
3i	258, 330, 422, 534
4b	263, 335, 429, 548
4g	262, 332, 431, 551
4h	261, 331, 434, 551
6b	263, 316, 426, 451, 543
6c	255, 315, 424, 459, 541
6g	255, 315, 425, 461, 543
6h	256, 316, 425, 465, 546

substituted azides that we synthesized containing either allylic (azides **1a,b,f—i)** or cyanoethyl (azides **1d,e)** substituents in positions 1 and 3 of the isocyanurate ring, in order to elucidate the effect of reaction temperature and the nature of the substituent on the monoadduct structure. The temperature of the reaction between C_{60} and azides **1a,b,d—i** varied from 50 to 100 °C. At 50 °C, azide **1c** was also involved in the reaction with C_{60}.

Fullerene C_{60} does not react with azides **1a,f,i** at 100 °C (4 h).

In the case of reaction of C_{60} with azide **1b**, two products were isolated apart from the unreacted C_{60} (Scheme 5). According to elemental analysis, both compounds are monoadducts (see Table 4). One product isolated in 5% yield differed from fullerenoaziridine **3b**,[1] formed at 180 °C, relying on the results of elemental analysis, TLC, and UV spectroscopy. The UV spectrum of this compound (see Table 6) exhibited a band at 426 nm, typical of monoadducts at a fullerene 6,6-bond, and a broad long-wavelength band at 451 nm (in the spectrum of compound **3b**,[1] the band of this type was

Table 7. ^{1}H NMR spectra (CDCl$_3$, δ, $^3J_{HH}$/Hz) of compounds **2e,i**, **3f,g**, **4b,g,h**, and **6c,g,h**

Compound	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(18)H$_2$ (2 H)	C(8,11)H$_2$ (2 H)	C(9,12)H$_{trans}$ (2 H)	C(9,12)H$_{cis}$ (2 H)
2e	4.25 (t, J = 6.8)	4.03* (m, J = 7.2)	3.81 (m, J = 6.5)	1.88 (m)	1.75 (m)	2.07 (m)	2.80 (t, 4 H, J = 6.5)		—	—
2i	4.48 (d, J = 6.0)	3.88 (m, J = 6.7)	3.82 (m, J = 7.0)	1.31—2.00 (m, C(15)H$_2$—C(22)H$_2$, 16 H)				5.83 (ddt)	5.29 (d, J = 17.1)	5.23 (d, J = 10.2)
3f	4.42 (d, J = 5.5)	4.60 (m, J = 6.0)	3.88 (m, J = 6.9)	—	—	—	—	5.76 (ddt)	5.24 (d, J = 17.1)	5.13 (d, J = 10.2)
3g	4.51 (d, J = 6.0)	4.11 (m, J = 7.4)	3.96 (m, J = 7.2)	2.06 (m)		—	—	5.89 (ddt)	5.35 (d, J = 17.2)	5.23 (d, J = 10.2)
4b	4.46 (d, J = 6.1)	4.38 (m, J = 6.5)	3.95 (m, J = 6.3)	2.35 (m)	—	—	—	5.87 (ddt)	5.33 (d, J = 18.4)	5.24 (d, J = 10.2)
4g	4.52 (d, J = 6.01)	4.11 (m, J = 7.8)	3.87 (m, J = 6.5)	2.07 (m)		—	—	5.90 (ddt)	5.33 (d, J = 16.5)	5.25 (d, J = 10.6)
4h	4.50 (d, J = 6.0)	3.95 (m, J = 6.5)	3.79(m) (m, J = 6.3)	1.55, 1.73, 1.77, 2.02 (все m)				5.89 (ddt)	5.32 (d, J = 17.6)	5.25 (d, J = 10.1)
6c	4.48 (d, J = 5.8)	4.39 (m, J = 7.7)	3.98 (m, J = 7.2)	1.79 (m)	1.58 (m)	2.27 (m)	—	5.88 (ddt)	5.32 (d, J = 17.0)	5.24 (d, J = 10.1)
6g	4.50 (d, J = 5.9)	4.08 (m, J = 6.3)	3.47 (m, J = 7.5)	2.07 (m)	2.19 (m)	—	—	5.89 (ddt)	5.32 (d, J = 17.6)	5.24 (d, J = 9.8)
6h	4.49 (d, J = 5.9)	4.41 (m, J = 7.0)	3.40 (m, J = 6.2)	2.26—1.53 (m)				5.88 (ddt)	5.30 (d, J = 17.2)	5.23 (d, J = 10.1)

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

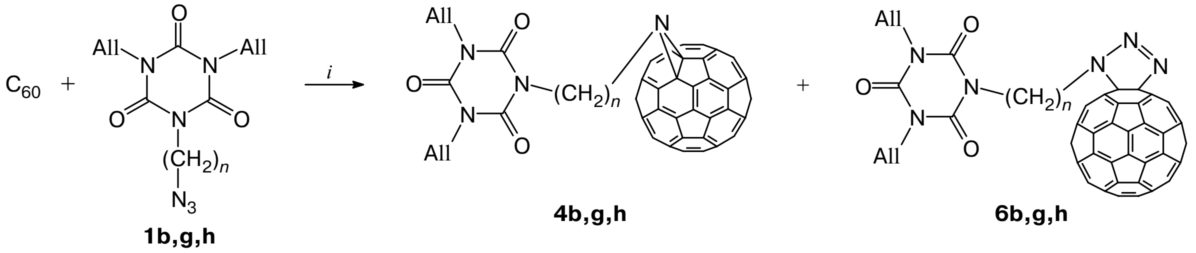
found at 538 nm). Therefore, we assume that this product has the structure of [60]fullereno[1,2-*d*]triazoline **6b**.

The second product isolated in 22% yield upon the reaction of C_{60} with azide **1b** also differed in R_f from compound **3b**;[1] however, the data of elemental analysis implied that this product was an isomer of **3b**. In the ^{13}C NMR spectrum (see Table 5) of this product, the fullerene fragment accounted for signals of both sp^2- and sp^3-hybridized carbon atoms; however, the UV spectrum (see Table 6) exhibited no band in the region of 420—430 nm, typical of 6,6-adducts. The ^{1}H NMR spectrum of this compound (see Table 7) showed no difference from the spectrum of the initial azide,[1] while the IR spectrum was indicative of the presence of both the fullerene fragments and the isocyanurate ring in the molecule. Previously,[3] we noted that the combination of these structural data corresponds to the structure of a monoadduct at a C—C bond between five- and six-membered rings formed without opening of the fullerene sphere. In our opinion, this monoadduct can be identified as [60]fullereno[1,6-*b*]aziridine **4b**.

In order to avoid a mistake in identification of product **4b**, we studied its thermolysis and compared the results with the thermal behavior of [60]fullereno[1,6-*b*]aziridine **4c**, which we prepared previously.[3] Refluxing a solution of compounds **4b** and **4c** in *o*-dichlorobenzene for 10 h resulted in the corresponding azahomo[60]fullerenes **2b** and **2c** (Scheme 6).[2]

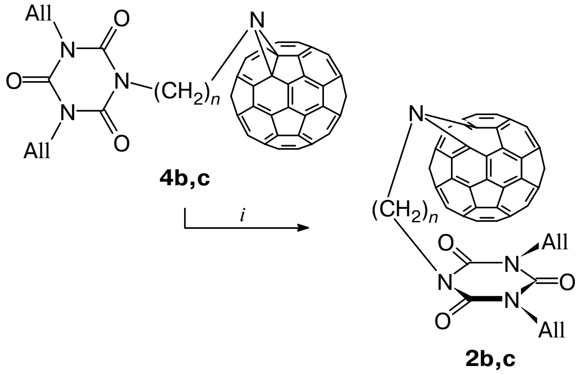
UV spectra and the R_f values of the azahomo[60]fullerene **2c** samples isolated upon thermolysis and prepared in our previous study[2] coincided. Previously, azahomo[60]fullerene **2b** has not been isolated upon the reaction of azide **1b** with C_{60}. The product obtained by thermal isomerization of **4b** was identified as azahomo[60]fullerene **2b** based on the data of UV spectroscopy and TLC. Indeed, the UV spectrum of this product (see Table 6) contained no bands in the region of 420—430 nm typical of 6,6-adducts and the long-wavelength band was detected in the same region

Scheme 5



i. *o*-DCB, 100 °C, 4 h.

Scheme 6



i. o-DCB, 180 °C, 10 h.

(λ_{max} 544 nm) as the corresponding bands in the spectra of azahomo[60]fullerenes **2c** [2] and **2i** (see Table 6).

Thus, on the basis of the data obtained, we believe that the reaction of azide **1b** with C_{60} at 100 °C gives [60]fullereno[1,6-*b*]aziridine **4b** as the major product. The results of thermal transformations indicate that on heating, isocyanurate-substituted fullerenoaziridines **4** are converted into azahomo[60]fullerenes **2**, while the latter are transformed into thermally stable [60]fullereno[1,2-*b*]aziridines **3**. This sequence of thermal transformations has previously been postulated in the literature[8] to explain the outcome of cycloaddition of organic azides with C_{60} but now it is proved experimentally for the first time.

The reactions of C_{60} with azides **1g,h**, like those with azide **1b**, were found to give two products; study of their structures showed that the corresponding [60]fullereno[1,2-*d*]triazolines **6g,h** are the major products exceeding other products, [60]fullereno[1,6-*b*]aziridines **4g** and **4h**, in the yield.

The conclusion concerning the structure of adducts **6g,h** was drawn from the following data. According to TLC, the R_f value of compound **6g** differs from that of [60]fullereno[1,2-*b*]aziridine **3g**, formed at 180 °C. The R_f value of compound **6h** does not coincide with the R_f values of products formed at 180 °C in the reaction of C_{60} with azide **1h**. The UV spectra (see Table 6) of the adducts **6g,h** indicate that the azide has been added to a bond between six-membered rings of fullerene. Thus, the data of TLC and UV spectroscopy ruled out both the azahomo[60]- and [60]fullereno[1,6-*b*]aziridine structures of the adducts. A high-quality ^{13}C NMR spectrum could be recorded only for compound **6h**. As expected, the ^{13}C NMR spectrum of [60]fullereno[1,2-*d*]triazoline having C_s symmetry of molecules (see Table 5) exhibited 30 signals (28 signals with a 2 C intensity and 2 signals with a 1 C intensity) in the region of the sp^2-hybridized carbon atoms of the fullerene sphere (δ 133—147) and one signal at δ 82.1 with a 2 C intensity corresponding to the sp^3-hybridized carbon atoms of the fullerene sphere incorporated in the triazoline heterocycle. The ^{1}H NMR spectra of these compounds (see Table 7) did not differ from the spectra of initial azides (see Table 2).

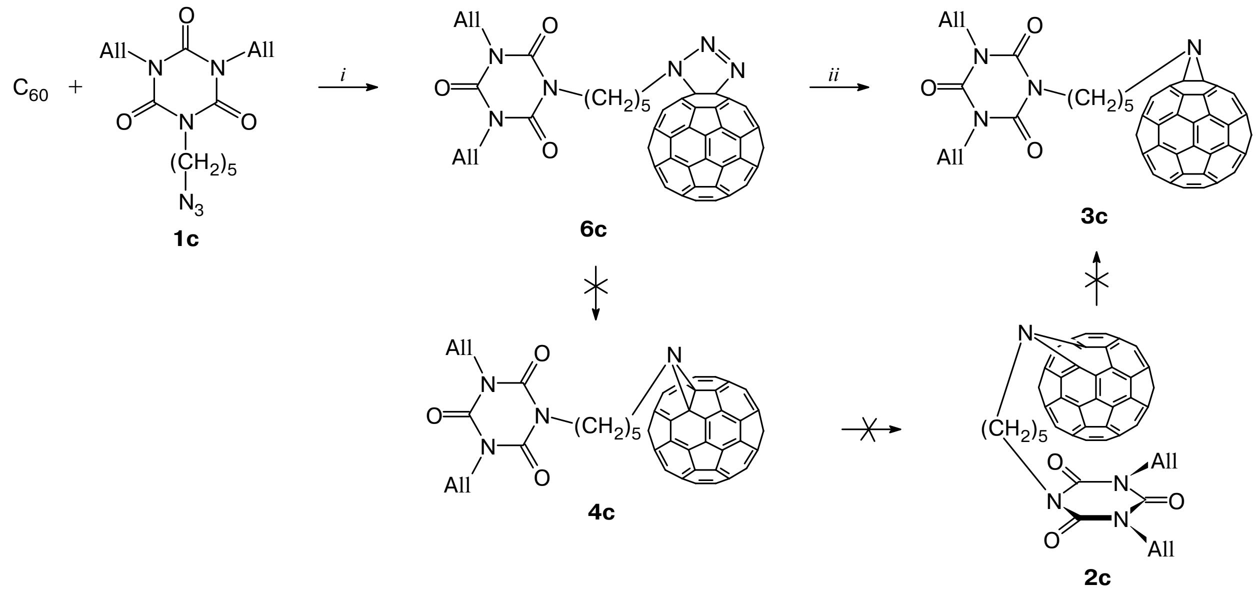
The R_f values of compounds **4g** and **4h** differ from the R_f values of the adducts produced in fullerene reactions with the corresponding azides at 180 °C; the UV spectra of these compounds (see Table 6) completely coincide with the UV spectra of [60]fullereno[1,6-*b*]aziridines **4b** [3] and **4c** (the absence of narrow bands at about 420—430 nm and the presence of a long-wavelength band at 461 and 465 nm, respectively); and the ^{1}H NMR spectra indicate that the azide has added to a bond between five- and six-membered rings[9] (a downfield shift of the signals of the C(14)H_2 methylene group (see Table 7) relative to their positions in the spectra of the starting azides **1g,h** (see Table 2)). Previously,[3] we noted that, due to the similarity of the UV spectra of [60]fullereno[1,6-*b*]aziridines and azahomo[60]fullerenes, these structures cannot be distinguished reliably without data of the ^{13}C NMR spectra. Therefore, now we can only suggest (with a rather high degree of probability) that products **4g,h** are [60]fullereno[1,6-*b*]aziridines.

Thus, our data concerning the reaction of C_{60} with diallylisocyanurato-substituted azides **1b,g,h** in combination with the data on the reaction with azide **1c** [3] demonstrate that the structures of adducts formed at 100 °C differ from the structures of adducts evolved at 180 °C. At 100 °C, cycloaddition of isocyanurato-substituted azides to C_{60} stop at the stage of thermally less stable products whose stability is dictated by the number of methylene groups in the hydrocarbon chain between the isocyanurate heterocycle and the fullerene sphere. Analysis of the results obtained shows that for odd *n* values (*n* = 3 and 5), the main reaction products are [60]fullereno[1,6-*b*]aziridines **4b,c**, whereas [60]fullereno[1,2-*d*]triazoline **6b** was isolated in a low yield and fullerenotriazoline **6c** was not detected at all. In the case of even *n* values (*n* = 4, 6), fullerenotriazolines **6g,h** become the predominant products. This difference between the structures of the major products of cycloaddition of diallylisocyanurato-substituted azides to C_{60} carried out at 100 °C is, apparently, due to the intramolecular interaction whose presence is determined by the inclination of the plane of the isocyanurate heterocycle relative to the fullerene sphere. This assumption is supported by isolation of fullerenoaziridines **4b,c**, which have not been isolated previously in the reactions of dipolarophiles with C_{60}, and fullerenotriazolines **6g,h**, stable at 100 °C. [60]Fullereno[1,2-*d*]triazolines known from the literature were stable at temperatures not exceeding 60 °C.[10]

The reactions of azides **1a—c,f—i** with C_{60} were also carried out at 50 °C. Under these conditions, monoadducts were isolated only in the reaction of azide **1c**. Study by ^{13}C and ^{1}H NMR, IR, and UV spectroscopy showed that this compound is *N*-isocyanurato-substituted [60]fullereno[1,2-*d*]triazoline **6c** (Scheme 7).

Previously,[1] the pathways to the adducts in the reaction of C_{60} to diallyl-substituted isocyanuratoalkyl azides

Scheme 7



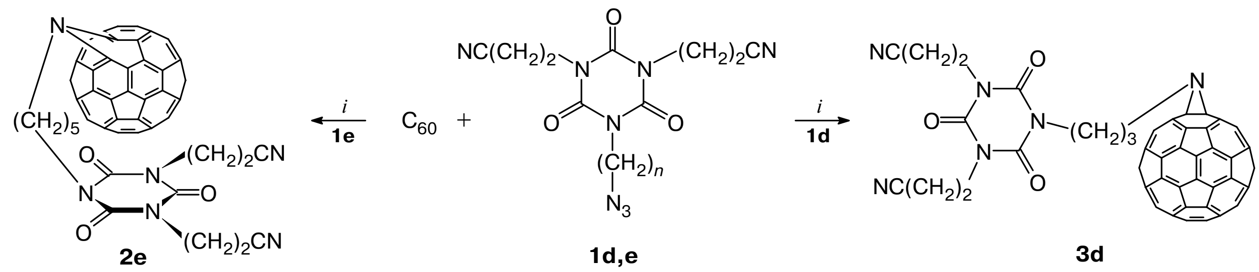
Reagents and conditions: *i. o*-DCB, 50 °C, 4 h; *ii.* 1) *o*-DCB, 70 °C, 1 h; 2) 100 °C, 1 h.

at 180 °C have been interpreted by assuming that the addition of these reagents to fullerene follows a [3+2]-cycloaddition scheme and involves the intermediate formation of fullerenotriazolines **6**, which undergo subsequent thermal transformations to give thermally stable fullerenoaziridines **3** (**6**→**4**→**2**→**3**). When the same reactions were carried out at 100 °C, not only were fullerenotriazolines **6**, fullerenoaziridines **4**, and azahomo[60]fullerenes **2** isolated in experiments, but the sequence of thermal transformations **4b,c**→**2b,c**→**3c**, confirming the assumed reaction scheme, was established. Thus, it was of interest to investigate the thermal behavior of isocyanurato-substituted fullerenotriazolines using compound **6c** as an example.

According to published data[10] and to the theoretical scheme[8] of the decomposition of [60]fullereno[1,2-*d*]triazolines, thermolysis of adduct **6c** could be expected to yield [60]fullereno[1,6-*b*]aziridine **4c** and, to a lesser extent, azahomo[60]fullerene **2c**. However, thermolysis gave [60]fullereno[1,2-*b*]aziridine **3c** as the only product. This was an unexpected result, and one can hardly assume that the **6c**→**4c**→**2c**→**3c** sequence of thermal transformations takes place under these mild conditions because the **4c**→**2c**→**3c** transformations proceed over longer periods of time (at least 10 h) and at higher temperatures (180 °C). Apparently, the decomposition routes of fullerenotriazoline **6c** in an individual state and in a reaction mixture are different.

We have also studied the reactions of C_{60} with dicyanoethyl-substituted isocyanuratoalkyl azides **1d** and **1e** at 100 and 50 °C. At 50 °C, the reaction did not take place, as indicated by quantitative recovery of unchanged fullerene. Study of the structures of the adducts isolated from the reaction mixtures at 100 °C showed that they differ from the products isolated upon the reactions of fullerene with the corresponding diallyl-substituted azides **1b** and **1c** under the same temperature conditions. At 100 °C, the reaction with azide **1d** gave [60]fullere-

Scheme 8



i. o-DCB, 50 °C, 4 h.

no[1,2-*b*]aziridine **3d**, which was prepared previously[1] at 180 °C. This is also indicated by TLC and UV-spectroscopy data.

Conversely, the reaction of C_{60} with azide **1e** yielded azahomo[60]fullerene **2e**, whose structure was confirmed by ^{1}H and ^{13}C NMR, UV, and IR spectroscopy (see Tables 5—7). Previously,[1] we found that fullerenoaziridine **3d** is thermally stable on prolonged refluxing in an *o*-dichlorobenzene solution. Under the same conditions, azahomo[60]fullerene **2e** decomposed to give fullerene, whereas the diallyl-substituted analog **2c** was converted into the corresponding fullerenoaziridine **3c**.[3]

In addition to fullereno-containing adducts, the corresponding azo compounds, 1,8-di[3,5-di(2-cyanoethyl)-2,4,6-trioxo-1,3,5-triazinyl]-4,5-diazaoct-4-ene **(7d)** and 1,12-di[3,5-di(2-cyanoethyl)-2,4,6-trioxo-1,3,5-triazinyl]-6,7-diazadodec-6-ene **(7e)**, were isolated upon the reaction of C_{60} with azides **1d** and **1e** at 100 °C; the parameters of these products (R_f and UV, IR, and ^{1}H NMR spectra) were identical to the characteristics of the same azo compounds isolated[1] upon similar reactions carried out at 180 °C. The isolation of azo compounds **7d** and **7e** suggests that azides **1d** and **1e** decompose during the reactions to nitrenes, which, in turn, react with C_{60} according to the [2+1]-cycloaddition pattern. In this case, the isolation of azahomofullerene **2e** does not contradict the formation of nitrenes if one assumes a stepwise mechanism of nitrene formation. However, we are still not inclined to explain the outcome of reactions of C_{60} with azides **1d** and **1c** at 100 °C by the presence of nitrenes alone. In view of the fact that cyanoethyl substituents are stronger electron acceptors than allyl substituents, the reaction outcome is also consistent with our previous assumption according to which an increase in the electron-withdrawing capacity of the organic fragment in the azide and its close arrangement to the azido group promote isomerization of the products of azide [3+2]-cycloaddition to fullerene into thermally more stable products.

Thus, our study showed that the structure and stability of the products formed in the reactions of isocyanurato-substituted azides with C_{60} are determined by several factors. First of all, these are the reaction temperature and stability of the azides, which are discussed in the literature. Our results show that besides these factors, one should also take into account the electronegativity of the organic fragment in azides, the remoteness of this fragment from the azido group, and, in some cases, the probability of intramolecular stabilizing interactions.

Experimental

IR spectra were measured on a Bruker IFS-113V FT spectrometer for pellets with KBr for fullerene derivatives and thin films or mineral oil mulls for liquid or solid samples of azides **1f,i** and haloalkylisocyanurates **5f—i**, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker WSL-400 instrument (400.13 MHz and 100.62 MHz, respectively). The δ values were referred to $CDCl_3$. UV spectra were measured on a Specord UV-VIS instrument.

1,3-Diallyl-5-(ω-azidoalkyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-triones (1f—i) and **1,3-diallyl-5-(ω-bromoalkyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-triones (5f—i)** were synthesized by a previously described procedure.[1] The compounds were purified by chromatography on a column with silica gel (the eluents used were: petroleum ether—Et_2O, 5 : 1, for compounds **1f—i** and petroleum ether—Et_2O, 2 : 1, for compounds **5f—i**). The yields, the data of elemental analysis, and spectroscopic characteristics are presented in Tables 1—3.

Reactions of C_{60} with 1,3-diallyl-5-(ω-azidoalkyl)-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-triones (1f—i) at 180 °C (general procedure). A mixture of C_{60} (72 mg, 0.1 mmol) and the corresponding azide **1f—i** (0.3 mmol) in 25 mL of anhydrous degassed *o*-DCB was heated at reflux for 4 h. The solvent was distilled off. The residue was chromatographed on a column with silica gel. Toluene was used as the eluent to isolate the unreacted fullerene (10—15% of the initial amount), the individual products **1,3-diallyl-5-{2′-([60]fullereno[1,2-*b*]aziridino)ethyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (3f)**, **1,3-diallyl-5-{4′-([60]fullereno[1,2-*b*]aziridino)butyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (3g)**, and **1,3-diallyl-5-[10′-(azahomo[60]fullereno)decyl]-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (2i)**, and a mixture of monoadducts **1,3-diallyl-5-{6′-([60]fullereno[1,2-*b*]aziridino)hexyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (3h)** and **1,3-diallyl-5-[6′-(azahomo[60]fullereno)hexyl]-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (2h)**; elution with a 10 : 1 mixture of toluene with Et_2O gave diadducts, which were detected in each reaction. TLC (R_f, Silufol plates, elution with toluene—Et_2O, 10 : 1): 0.41 **(3f)**, 0.61 **(3g)**, 0.59 **(2h)**, 0.61 **(3h)**, 0.52 **(2i)**. The yields, the data of elemental analysis and spectroscopic characteristics are presented in Tables 4—7. IR (KBr), ν/cm^{-1}: for **3f**, 1647 (ν(C=C)); 930, 989 (δ =CH); 1692 (ν(C=O)); 528 (fullerene fragment); for **3g**, 1646 (ν(C=C)); 929, 989 (δ =CH); 1689 (ν(C=O)); 525 (fullerene fragment); for **2i**, 1645 (ν(C=C)); 993, 1000 (δ =CH); 1690 (ν(C=O)); 527 (fullerene fragment); for a mixture of **3h** and **2h**, 1644 (ν(C=C)); 929, 990 (δ =CH); 1691 (ν(C=O)); 527 (fullerene fragment).

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 1b,g,h,d,e at 100 °C (general procedure). A mixture of C_{60} (86 mg, 0.12 mmol) and the corresponding azide **1b,d,e,g,h** (0.3 mmol) in 25 mL of anhydrous degassed *o*-DCB was heated for 5 h at 100 °C. The solvent was evaporated *in vacuo*. The residue was chromatographed on a column with silica gel. Toluene was used as the eluent to isolate unreacted fullerene (30 to 50% of the initial amount) and the corresponding individual compounds: **1,3-diallyl-5-{3′-([60]fullereno[1,6-*b*]aziridino)propyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (4b)**, **1,3-diallyl-5-{4′-([60]fullereno[1,6-*b*]aziridino)butyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (4g)**, **1,3-diallyl-5-{6′-([60]fullereno[1,6-*b*]aziridino)hexyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (4h)**; a 20 : 1 mixture of toluene with Et_2O was used to isolate the following individual compounds: **1,3-diallyl-5-{3′-([60]fullereno[1,2-*d*]triazolino)propyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (6b)**, **1,3-diallyl-5-{4′-([60]fullereno[1,2-*d*]triazolino)butyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (6g)**, **1,3-diallyl-5-{6′-([60]fullereno[1,2-*d*]triazolino)hexyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (6h)** and **1,3-di(2′-cyanoethyl)-5-[5′-(azahomo[60]fullereno)pentyl]-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (2e)**; elution with a 6 : 1 toluene—Et_2O mixture afforded **1,3-di(2′-cyanoethyl)-5-{3′-([60]fullereno[1,2-*b*]aziridino)propyl}-1,3,5-triazine-**

2,4,6-(1*H*,3*H*,5*H*)-trione (3d), acetone was used to isolate **1,8-di[2,4,6-trioxo-3,5-di(2-cyanoethyl)-1,3,5-triazinyl]-4,5-diazaoct-4-ene (7d)** and **1,12-di[2,4,6-trioxo-3,5-di(2-cyanoethyl)-1,3,5-triazinyl]-6,7-diazadodec-6-ene (7e)**. Characteristics of compounds **3d** and **7d,e** coincide with those reported previously.[1] TLC (R_f, Silufol plate, elution with toluene—Et_2O, 10 : 1): 0.80 (**4b**), 0.77 (**4g**), 0.77 (**4h**), 0.62 (**6b**), 0.53 (**6g**), 0.60 (**6h**), 0.48 (toluene—acetone, 10 : 1) (**2e**), 0.61 (**3d**) (toluene—Et_2O—acetone, 10 : 2 : 2), 0.21 (acetone) (**7d**), 0.30 (acetone) (**7e**). The yields, the data of elemental analysis, and spectroscopic characteristics are presented in Tables 4—7. IR (KBr), ν/cm^{-1}: for **4b**, 1647 (ν(C=C)); 931, 990 (δ =CH); 1691 (ν(C=O)); 527 (fullerene fragment); for **6g**, 1633 (ν(C=C)); 935, 1000 (δ =CH); 1693 (ν(C=O)), 527 (fullerene fragment); for **6h**, 1645 (ν(C=C)); 993, 984 (δ =CH); 1693 (ν(C=O)); 527 (fullerene fragment); for **2e**, 1691 (ν(C=O)); 2251 (ν(CN)); 527 (fullerene fragment).

1,3-Diallyl-5-{5′-([60]fullereno[1,2-*d*]triazolino)pentyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (6c). Azide **1c** (0.12 g, 0.33 mmol) was added dropwise to a solution of C_{60} (96 mg, 0.13 mmol) in 25 mL of anhydrous degassed *o*-DCB and the mixture was heated with stirring for 6 h at 50 °C. The solvent was evaporated *in vacuo* and the residue was chromatographed on a column with silica gel. Elution with toluene afforded 36 mg (38%) of C_{60}, while the use of a 20 : 1 toluene—Et_2O mixture gave compound **6c**. TLC (R_f, Silufol plates, elution with toluene—Et_2O, 10 : 1): 0.52. The yield, the data of elemental analysis, and spectroscopic characteristics are presented in Tables 4—7. IR (KBr), ν/cm^{-1}: 1643 (ν(C=C)); 929, 989 (δ =CH); 1689 (ν(C=O)); 527 (fullerene fragment).

Thermolysis of 1,3-diallyl-5-[10′-(azahomo[60]fullereno)decyl]-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (2i). A solution of compound **2i** (10 mg) in 5 mL of anhydrous degassed *o*-DCB was heated at reflux for 10 h. The mixture was chromatographed on a column with silica gel using toluene as the eluent to give C_{60} (3 mg, yield 45%) and compound **3i** (4 mg, 40%). TLC (R_f, Silufol plates, elution with toluene—Et_2O, 10 : 1): 0.70. The UV spectrum is given in Table 6.

Thermolysis of 1,3-diallyl-5-[3′-([60]fullereno[1,6-*b*]aziridino)propyl]- and 1,3-diallyl-5-[5′-([60]fullereno[1,6-*b*]aziridino)pentyl]-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-triones (4b,c). A solution of compound **4b,c** (10 mg) in 5 mL of anhydrous degassed *o*-DCB was heated at reflux for 10 h. The mixture was chromatographed on a column with silica gel using toluene as the eluent to give (in the case of **4b**) 3 mg (yield 30%) of **1,3-diallyl-5-[3′-(azahomo[60]fullereno)propyl]-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (2b)** or (in the case of **4c**) 5 mg (50%) of C_{60} and 4 mg (40%) of **1,3-diallyl-5-[5′-(azahomo[60]fullereno)pentyl]-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (2c)**. TLC (R_f, Silufol plates, elution with toluene—Et_2O, 10 : 1): 0.35 (**2b**) and 0.59 (**2c**). The UV spectrum of compound **2b** is given in Table 6. Characteristics of compound **2c** corresponded to those of the sample obtained previously.[2]

Thermolysis of 1,3-diallyl-5-{6′-([60]fullereno[1,2-*d*]triazolino)hexyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (6c). A solution of compound **6c** (10 mg) in 5 mL of anhydrous degassed *o*-DCB was heated at reflux for 10 h. The mixture was chromatographed on a column with silica gel using toluene as the eluent to give 3 mg (45%) of C_{60} and 4 mg (40%) of **1,3-diallyl-5-{5′-([60]fullereno[1,2-*b*]aziridino)pentyl}-1,3,5-triazine-2,4,6-(1*H*,3*H*,5*H*)-trione (3c)**, whose characteristics corresponded to those of the product prepared previously.[3]

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