Synthesis and study of trannulene derivatives of fullerenes

*E. A. Khakina,[a] A. S. Peregudov,[b] S. I. Troyanov,[c] and P. A. Troshin[a]**

[a]*Institute of Problems of Chemical Physics, Russian Academy of Sciences, 1 prosp. Akad. Semenova, 142432 Chernogolovka, Moscow Region, Russian Federation. Fax +7 (496) 522 1852. E-mail: troshin@cat.icp.ac.ru*
[b]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991 Moscow, Russian Federation. Fax: +7 (495) 135 6549. E-mail: asp@ineos.ac.ru*
[c]*Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119991 Moscow, Russian Federation. Tel.: +7 (495) 939 5396. E-mail: stroyano@thermo.chem.msu.ru*

A series of trannulenes $C_{60}F_{15}[CX(COOR)_2]_3$ (X = COOMe, Br; R = Me, Et, Pr^n, *n*-Hex, Bu^t, $(CH_2)_3NHCOOBu^t$) was synthesized. The first water-soluble trannulenes containing six carboxyl groups ($C_{60}F_{15}[C(COOMe)(COOH)_2]_3$) or six protonated amino groups ($C_{60}F_{15}[C(COOMe)(COO(CH_2)_3NH_3^+CF_3COO^-)_2]_3$) were obtained. The compositions and structures of all compounds were proved by mass spectrometry, ^1H, ^{13}C, and ^{19}F NMR spectroscopy, and other physicochemical methods. The reactivity of trannulenes was studied for the first time. The unique isomerization of trannulenes to triumphenes accompanied by the migration of three organic addends from one hemisphere of the fullerene cage to another hemisphere was discovered. The structures of the isomerization products were proved using single-crystal X-ray diffraction analysis and ^1H, ^{13}C, and ^{19}F NMR spectroscopy. The concerted cascade of isomerization, elimination, and addition reactions was accomplished, which made it possible to obtain photoactive dyads $C_{60}F_{14}R_2$=**A** (R = C(X)(COOR)$_2$, **A** is a fragment of fullerenes C_{60} or C_{70}, anthracene, or pentacene). These dyads contain the electron-deficient fluorofullerene core and electron-donor (with respect to the fluorofullerene core of the molecule) addend **A**. Photoinduced charge separation can occur in these systems, which makes them analogs of natural photosynthetic antennas.

Key words: fullerenes, annulenes, fluorination, nucleophilic substitution, isomerization.

Halofullerenes are promising precursors for the synthesis of diverse polyfunctional fullerene derivatives. Fluorofullerene $C_{60}F_{18}$ is of special interest, since it is highly symmetric and a powerful electron acceptor. One of the most remarkable reactions[1] of fluorofullerene $C_{60}F_{18}$ is its reaction with such CH acids as $HCBr(COOEt)_2$ in the presence of a base, resulting in the unusual fullerene derivative named "trannulene" (Scheme 1).

Trannulenes are fullerene derivatives containing the aromatic 18-membered macrocycle encircling the molecule along the equator. The cyclic system of trannulenes is nonplanar. All conjugated π-bonds of the macrocycle are in the *trans*-configuration due to rigidity of the fullerene macrocycle. Unlike classical [18]annulenes containing the planar aromatic ring, the π-orbitals in trannulenes are overlapped not above and below the ring plane but by parallel to the plane (Fig. 1). This variant of π-conjugation was named "planar aromaticity." [2]

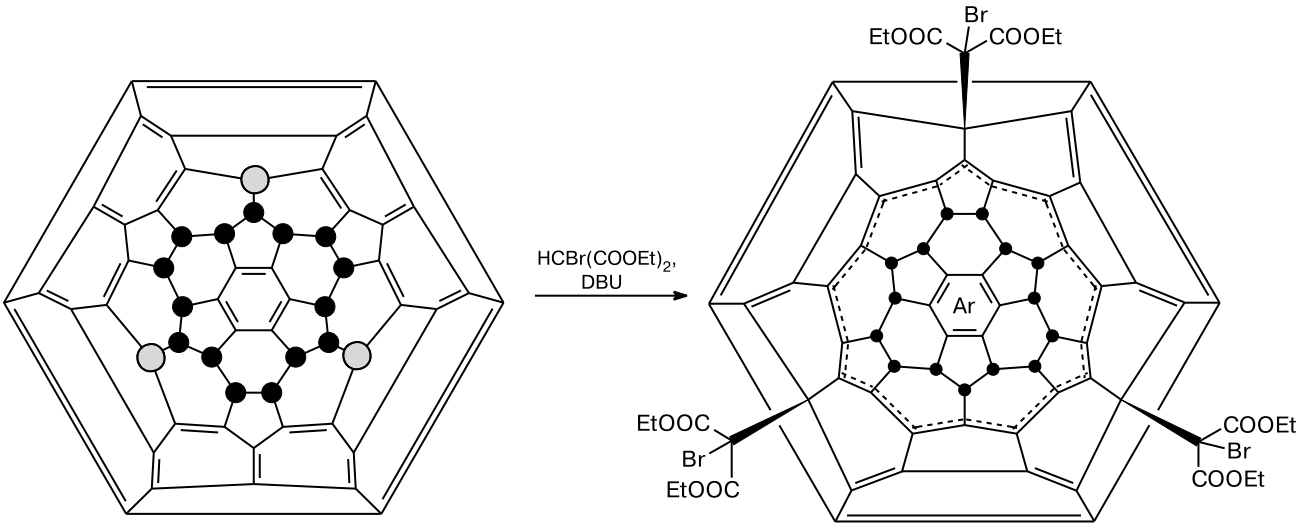
Interest in trannulenes is not only theoretical. Trannulenes are highly stable and demonstrate interesting electronic properties, which can form a basis for a series of practical applications. Several works on the synthesis of new types of trannulene derivatives of fullerenes containing no fluorine atoms[3,4] and on the study of properties of various trannulenes[5—7] have recently been published.

Many fullerene derivatives are biologically active and can be used in medicine. They are good photosensitizers capable of transforming oxygen into the active singlet form in nearly 100% quantum yield.[8] At the same time, the fullerene derivatives can selectively be accumulated in cells of cancer tumors.[9] These properties favor to use the fullerene derivatives in photodynamic anticancer therapy.[10,11] Fullerene and its simplest derivatives absorb light only in the short-wavelength range. However, this radiation does not penetrate deeply into living tissues. This problem can be solved if trannulene derivatives of fullerenes absorbing in the red and near-IR spectral ranges are used as photosensitizers.

It is known that some fullerene derivatives can selectively be accumulated in the bone tissue.[12] Therefore, the

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 264—279, February, 2012.
1066-5285/12/6102-264

Scheme 1



use of trannulenes for drug delivery to bones, for instance, at osteoporosis can be promising. In particular, water-soluble fluorinated trannulenofullerenes can be used as carriers of labile fluorine atoms that are attached to the cage and can readily be eliminated in the bone tissue to form fluorophosphates. Thus, water-soluble trannulenes can become valuable compounds for biomedical applications.

A restricted range of trannulene derivatives of fullerene has already been prepared to date in milligram amounts.[13,14] However, the chemistry of trannulenes remains unstudied so far.

In this work, we synthesized a series of new trannulenes, including water-soluble, and studied their chemical transformations.

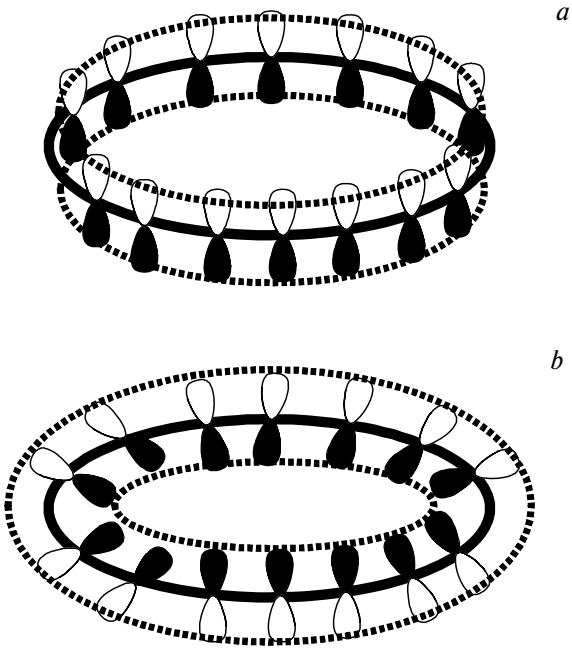


Fig. 1. Orbital overlap in classical annulenes (*a*) and trannulenes (*b*).

Results and Discussion

Synthesis of fluorinated trannulenofullerenes

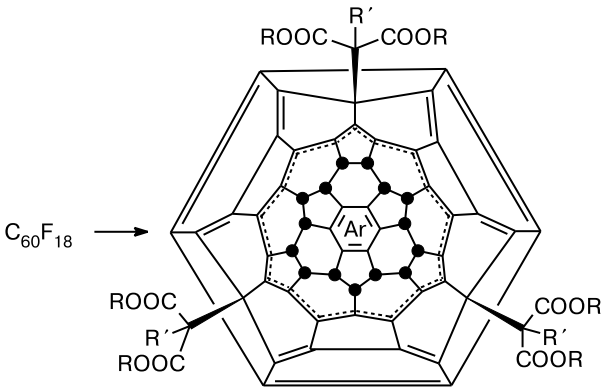
Trannulenes **1**—**6** were synthesized by the reaction of $C_{60}F_{18}$ with compounds of the $CHR'(COOR)_2$ type in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as a base (Scheme 2). The trannulenes were isolated and purified using column chromatography on silica gel.

We have synthesized compounds **3**—**6** for the first time. Note that earlier trannulenes were obtained only in amounts of 3—30 mg. The procedures developed by us make it possible to synthesize trannulenes in gram amounts. Particularly, 700 mg of pure trannulene **5** was synthesized from fluorofullerene $C_{60}F_{18}$ within several hours in a yield higher than 50%. This example shows that trannulenes become accessible compounds for various studies and practical applications.

The structures of trannulenes **1**—**6** were proved by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. This is exemplified by the ^1H, ^{13}C, and ^{19}F NMR spectra of compound **6** (Fig. 2).

An analysis of the ^{19}F NMR spectra of compound **6** suggests that **6** contains three types of fluorine atoms and its molecule belongs to the point symmetry group C_{3v} characteristic of trannulenes. The ^1H NMR spectrum of compound **6** exhibits two signals corresponding to the protons of the *tert*-butyl and methyl groups. The

Scheme 2



1—6

Compound	R	R´	Yield
1	Me	Br	37
2	Et	Br	40
3	Pr^n	Br	47
4	C_6H_{13}	Br	33
5	Me	COOMe	68
6	Bu^t	COOMe	48

Reactants and conditions: $HCR´(COOR)_2$ (5 equiv.), DBU (0.9 equiv.), toluene.

^{13}C NMR spectrum of compound **6** also confirms the structure proposed.

Synthesis of water-soluble trannulenes

Reflux of trannulene **6** in trifluoroacetic acid for 2 h results in the cleavage of the protective *tert*-butyl ester groups in the addends to form trannulene **7** containing six carboxyl groups in a quantitative yield (Scheme 3).

The structure of the synthesized compound was determined by ^1H, ^{13}C, and ^{19}F NMR spectroscopy (Fig. 3).

The ^1H NMR spectrum of trannulene **6** contains two singlets at δ 1.67 (OBu^t) and 4.05 (OMe) with the intensity ratio 1 : 6 (see Fig. 2, *a*). The ^1H NMR spectrum of compound **7** (see Fig. 3, *a*) exhibits only a singlet at δ 3.31 belonging to the protons of the COOMe group. The ^{13}C NMR spectra of compounds **6** and **7** turned out to be similar, which confirms their C_{3v} symmetry and the presence of the trannulene fragment in it. The spectrum of compound **6** differs only by the presence of signals from the *tert*-butyl groups (δ 27.96 and 85.89). The ^{19}F NMR spectra of compounds **6** and **7** contain three signals with the intensity ratio 3 : 6 : 6, which corresponds to the trannulene structure. Thus, the ^1H, ^{13}C, and ^{19}F NMR spectra confirm the structure of trannulene **7**.

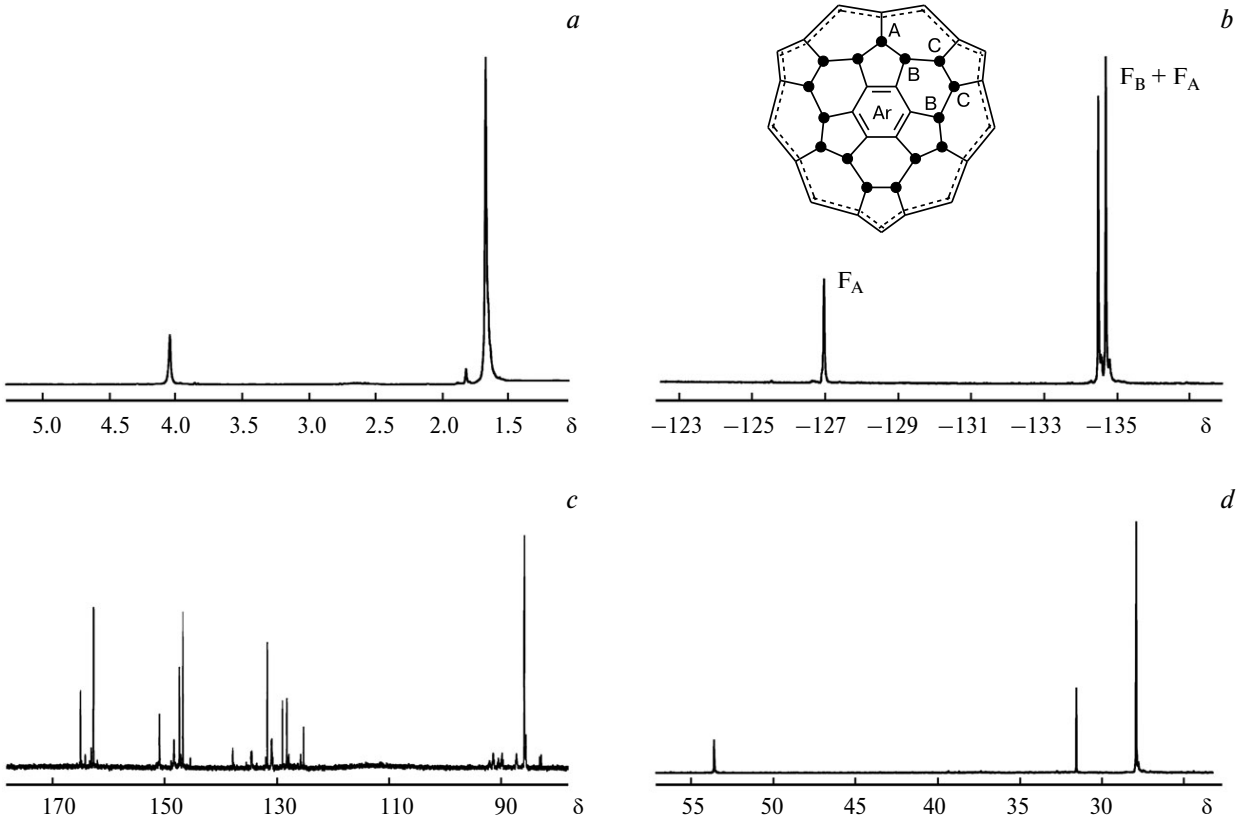
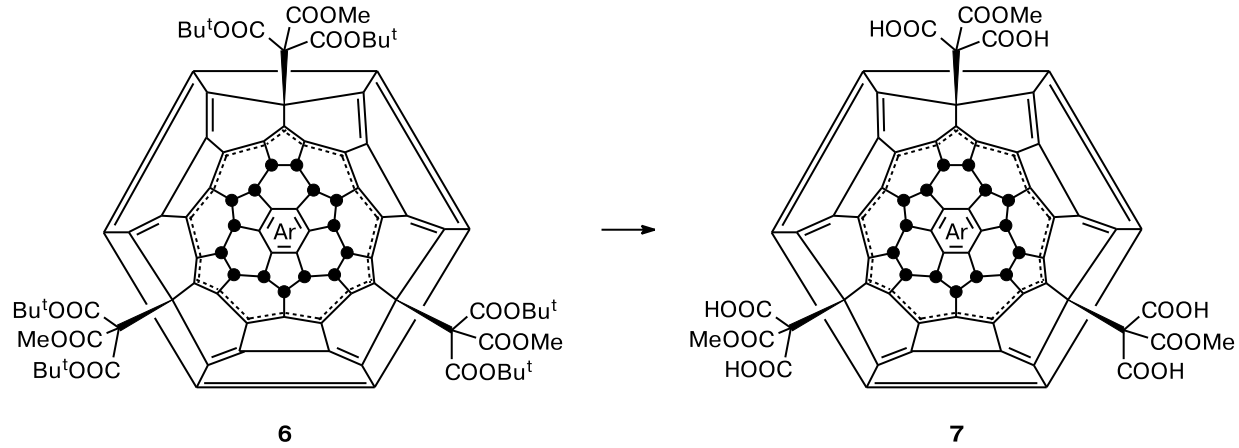


Fig. 2. ^1H (*a*), ^{19}F (*b*), and ^{13}C (*c*, *d*) NMR spectra of trannulene **6** in $CDCl_3$.

Scheme 3



6 **7**

Reactants and conditions: CF_3COOH, 72 °C, 2 h.

The precursor for the synthesis of trannulene **8** (Scheme 4) was prepared in several steps. The first step was the Boc-protection of 3-aminopropan-1-ol. The subsequent acylation of the formed product **9** with malonic acid in the presence of dicyclohexylcarbodiimide as a condensing agent gave ester **10** with two protected amino groups. Compound **10** was treated with sodium hydride and methyl chloroformate, giving key precursor **11**.

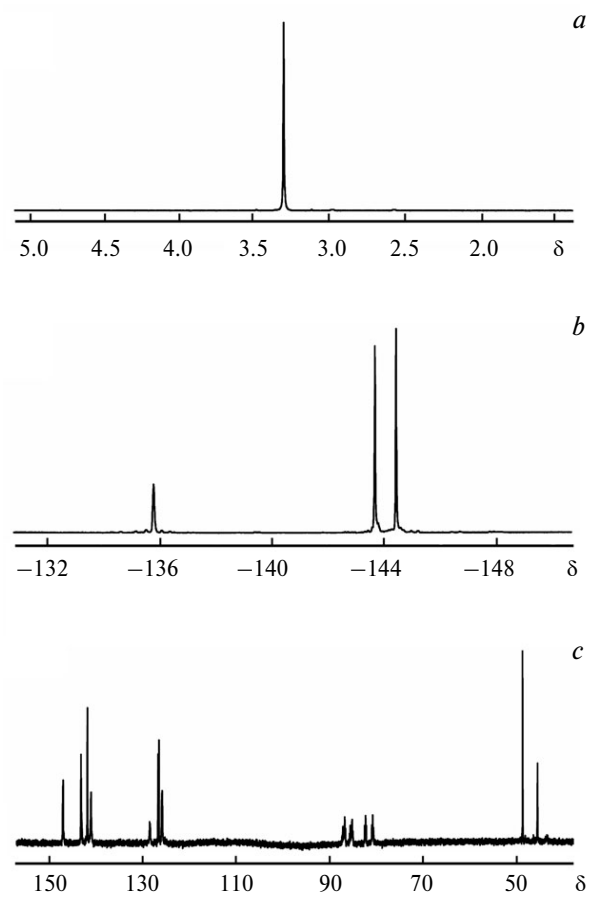


Fig. 3. ^1H (*a*), ^{19}F (*b*), and ^{13}C (*c*) NMR spectra of trannulene **7** in DCOOD.

The reaction of $C_{60}F_{18}$ with an excess of compound **11** (5 equiv.) yields trannulene **12** containing six Boc-protected amino groups. The protective groups are easily removed by treatment of **12** with trifluoroacetic acid for 10 min at ambient temperature. The reaction product is the first water-soluble trannulene **8** containing cationoid solubilizing groups, which was isolated as an emerald-green powder.

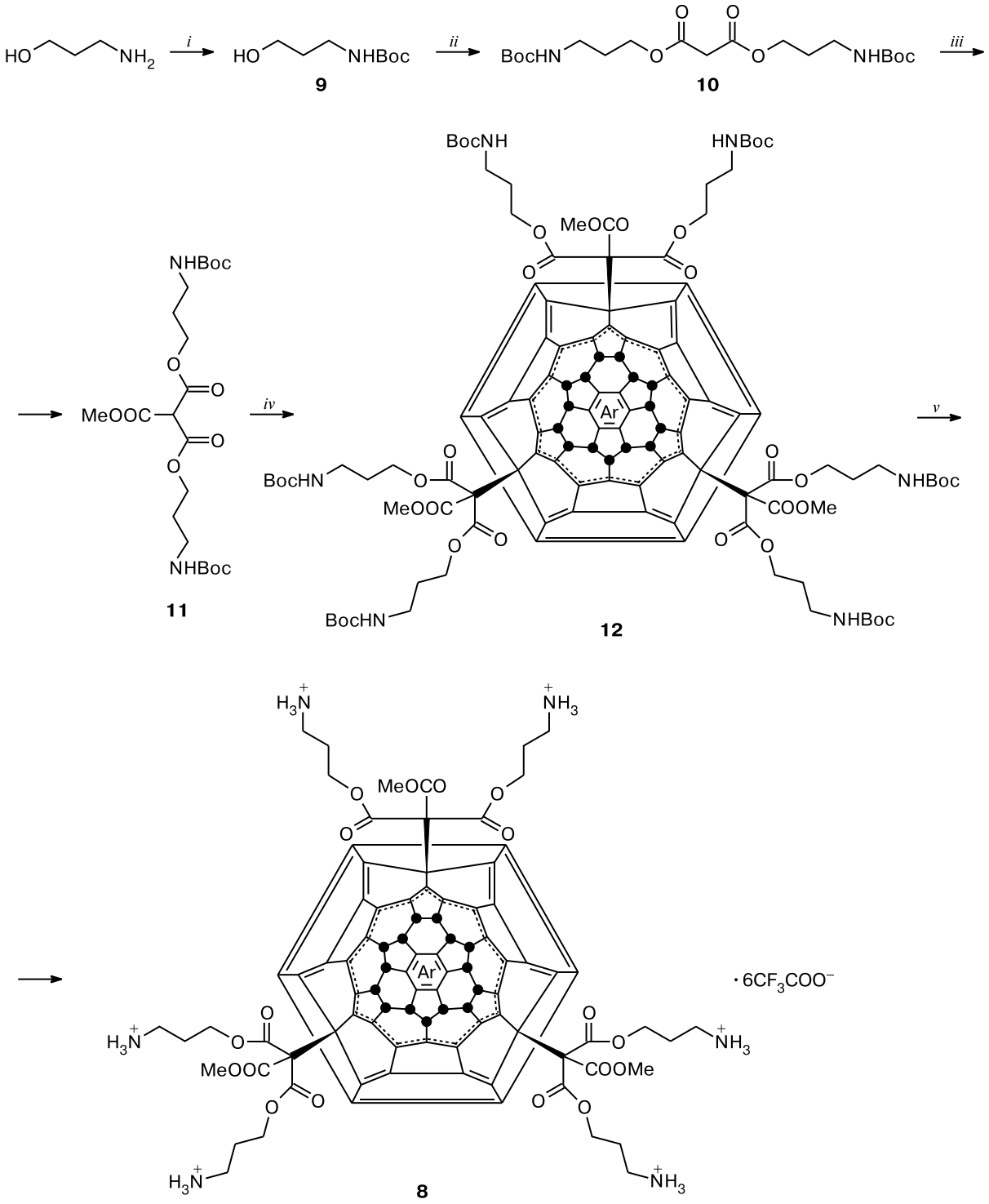
The ^{19}F NMR spectra of compounds **8** and **12** are very similar: they contain three signals with the intensity ratio 1 : 2 : 2, which is characteristic of trannulenes. The ^1H and ^{13}C NMR spectra turned out to be non-informative, possibly, because of the complicated structures of compounds **8** and **12** exhibiting hindered rotation of the attached organic addends.

Solubility of trannulenes **7** and **8** in water differs sharply. Trannulene **7** is hydrophobic, although its structure includes six polar carboxyl groups. However, it is highly soluble in polar organic solvents, for instance, in acetic, formic, and trifluoroacetic acids, 1,4-dioxane, and THF. Solutions of trannulene **7** in an aqueous medium were obtained by its primary dissolution in a minimum amount of an appropriate organic solvent followed by the addition of 10—100 volumes of distilled water. By contrast to **7**, trannulene **8** is hydrophilic: 15 mg of **8** are dissolved in one droplet of distilled water.

The absorption spectra of compounds **7** and **8** in water compared to the spectra of the starting trannulenes **6** and **12** in toluene are shown in Fig. 4.

It is seen that these spectra are similar. The spectra of **7** and **8** almost are not broadened, suggesting that compounds **7** and **8** are not prone to form large aggregates in water.

Scheme 4



Reactants and conditions: *i.* Boc_2O, CH_2Cl_2; *ii.* $CH_2(COOH)_2$, DCC, DMAP, DMF, 5 h; *iii.* 1) NaH, DMF, 2) ClCOOMe; *iv.* $C_{60}F_{18}$, DBU, toluene; *v.* CF_3COOH, 20 °C, 10 min.

This distinguish them from many other water-soluble fullerenes with high affinity to association in aqueous solutions.

Unfortunately, trannulenes **7** and **8** are unstable in an aqueous medium. Aqueous solutions of these trannulenes

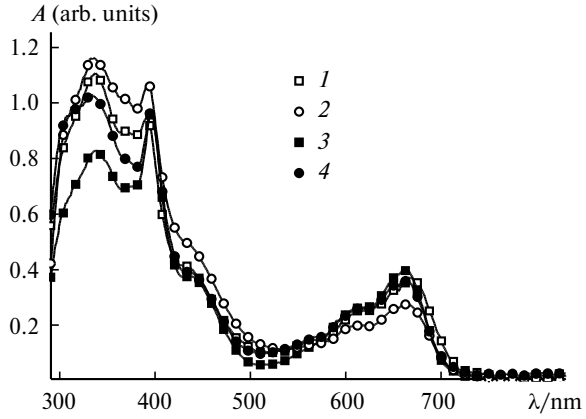


Fig. 4. Absorption spectra of trannulenes **7** (*1*) and **8** (*2*) in water and the starting trannulenes **6** (*3*) and **12** (*4*) in toluene.

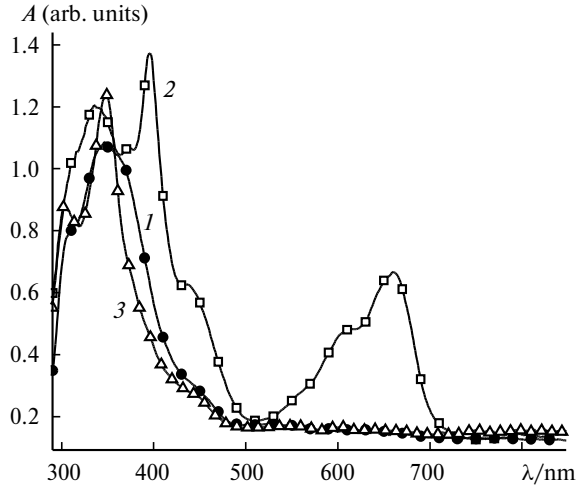


Fig. 5. Absorption spectra of $C_{60}F_{18}$ (*1*), trannulene **5** (*2*), and triumphene **17** (*3*) in toluene.

(concentration ~10^{-6} mol L^{-1}) are completely bleached within 24 h. Similar degradation occurs within several minutes only, if a small amount of water is added to a solution of trannulenes **7** and **8** in dimethyl sulfoxide.

On the contrary, solutions **7** and **8** in aqueous acids are stable and show no signs of degradation within one year. Therefore, we hope that the problem of low stability of trannulenes will be solved and they will become accessible objects for biomedical research.

Isomerization of trannulenes to triumphenes

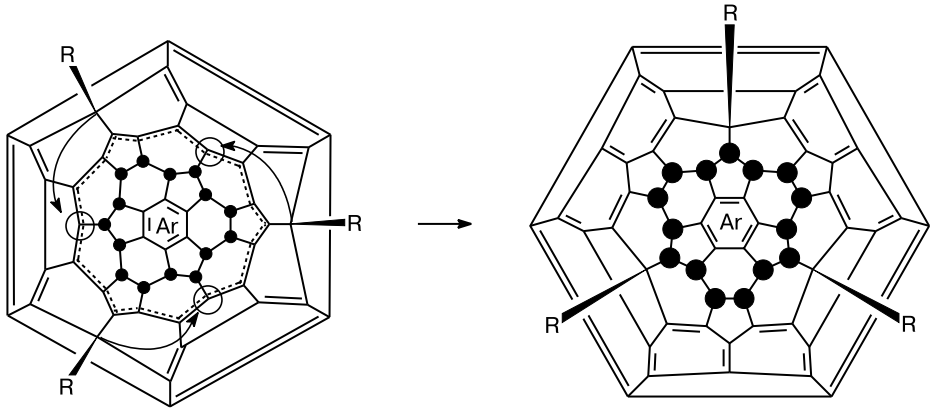
Isomerization of trannulenes 1—6. We found[15,16] a unique isomerization of trannulenofullerenes $C_{60}F_{15}[CX(COOR)_2]_3$ (X = Br, R = Alk) to compounds named "triumphenes." Triumphenes are isostructural to the starting fullerene fluoride $C_{60}F_{18}$ with the only distinction that three peripheral fluorine atoms are replaced by organic residues.

Isomerization occurs on reflux of a trannulene solution in 1,2-dichlorobenzene for several hours. The isomerization is accompanied by the migration of three addends from one hemisphere of the fullerene cage to another hemisphere (Scheme 5).

Trannulenes **1**—**6** were isomerized to give triumphenes **13**—**17** in 70—95% yields (Scheme 6). Triumphene **18** was not isolated from the reaction mixture. Perhaps, compound **18** is not formed at all because of high steric shielding by the bulky *tert*-butyl groups.

During isomerization, the emerald-green color of the reaction mixture changes to olive-green (a mixture of trannulene with triumphene) and then to lemon-yellow (pure triumphene). The absorption spectra of $C_{60}F_{18}$, trannulene **5**, and triumphene **17** are shown in Fig. 5.

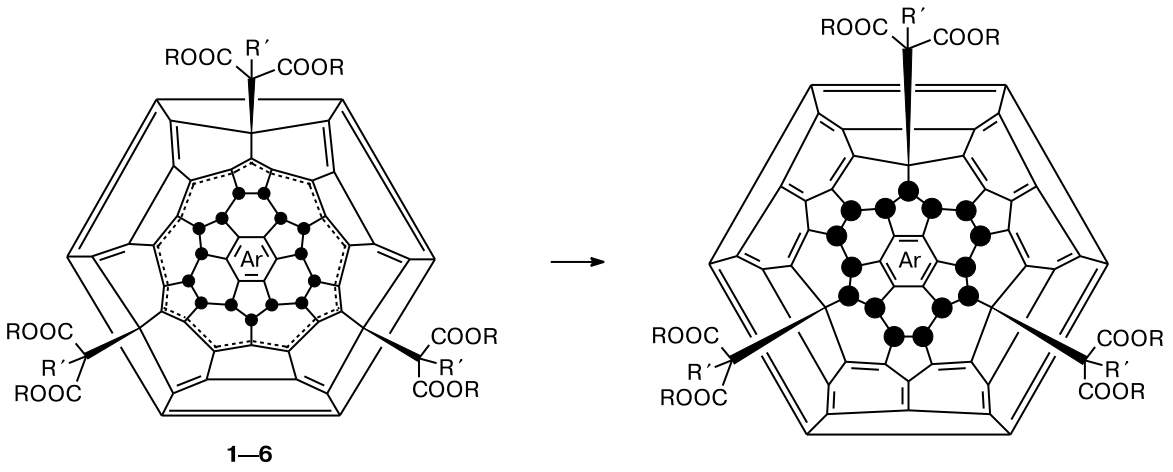
Scheme 5



Trannulene Triumphene

Reactants and conditions: 1,2-ClC_6H_4, 180 °C, 2 h.

Scheme 6



1—6 **13—18**

Compound	R	R′
1, **13**	Me	Br
2, **14**	Et	Br
3, **15**	Pr^n	Br
4, **16**	C_6H_{13}	Br
5, **17**	Me	COOMe
6, **18**	Bu^t	COOMe

Reactants and conditions: 1,2-ClC_6H_4, 180 °C, 2—3 h.

Single crystals of compound **17** useful for X-ray diffraction analysis were obtained by recrystallization from chlorobenzene. It turned out that molecule **17** has a triumphene structure with three trimethoxycarbonylmethyl substituents (Fig. 6).

Addends $C(COOMe)_3$ were detected to exist in a trannulene molecule in such a way that two COOMe groups are directed to the fluorinated part of the cage and the third COOMe group is oriented to the opposite side. The orientation of the addends in form **I** is more energetically favorable than in form **II** (Fig. 7). This is explained by the minimization of steric interactions between the adjacent fluorine atom and COOMe groups.

The structures of compounds **13**—**17** were confirmed by ^1H, ^{13}C, and ^{19}F NMR spectroscopy. The ^1H, ^{13}C, and ^{19}F NMR spectra of compound **17** are compared to those of the starting trannulene **5** in Fig. 8. The NMR spectra of compound **17** show that the rotation of addend $C(COOMe)_3$ is hindered at room temperature. The presence of two signals from protons of the methoxycarbonyl groups with the intensity ratio 2 : 1 in the ^1H NMR spectrum confirms that compound **17** exists in form **I**. The ^1H NMR spectrum of triumphene **17** remained unchanged with the temperature increase to 120 °C (measured in C_6D_5Br) and, hence, it can be concluded that the energy barrier of rotation of the $C(COOMe)_3$ substituents is high. The high rotation barrier is due to the repulsion of the F atom and COOMe group in conformation **II**.

The situation with hindered rotation becomes more complicated for triumphenes **13**—**16**, since addends $CR(COOAlk)_2$ are less symmetric in this case. A decrease in symmetry of the addends allows a more possible conformations to exist for the corresponding

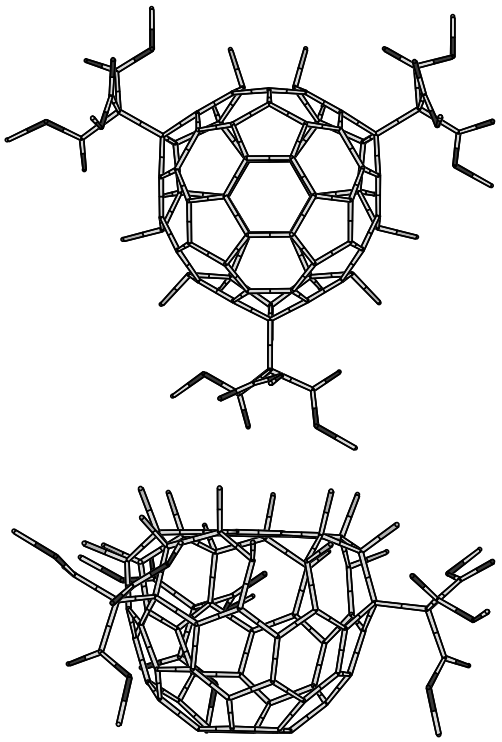


Fig. 6. Molecular structure of triumphene **17** according to X-ray diffraction data. Two projections are shown.

I **II**

Fig. 7. Two possible conformations (**I** and **II**) of the $FCCC(COOMe)_3$ fragment with different arrangements of the $C(COOMe)_3$ groups relative to the adjacent fluorine atom.

triumphenes, which is completely confirmed by the obtained NMR spectra.

Kinetics of isomerization of trannulenes to triumphenes. To reveal possible intermediates formed by the isomerization of trannulene **5** to triumphene **17**, we studied the reaction *in situ* using optical absorption spectroscopy. The change in the absorption spectra of the reaction mixture during the reaction is shown in Fig. 9.

Figure 9 shows that the intensity of the band characteristic of the trannulene fragment (550—750 nm) decreases fourfold 15 min after the beginning of reflux. The complete conversion of the starting trannulene **5** occurs within 2—3 h. No additional bands are observed in the spectra, indicating the absence of any intermediates accumulated in the system.

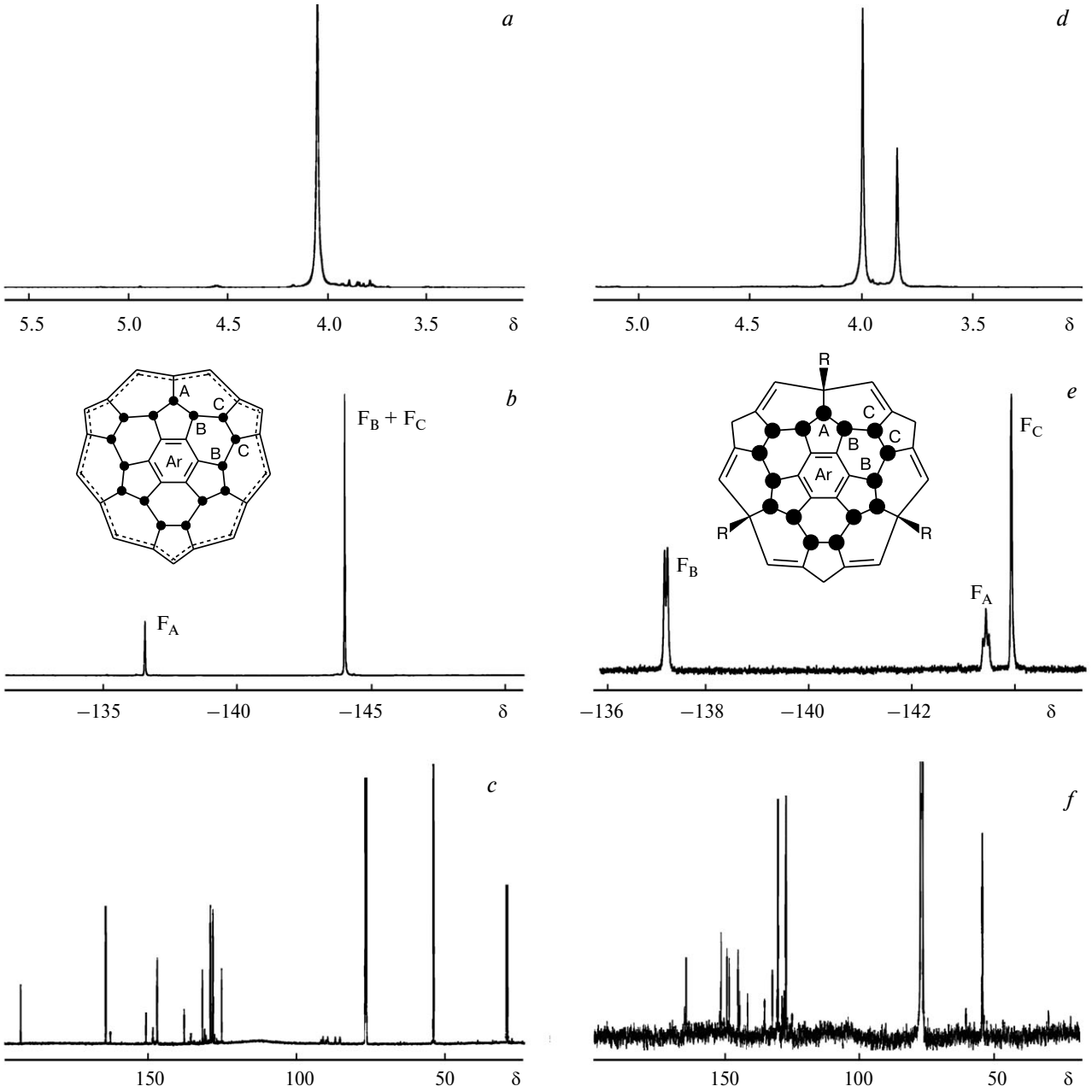


Fig. 8. ^1H (*a*, *d*), ^{19}F (*b*, *e*), and ^{13}C (*c*, *f*) NMR spectra of trannulene **5** (*a*—*c*) and triumphene **17** (*d*—*f*) in $CDCl_3$.

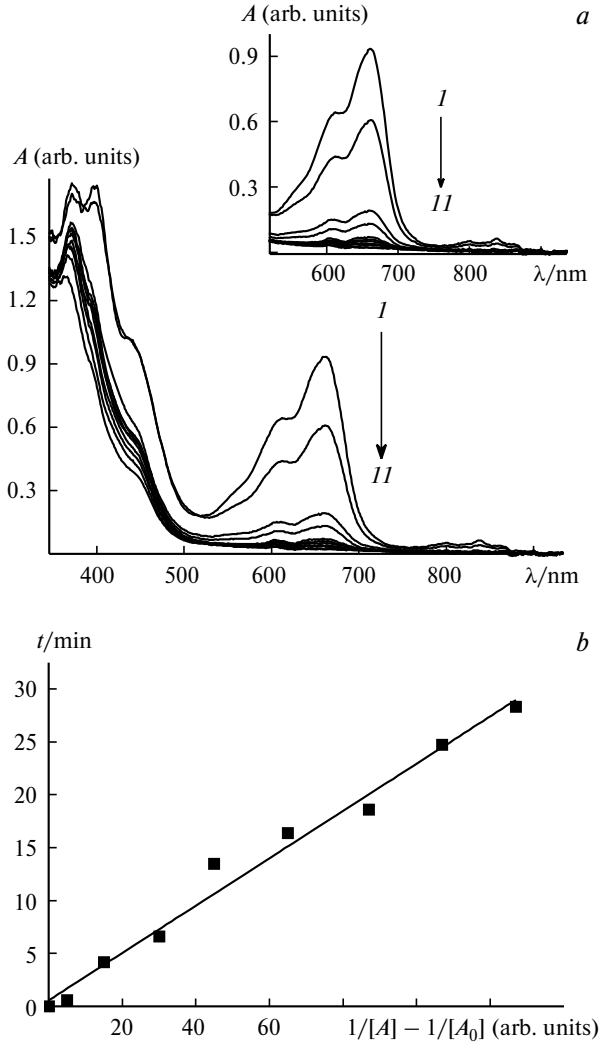


Fig. 9. *a*. Absorption spectra of a solution of trannulene **5** in 1,2-dichlorobenzene recorded before reaction (*1*) and 5 (*2*), 15 (*3*), 30 (*4*), 45 (*5*), 65 (*6*), 87 (*7*), 107 (*8*), 127 (*9*), 147 (*10*), and 173 min (*11*) after the beginning of reflux. The fragment of the absorption spectrum for the wavelengths from 500 to 900 nm in an enlarged scale is shown in inset. *b*. Linear dependence of the reciprocal concentration expressed as $1/[A] - 1/[A_0]$ on the reaction time.

Some information on the kinetics of transformation of trannulene into triumphene was obtained by the analysis of the change in the absorption spectra of the reaction system with time. The experimental data obtained do not obey the logarithmic dependence of changing the trannulene concentration (in this case, the change in the absorbance at 661 nm) with time, which is characteristic of first-order molecular reactions

$$kt = \ln(c_0/c) = \ln([A]/[A_0]),$$

where k is the isomerization constant of trannulene, t is the reaction time, c_0 is the initial concentration of trannulene in the reaction mixture, c is the trannulene concentration in the reaction mixture at moment t, A is the absorption of the reaction mixture at time t, and A_0 is the absorption of the initial trannulene solution.

It is most likely that the reaction is more complicated than the simple monomolecular decomposition or isomerization. Moreover, experimental points fall well onto the linearization coordinates for second-order reactions, where the linear dependence of $1/c$ (in our case, $1/[A]$) on time is observed

$$kt = 1/[A] - 1/[A_0].$$

The rate constant for isomerization of trannulene **5** was determined from the slope ratio of the straight line presented in Fig. 9, c was turned out to be $3.7 \cdot 10^{-3}$ mol^{-1} s^{-1}.

Thus, the isomerization of trannulene **5** has the second order with respect to the reactant. This result seems unexpected, since indicates that two trannulene molecules interact, most likely, in the rate-determining step. Perhaps, they change their organic radicals, finally resulting in the isomerization of trannulene to triumphene. This aspect requires an additional comprehensive examination.

Concerted cascades of isomerization, elimination, and addition reactions. Earlier trannulenes were considered to be very stable due to the aromatic 18-membered cyclic moiety. However, the isomerization of trannulenes to triumphenes discovered by us proves the opposite thesis. Triumphenes are thermodynamically more stable than trannulenes.

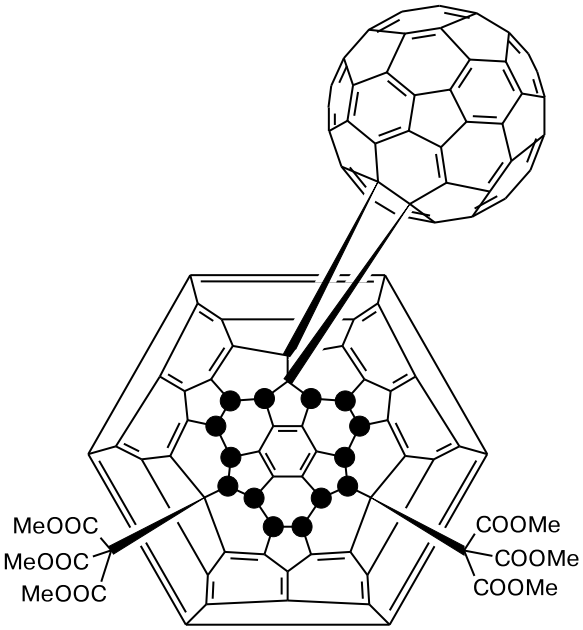
The migration of three organic addends during trannulene isomerization to triumphenes can proceed either as an intramolecular reaction or *via* the dissociation—addition mechanism. In the latter case, the reaction should be accompanied by the formation of free radicals or carbanions.

In order to clarify the mechanism of trannulene isomerization to triumphenes, we attempted to carry out the reaction in the presence of a large excess of unsaturated compounds [A], being traps of free radicals and/or carbanions. It turned out that the isomerization product is formed in fairly high yields even in the presence of the traps. When the reaction was carried out in the presence of maleic anhydride (strong Michael acceptor), the yield of triumphene **17** was 90%. In addition, we found that the isomerization of trannulene **5** in the presence of a series of unsaturated compounds (**A** are fullerenes C_{60} and C_{70}, anthracene, and pentacene) afforded adducts $C_{60}F_{14}R_2$=**A** along with triumphene **17** (Scheme 7).

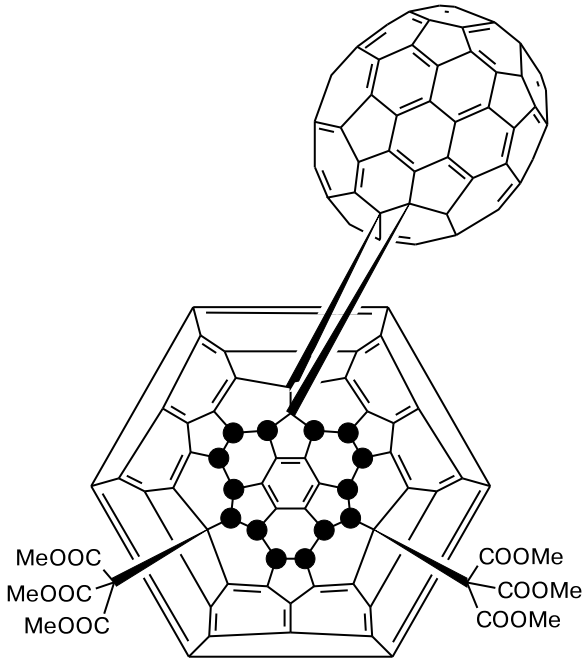
The compositions and structures of the synthesized compounds were determined by ^{1}H, ^{13}C, and ^{19}F NMR spectroscopy, 2D correlation NMR spectroscopy, and mass spectrometry. The ^{19}F NMR spectra of compounds **19**—**22** confirming the C_s symmetry of the obtained adducts are presented in Fig. 10.

Scheme 7

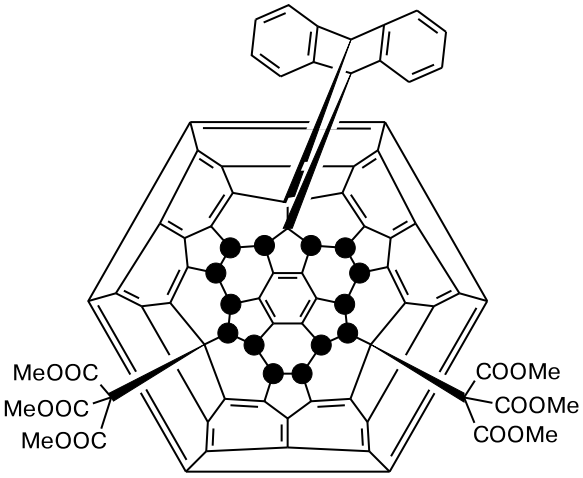
5 ⟶ **19—22** + **17**



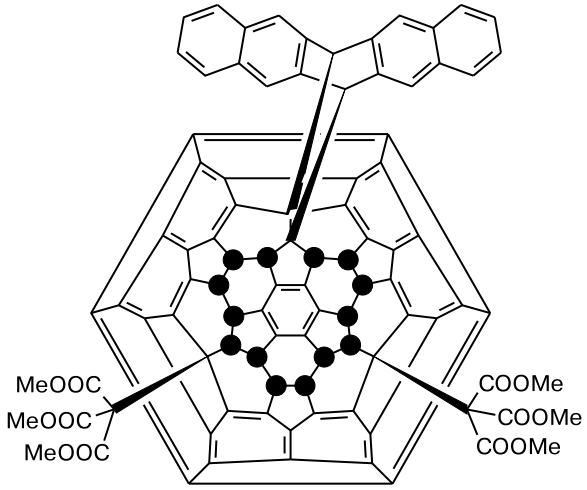
19



20



21



22

Adduct	Yield of adduct (%)	Yield of **17** (%)
19	55—65	30—40
20	50—60	20—25
21	45	20—25
22	35—40	20—30

The experiments indicate that no free radicals or carbanions are formed, most likely, in the isomerization of trannulenes to triumphenes. Thus, the reaction can proceed as an intramolecular process (in this case, the addends migrate as a sequence of sigmatropic shifts) or through the formation of a tight ion pair between the malonate groups formed by dissociation and the fullerene cage. It seems an interesting future task to establish the mechanism of isomerization of trannulenes to triumphenes.

The 12-h reflux of triumphene **17** with a large excess of fullerene C_{60} in 1,2-dichlorobenzene gave 90% of the starting triumphene and only small amounts (5%) of com-

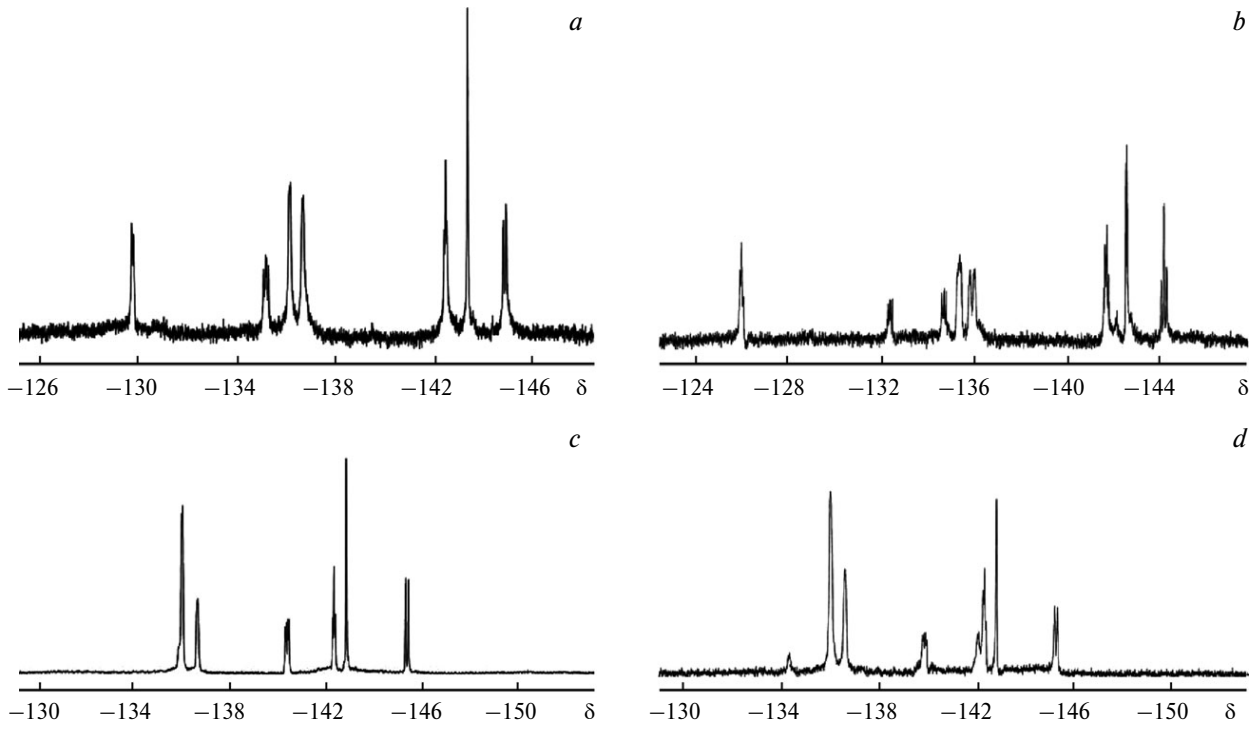


Fig. 10. ^{19}F NMR spectra of compounds **19** (*a*), **20** (*b*), **21** (*c*), and **22** (*d*) in $CDCl_3$.

pound **19**. Thus, it can be assumed that adducts **19**—**22** are formed not from triumphenes but from trannulenes and intermediate products of their isomerization.

Based on the obtained experimental data, we proposed the mechanism for the formation of adducts $C_{60}F_{14}R_2$=**A** (Scheme 8). It is not principal for the consideration of this mechanism how does the migration of addends from one hemisphere of the fullerene cage to another proceed: by the intramolecular reaction, *via* consecutive sigmatropic shifts, or through the formation of a tight ion pair.

The δ-shift of one addend in trannulene **5** affords intermediate **I1**, which can eliminate an R—F molecule to form product **E1**. Intermediates **I2** and **17** are formed due to the successive migration of two remained organic addends in **E1**. Upon the elimination of the R—F molecule, these intermediates can transform into **E2** and **E3**, respectively. All the three elimination products **E1**, **E2**, and **E3** have the same composition ($C_{60}F_{14}R_2$) and can potentially enter [2+2] and [2+4] cycloaddition with unsaturated compounds **A** to form products **A1**, **A2**, and **19**, respectively.

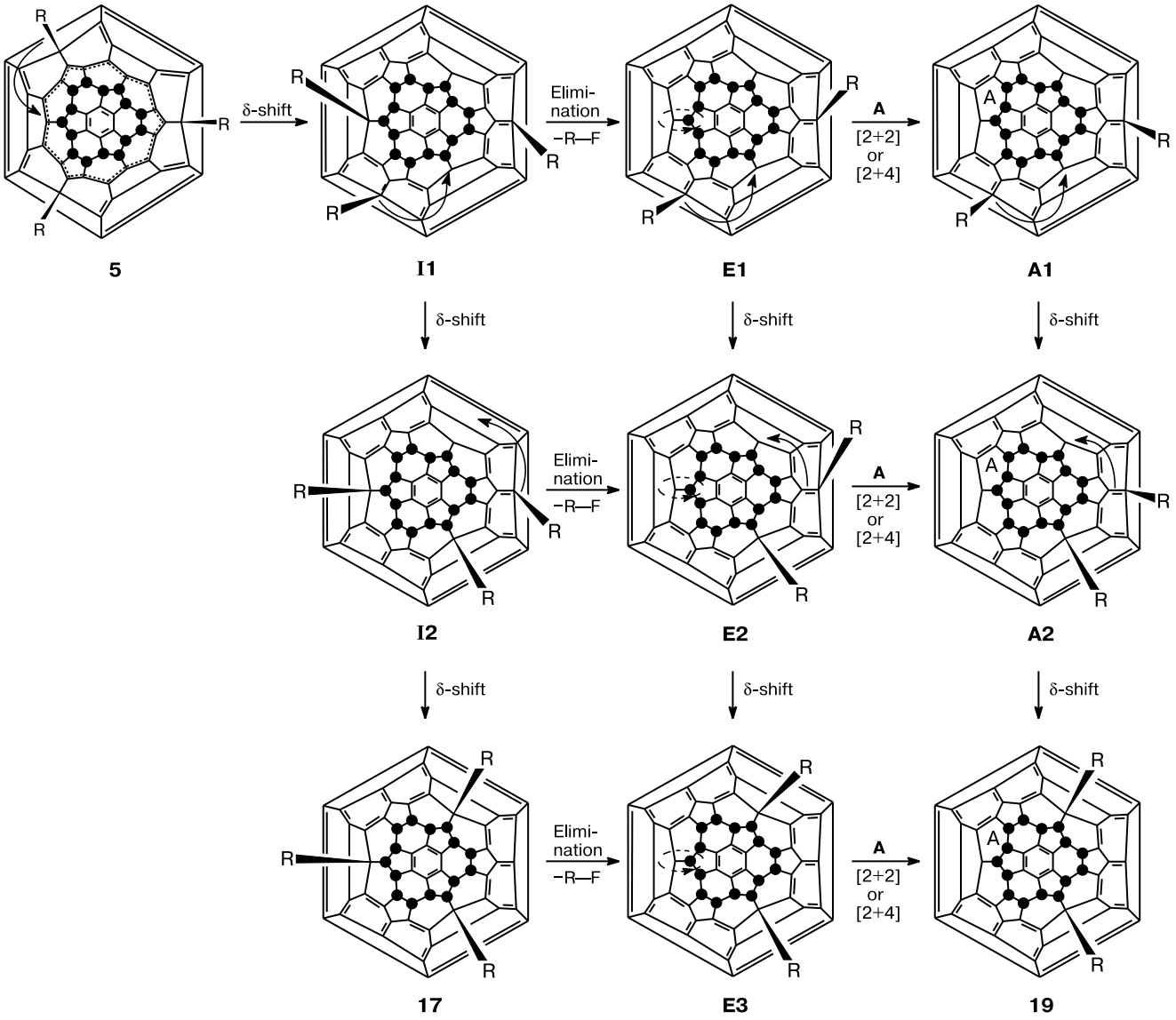
Intermediate **A1** can transform into intermediate **A2** and into compound **19** due to one or two δ-shifts of organic addends R, respectively. Thus, each of three possible intermediates **E1**, **E2**, and **E3** can transform into compound **19**. However, these three reaction directions are not equally efficient. The transformations of trannulene **5** into **I1**, **I1** into **I2**, and **I2** into **17** are thremodynamically controlled. Therefore, stability of these compounds increases in the series **5** < **I1** < **I2** < **I3**.It can be assumed that the activation barriers of the elimination reactions for compounds **I1**—**I3** will increase in the same order. Therefore, the formation of **E1** can be faster than that of **E2**, and **E2** can be formed more rapidly than **E3**. These considerations suggest that the transformation of **5** into **19** proceeds predominantly through the formation of **E1** and **E2** as intermediates. This is also confirmed by experimental data, indicating that **19** is formed from trannulene **5** with considerably higher yields (through **E1**, **E2**, and **E3**) than from triumphene **17** (intermediate **I3**) (only through **E3**).

Thus, adducts $C_{60}F_{14}R_2$=**A** are formed from trannulene **5** as a concerted cascade of consecutive reactions including: (1) isomerization (δ-shift of one or two organic addends), (2) elimination of $FC(COOMe)_3$, (3) [2+2] or [2+4] cycloaddition, and (4) isomerization (δ-shift of one or two organic addends).

Experimental

The ^1H, ^{13}C, and ^{19}F NMR spectra of the synthesized compounds were recorded on Bruker AVANCE 300 (282 MHz (^{19}F)), AMX 400 (400 MHz (^1H)), and Bruker AVANCE 600 (600 MHz (^1H) and 150 MHz (^{13}C)) spectrometers in $CDCl_3$ and DCOOD. Trichlorofluoromethane was used as an external standard for recording ^{19}F NMR spectra. Absorption spectra were obtained on an Avantes AvaSpec-2048 two-channel optofiber spectrometer equipped with a 2D matrix photodetector. IR spectra were measured on a Spectrum BX spectrometer (Perkin—Elmer).

Scheme 8



Mass spectra (electrospray ionization, ESI) were obtained on an Shimadzu LCMS-2020 spectrometer.

Commerically available dimethyl bromomalonate $CHBr(COOMe)_2$, diethyl bromomalonate $CHBr(COOEt)_2$, malonic acid, propan-1-ol, hexan-1-ol, methyl chloroformate, trifluoroacetic acid, Boc_2O, 3-aminopropan-1-ol, DCC, sodium hydride, and maleic anhydride (Acros organics); fullerenes C_{60} and C_{70} (ZAO Fulleren-tsentr, Nizhny Novgorod, Russia); anthracene (Fluka); and pentacene (Aldrich) were used. Dipropyl bromomalonate, dihexyl bromomalonate, tricarbomethoxymethane $CH(COOMe)_3$, and 1,1-dicarbo-*tert*-butoxy-1-carbomethoxymethane $CH(COOMe)(COOBu^t)_2$ were synthesized using known procedures.[17—19] Fluorofullerene $C_{60}F_{18}$ was synthesized by the reaction of fullerene C_{60} with potassium, rubidium, and cesium hexafluoroplatinates according to an earlier published procedure.[20] The compounds synthesized were purified from admixtures by column chromatography on silica gel (Acros organics, 40—60 μm, 60 Å).

Synthesis of trannulenes 1—6 (general procedure). The corresponding CH acid (3—5 equiv.) was added to a solution of $C_{60}F_{18}$ (150 mg, 0.14 mmol) in anhydrous toluene (150 mL). The resulting solution was degassed, and the reaction system was filled with argon. Then, a solution of DBU in toluene (30 mL) was added dropwise with vigorous stirring for 10—15 min to the mixture of reactants (mole ratio of DBU and CH acid was 1 : 2). The mixture was stirred for 10 min and applied onto a chromatographic column packed with silica gel (eluent toluene—ethyl acetate (from 0.5 to 4% vol/vol)). After the solvent was distilled off, the residue was washed with hexane and dried in air. Trannulenes **1—6** were obtained as emerald-green crystalline powders.

Hexamethyl 2,2′,2′′-[23,24,25,26,27,28,41,42,47,48,49, 55,56,59,60-pentadecafluoro-24,25,26,27,28,41,42,47,48,49,

55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]tris(2-bromomalonate) (1). The yield was 37%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.56 (s, 18 H, $CBr(COOC\underline{H}_3)_2$). ^{19}F NMR ($CDCl_3$), δ: −136.20 (s, 3 F); −143.30 (s, 6 F); −143.45 (s, 6 F).

Hexaethyl 2,2′,2′′-[23,24,25,26,27,28,41,42,47,48,49,55,56,59,60-pentadecafluoro-24,25,26,27,28,41,42,47,48,49,55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]tris(2-bromomalonate) (2). The yield was 40%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.51 (t, 18 H, $CBr(COOCH_2C\underline{H}_3)_2$, J = 6.99 Hz); 4.59 (m, 12 H, $CBr(COOC\underline{H}_2CH_3)_2$). ^{19}F NMR ($CDCl_3$), δ: −136.15 (s, 3 F); −143.20 (s, 6 F); −143.53 (s, 6 F).

Hexapropyl 2,2′,2′′-[23,24,25,26,27,28,41,42,47,48,49,55,56,59,60-pentadecafluoro-24,25,26,27,28,41,42,47,48,49,55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]tris(2-bromomalonate) (3). The yield was 47%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.05 (t, 18 H, $CBr(COOCH_2CH_2C\underline{H}_3)_2$, J = 7.47 Hz); 1.87 (m, 12 H, $CBr(COOCH_2C\underline{H}_2CH_3)_2$); 4.46 (m, 12 H, $CBr(COOC\underline{H}_2CH_2CH_3)_2$). ^{19}F NMR ($CDCl_3$), δ: −137.37 (s, 3 F); −144.50 (s, 12 F). ^{13}C NMR ($CDCl_3$), δ: 10.27 ($CBr(COOCH_2CH_2\underline{C}H_3)_2$); 21.82 ($CBr(COOCH_2\underline{C}H_2CH_3)_2$); 70.08 ($\underline{C}Br(COOCH_2CH_2CH_3)_2$); 76.69 ($sp^3$-C of cage); 77.01 (CF); 77.22 (CF); 77.33 (CF); 131.30, 146.71, 147.40, 164.28.

Hexahexyl 2,2′,2′′-[23,24,25,26,27,28,41,42,47,48,49,55,56,59,60-pentadecafluoro-24,25,26,27,28,41,42,47,48,49,55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]tris(2-bromomalonate) (4). The yield was 33%. ^{19}F NMR ($CDCl_3$), δ: −136.28 (s, 3 F); −143.47 (s, 12 F). ^{13}C NMR ($CDCl_3$), δ: 14.00 ($CBr(COO(CH_2)_5\underline{C}H_3)_2$); 22.50 ($CBr(COO(\underline{C}H_2)_5CH_3)_2$); 25.31 ($CBr(COO(\underline{C}H_2)_5CH_3)_2$); 28.28 ($CBr(COO(\underline{C}H_2)_5CH_3)_2$); 31.33 ($CBr(COO(\underline{C}H_2)_5CH_3)_2$); 42.48 ($CBr(COO(\underline{C}H_2)_5CH_3)_2$); 67.31 ($\underline{C}Br(COO(\underline{C}H_2)_5CH_3)_2$); 68.76 ($CBr(COO(\underline{C}H_2)_5CH_3)_2$); 76.81 ($sp^3$-C of cage); 77.02 (CF); 77.23 (CF); 125.29, 128.22, 129.03, 131.30, 146.72, 147.42, 164.24, 164.67.

Nonamethyl [23,24,25,26,27,28,41,42,47,48,49,55,56,59,60-pentadecafluoro-24,25,26,27,28,41,42,47,48,49,55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]-trimethanetricarboxylate (5). The yield was 68%. ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 4.06 (s, 27 H, $C(COOC\underline{H}_3)_3$). ^{19}F NMR ($CDCl_3$, δ: −137.14 (s, 3 F); −144.58 (s, 12 F). ^{13}C NMR ($CDCl_3$), δ: 29.68 ($\underline{C}(COOMe)_3$); 54.3 (OMe); 70.99 (sp^3-C of cage); 85.69 (CF); 87.23 (CF); 89.72 (CF); 90.39 (CF); 91.3 (CF); 91.99 (CF); 125.26; 128.19, 129, 130.96, 131.71, 135.45, 135.58, 137.84, 146.80, 146.94, 148.30, 150.62, 162.54, 164.13. UV (toluene), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 335 ($24.2\cdot10^3$), 397 ($26.8\cdot10^3$), 438 ($11.3\cdot10^3$), 567 ($4.2\cdot10^3$), 611 ($7.7\cdot10^3$), 661 ($12.5\cdot10^3$). IR (KBr), ν/cm^{-1}: 465 (v.w), 540 (v.w), 562 (w), 584 (w), 658 (w), 671 (w), 688 (w), 732 (w), 764 (v.w), 814 (m), 861 (v.w), 935 (w), 946 (w), 968 (w), 1008 (w), 1026 (m), 1034 (m), 1056 (m), 1078 (v.s), 1119 (v.s), 1147 (s), 1168 (m), 1184 (m), 1244 (s), 1281 (v.s), 1363 (v.w), 1400 (w), 1437 (m), 1459 (m), 1630 (w), 1748 (v.s), 2957 (w).

Tris-(1′,1′-di-*tert*-butyl-1′-methyl) [23,24,25,26,27,28,41,42,47,48,49,55,56,59,60-pentadecafluoro-24,25,26,27,28,41,42,47,48,49,55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]trimethanetricarboxylate (6). The yield was 48%. ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 1.67 (s, 54 H, $C(COOC(C\underline{H}_3)_3)_2(COOCH_3)$); 4.06 (s, 9 H, $C(COOC(CH_3)_3)_2(COOC\underline{H}_3)$). ^{19}F NMR ($CDCl_3$), δ: −137.05 (s, 3 F); −144.56 (s, 6 F); −144.78 (s, 6 F). ^{13}C NMR ($CDCl_3$), δ: 27.96 (Bu^t); 31.6 ($\underline{C}(COOBu^t)_2COOMe$); 53.61 (OMe); 71.87 ($sp^3$-C of cage); 85.75 ($Bu^t$); 85.89 (CF); 87.23 (CF); 89.89 (CF); 90.48 (CF); 91.41 (CF); 92.07 (CF); 125.31, 128.24, 129.05, 130.94, 131.76, 146.85, 147.46, 148.42, 150.99, 162.83, 163.24, 165.14. UV (toluene), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 338 ($23.8\cdot10^3$), 397 ($27.5\cdot10^3$), 438 ($10.9\cdot10^3$), 565 ($4.0\cdot10^3$), 617 ($7.9\cdot10^3$), 661 ($11.6\cdot10^3$). IR (KBr), ν/cm^{-1}: 473 (w), 562 (w), 668 (w), 729 (w), 816 (w), 836 (w), 842 (w), 1078 (s), 1120 (v.s), 1147 (v.s), 1252 (s), 1295 (s), 1372 (m), 1396 (w), 1436 (w), 1462 (w), 1739 (s), 2334 (v.w), 2359 (w), 2981 (w).

2,2′,2′′-{[23,24,25,26,27,28,41,42,47,48,49,55,56,59,60-Pentadecafluoro-24,25,26,27,28,41,42,47,48,49,55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]tris-(2-methoxycarbonyl)malonic acid} (7). A solution of trannulene **6** (50 mg, 0. 047 mmol) in trifluoroacetic acid (30 mL) was refluxed for 2 h. An excess acid was distilled off *in vacuo*, and the dry residue that formed was washed with dichloromethane and dried in air. Trannulene **7** was obtained as dark green crystalline powder in quantitative yield (100%, 70 mg). ^{1}H NMR (DCOOD, 600 MHz), δ: 3.31 (s, 9 H, $C(COOH)_2(COOC\underline{H}_3)$). ^{19}F NMR (DCOOD), δ: −135.97 (s, 3 F); −143.86 (s, 6 F); −144.61 (s, 6 F). ^{13}C NMR (DCOOD), δ: 45.62 ($\underline{C}(COOMe)_3$); 48.81 (OMe); 80.84 (CF); 82.36 (CF); 85.24 (CF); 86.81 (CF); 125.78, 125.89, 126.47, 126.66, 128.37, 128.51, 141.02, 141.11, 141.79, 141.82, 143.05, 143.13, 143.16, 146.97, 147.06. UV (AcOH—H_2O, 1 : 1), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 338 ($25.1\cdot10^3$), 373 ($22.8\cdot10^3$), 391 ($24.5\cdot10^3$), 433 ($10.7\cdot10^3$), 569 ($4.6\cdot10^3$), 610 ($7.7\cdot10^3$), 663 ($10.9\cdot10^3$). IR (KBr), ν/cm^{-1}: 478 (w), 562 (w), 663 (w), 728 (w), 816 (w), 1032 (m), 1069 (s), 1116 (v.s), 1142 (s), 1166 (m), 1230 (m), 1327 (m), 1400 (w), 1732 (m), 1738 (m), 2855 (w), 2925 (w), 2956 (w), 3426 (m).

***tert*-Butyl-3-hydroxypropyl carbamate (9).** A solution of Boc_2O (30.8 g, 0.14 mol) in anhydrous dichloromethane (250 mL) was added dropwise within 2 h with vigorous stirring to a solution of 3-aminopropan-1-ol (22.5 g, 0.3 mol). After the end of the reaction, the reaction mixture was washed with water and the organic phase was dried with anhydrous manganese sulfate. After the solvent was distilled off, compound **9** was obtained as an oily liquid in a yield of 19.8 g (80%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.45 (s, 9 H, $C(C\underline{H}_3)_3$); 1.67 (m, 2 H, H(1)); 3.28 (m, 2 H, H(3)); 3.67 (m, 2 H, H(2)); 4.83 (br.s, 1 H, N<u>H</u>).

Bis[3-(*tert*-butoxycarbonylamino)propyl] malonate (10). Malonic acid (5 g, 49 mmol) was placed in a two-necked round-bottom 500-mL flask equipped with a dropping funnel. The system was evacuated, filled with argon, and anhydrous DMF (50 mL) was added. A solution of compound **9** (19 g, 108.5 mmol) in DMF (20 mL) was added dropwise with vigorous stirring to the resulting solution of malonic acid. Then, a catalytic amount (10—30 mg) of 4-(dimethylamino)pyridine was introduced into the reaction mixture under argon and a solution of dicyclohexylcarbodiimide (20.7 g, 100 mmol) in DMF (30 mL) was added dropwise. The reaction mixture was stirred for 5 h, after which a precipitate of dicyclohexylurea was filtered off. The filtrate was diluted with dichloromethane (200 mL) and washed three times with distilled water. The organic phase was dried with anhydrous sodium sulfate. After evaporation of the solvent, compound **10** was obtained as an oily yellowish liquid in a yield of 16.6 g (81%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.41 (s, 18 H, $C(C\underline{H}_3)_3$); 1.82 (m, 4 H, ($CH_2C\underline{H}_2CH_2$)); 3.17 (m, 4 H, $NH(C\underline{H}_2)$); 3.37 (s, 2 H, $C\underline{H}_2(COOR)_2$); 4.19 (t, 4 H, $(C\underline{H}_2)O$, J = 6.20 Hz); 4.81 (br.s, 2 H, NH).

1,1-Bis[3-(*tert*-butoxycarbonylamino)propyl]-1-methyl methanetricarboxylate (11). A two-necked round-bottom 250-mL flask equipped with a dropping funnel was evacuated and filled with argon. A solution of compound **10** (6 g, 14 mmol) in DMF (45 mL) was added under argon, and the system was cooled to 0 °C. Then, NaH (450 mg, 18.75 mmol) was added under argon, and the mixture was stirred for 10 min at 0 °C and 1 h at ambient temperature. The reaction mixture was again cooled to 0 °C and a solution of methyl chloroformate (1.7 g, 17 mmol) in DMF (10 mL) was added dropwise. The mixture was stirred for 15 min at 0 °C and 2 h at ambient temperature. After the reaction completion, a solution of ammonium chloride (2 g per 50 mL of water) was added to the reaction mixture and the reaction product was extracted with dichloromethane. The organic phase was washed with water and dried with anhydrous sodium sulfate. After the solvent was distilled off *in vacuo*, compound **11** was obtained in a yield of 2.2 g (33%). ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.41 (s, 18 H, $C(C\underline{H}_3)_3$); 1.48 (s, 3 H, $COOC\underline{H}_3$); 1.81 (m, 4 H, ($CH_2C\underline{H}_2CH_2$)); 3.17 (m, 4 H, $NH(C\underline{H}_2)$); 3.37 (s, 1 H, $C\underline{H}(COOCH_3)(COOR)_2$); 4.19 (t, 4 H, $(C\underline{H}_2)O$, J = 6.18 Hz); 4.81 (br.s, 2 H, NH).

1,1-Hexakis[3-(*tert*-butoxycarbonylamino)propyl]-1-trimethyl [23,24,25,26,27,28,41,42,47,48,49,55,56,59,60-pentadecafluoro-24,25,26,27,28,41,42,47,48,49,55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]trimethanetricarboxylate (12). A solution of compound **11** (449.7 mg, 0.94 mmol) in toluene (20 mL) was added to a solution of fluorofullerene $C_{60}F_{18}$ (200 mg, 0.188 mmol) in anhydrous toluene (150 mL). Then, a solution of DBU (25.8 mg, 0.17 mmol) in toluene (20 mL) was added dropwise under argon for 15 min with vigorous stirring. After addition of DBU, the reaction mixture was applied on a chromatographic column with silica gel. Trannulene **12** was eluted with toluene—ethyl acetate (1 : 4 vol/vol). After the solvent was distilled off, the residue was washed with hexane and dried in air. Trannulene **12** was obtained as a dark green powder in a yield of 50.3 mg (11%). ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 1.50 (s, 18 H, $C(C\underline{H}_3)_3$); 1.52 (s, 36 H, $C(C\underline{H}_3)_3$); 1.75 (m, 12 H, CH_2); 2.09 (m, 12 H, CH_2); 3.33 (m, 12 H, CH_2); 4.59 (m, 9 H, COOMe); 5.07 (br.s, 6 H, NH). ^{19}F NMR ($CDCl_3$), δ: −136.27 (s, 3 F); −143. 57 (m, 12 F). ^{13}C NMR ($CDCl_3$), δ: 28.45 (Bu^t); 29.01 ($CH_2\underline{C}H_2CH_2$); 33.87 ($\underline{C}(COOR)_2COOMe$); 37.3 ($\underline{C}H_2NHBoc$); 53.48 (OMe); 54.32 (OMe); 65.64 ($COO\underline{C}H_2$); 79.47 ($\underline{C}(CH_3)_3$); 79.51 ($\underline{C}(CH_3)_3$); 83.36 (CF); 85.68 (CF); 87.23 (CF); 89.82 (CF); 91.39 (CF); 92.03 (CF); 125.30, 127.72, 128.23, 129.04, 130.54, 130.91, 131.02, 131.70, 131.77, 137.88, 146.80, 146.88, 148.26, 150.80, 156.00, 156.09, 156.17, 163.79, 164.19, 165.10. UV (toluene), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 335 ($27.2\cdot10^3$), 396 ($29.6\cdot10^3$), 438 ($12.0\cdot10^3$), 571 ($5.3\cdot10^3$), 613 ($7.8\cdot10^3$), 662 ($10.7\cdot10^3$). IR (KBr), ν/cm^{-1}: 555 (w), 668 (w), 781 (w), 815 (m), 861 (m), 970 (m), 1034 (m), 1076 (s), 1119 (v.s), 1147 (s), 1168 (s), 1218 (s), 1252 (s), 1275 (s), 1368 (m), 1393 (m), 1436 (w), 1455 (m), 1462 (m), 1506 (m), 1520 (m), 1538 (m), 1698 (cp), 1713 (m), 1746 (m), 2869 (w), 2933 (m), 2975 (m).

2,2′,2′′-[23,24,25,26,27,28,41,42,47,48,49,55,56,59,60-Pentadecafluoro-24,25,26,27,28,41,42,47,48,49,55,56,59,60-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,33,38(23*H*)-triyl]tris[3-(3-ammoniopropoxy-2-methoxycarbonyl-3-oxopropanoyloxy)-propan-1-aminium hexafluoroacetate (8). A solution of trannulene **12** (15 mg, 6 μmol) in trifluoroacetic acid (5 mL) was magnetically stirred for 10 min, and an acid excess was distilled off *in vacuo*. The residue was washed with dichloromethane and dried in air. Trannulene **8** was obtained as an emerald-green crystalline powder in a yield of 15.5 mg (100%). ^{1}H NMR (DCOOD), δ: 2.88 (m, 12 H, CH_2); 2.95 (m, 12 H, CH_2); 3.86 (m, 12 H, CH_2); 4.84 (m, 9 H, COOMe); 5.24 (br.s, 6 H, NH). ^{19}F NMR (DCOOD), δ: −76.06 (CF_3COO^-, 18 F); −136.14 (m, 3 F); −143.32 (m, 6 F), −143.96 (m, 6 F). We failed to obtain the ^{13}C NMR spectrum of compound **8** because of its low solubility in organic solvents (including organic acids) and insufficient stability in an aqeuous medium. UV (AcOH—H_2O, 1 : 1), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 338 ($22.1\cdot10^3$), 369 ($19.2\cdot10^3$), 393 ($20.1\cdot10^3$), 436 ($9.4\cdot10^3$), 606 ($4.7\cdot10^3$), 665 ($7.4\cdot10^3$). MS (ESI), *m/z*: 1831 $[M + H]^+$, 916 $[M + 2H]^{2+}$. IR (KBr), ν/cm^{-1}: 483 (m), 604 (m), 659 (m), 723 (m), 760 (m), 801 (s), 839 (s), 890 (s), 1062 (v.s), 1124 (v.s), 1203 (v.s), 1270 (s), 1688 (m), 1732 (m), 1736 (m), 2949 (s), 3108 (s).

Isomerization of trannulenes 1—6 (general procedure). Solutions of trannulenes **1**—**6** (0.03 mmol) in anhydrous 1,2-dichlorobenzene (50 mL) were degassed and then refluxed for 2 h under argon. During reflux, the emerald-green color of the reaction mixture changed to lemon-yellow or yellow-orange. After the reaction completion, the mixture was cooled down and applied on a chromatographic column with silica gel. Triumphenes **13**—**17** were eluted with toluene—ethyl acetate (98 : 2 vol/vol). The solvent was evaporated *in vacuo* and dry residues were washed with hexane and dried in air. Triumphenes **13**—**17** were obtained as yellow crystalline powders in 70—95% yields.

Hexamethyl 2,2′,2′′-[7,8,9,10,11,22,23,28,29,42,43,46,47,57,58-pentadecafluoro-8,9,10,11,22,23,28,29,42,43,46,47,57,58-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,41,48(7*H*)-triyl]tris(2-bromomalonate) (13). The yield was 92%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 3.81 (s, 6 H, $COOC\underline{H}_3$); 4.03 (m, 12 H, $COOC\underline{H}_3$). ^{19}F NMR ($CDCl_3$), δ: −135.34 (m, 2 F); −136.09 (m, 2 F); −137.55 (m, 2 F); −142.40 (m, 2 F); −144.07 (m, 7 F). ^{13}C NMR ($CDCl_3$), δ: 55.15 (OMe); 55.19 (OMe); 55.38 (OMe); 90.22 (br.m, CF); 91.34 (br.m, CF); 91.79 (br.m, CF); 94.74 (br.m, CF); 96.37 (br.m, CF); 102.02 (br.m, CF); 103.72 (br.m, CF); 105.6 (br.m, CF); 125.3, 127.02, 127.70, 128.22, 128.50, 128.54, 128.58, 128.62, 128.85, 128.97, 129.02, 129.41, 129.53, 129.77, 130.15, 130.72, 133.62, 134.50, 135.18, 135.29, 135.78, 136.40, 140.59, 140.77, 141.63, 141.79, 142.65, 144.74, 144.77, 144.82, 144.99, 145.02, 145.19, 145.20, 145.24, 145.27, 145.35, 145.49, 145.68, 145.83, 145.90, 145.96, 146.04, 146.64, 146.77, 146.82, 146.88, 146.95, 146.99, 147.11, 147.14, 147.2, 147.63, 147.71, 147.79, 147.86, 147.95, 148.06, 148.22, 148.26, 148.31, 148.35, 148.42, 148.50, 148.63, 148.83, 148.87, 148.91, 149.08, 149.13, 149.21, 149.25, 149.38, 150.26, 150.38, 150.44, 150.56, 151.26, 151.38, 151.45, 151.56, 151.61, 151.64, 151.73, 151.81, 151.92, 152.00, 152.06, 162.66, 165.22 (C=O), 165.45 (C=O), 165.60 (C=O), 165.62 (C=O), 165.65 (C=O).

Hexaethyl 2,2′,2′′-[7,8,9,10,11,22,23,28,29,42,43,46,47,57,58-pentadecafluoro-8,9,10,11,22,23,28,29,42,43,46,47,57,58-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,41,48(7*H*)-triyl]tris(2-bromomalonate) (14). The yield was 83%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.27 (m, 9 H); 4.26 (m, 3 H); 4.37 (m, 3 H); 4.52 (m, 6 H). ^{19}F NMR ($CDCl_3$), δ: −135.13 (m, 3 F); −136.07 (m, 1 F); −137.44 (m, 3 F); −142.74 (m, 1 F); −143.88 (m, 7 F). ^{13}C NMR ($CDCl_3$), δ: 21.45, 22.69, 29.70, 31.93, 62.54, 62.68, 63.09, 63.55, 64.68, 64.81, 65.17, 91.88, 125.30, 127.00, 127.68, 127.73, 128.23, 128.50, 128.58, 128.62, 128.97, 129.04, 129.37, 129.76, 130.55, 134.48, 137.87, 141.81, 144.82, 144.91, 144.98,

145.13, 148.11, 148.25, 148.61, 148.79, 149.01, 149.26, 149.41, 151.31, 151.47, 151.63, 151.80, 151.98, 164.98, 165.12, 165.19.

Hexapropyl 2,2´,2´´-[7,8,9,10,11,22,23,28,29,42,43,46,47,57,58-pentadecafluoro-8,9,10,11,22,23,28,29,42,43,46,47,57,58-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,41,48(7*H*)-triyl]tris(2-bromomalonate) (15). The yield was 78%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 0.88 (m, 9 H); 1.01 (m, 9 H); 1.64 (m, 6 H); 1.81 (m, 6 H); 4.13 (m, 2 H); 4.31 (m, 10 H). ^{19}F NMR ($CDCl_3$), δ: −134.11 (m, 3 F); −135.48 (m, 1 F); −137.02 (m, 3 F); −141.99 (m, 1 F); −143.51 (m, 7 F). ^{13}C NMR ($CDCl_3$), δ: 10.17, 10.23, 14.11, 21.57, 21.65, 22.64, 22.69, 29.35, 29.69, 31.58, 31.93, 62.54, 62.68, 69.97, 70.07, 70.48, 70.51, 89.79, 91.91, 94.33, 95.95, 102.05, 103.76, 127.73, 128.61, 128.96, 129.01, 129.54, 129.75, 130.54, 132.55, 135.14, 140.79, 140.94, 141.82, 142.85, 144.58, 144.88, 145.04, 145.14, 145.35, 146.52, 146.69, 146.83, 146.99, 147.85, 148.02, 148.17, 148.60, 148.86, 149.10, 149.21, 149.35, 149.49, 151.30, 151.46, 151.60, 151.63, 151.78, 151.95, 164.99, 165.09, 165.24, 165.30.

Hexahexyl 2,2´,2´´-[7,8,9,10,11,22,23,28,29,42,43,46,47,57,58-pentadecafluoro-8,9,10,11,22,23,28,29,42,43,46,47,57,58-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,41,48(7*H*)-triyl]tris(2-bromomalonate) (16). The yield was 70%. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 0.91 (m, 18 H); 1.36 (m, 36 H); 1.64 (m, 6 H); 1.81 (m, 6 H); 4.22 (m, 2 H); 4.31 (m, 2 H); 4.37 (m, 2 H); 4.41 (m, 2 H); 4.46 (m, 2 H); 4.53 (m, 2 H). ^{19}F NMR ($CDCl_3$), δ: −135.2 (m, 3 F); −136.08 (m, 1 F); −137.5 (m, 3 F); −142.52 (m, 1 F); −143.88 (m, 7 F). ^{13}C NMR ($CDCl_3$), δ: 13.97, 22.45, 25.33, 28.13, 31.19, 31.32, 62.56, 62.70, 67.31, 68.68, 69.13, 89.78, 90.27, 91.89, 94.56, 95.95, 101.79, 103.75, 127.73, 129.56, 130.54, 130.91, 132.56, 134.99, 140.80, 140.97, 141.81, 142.83, 144.54, 144.84, 145.01, 145.12, 145.17, 145.27, 145.33, 146.48, 146.65, 146.81, 146.93, 146.98, 147.92, 148.07, 148.22, 148.60, 149.10, 149.25, 149.39, 149.54, 150.51, 151.30, 151.48, 151.61, 151.65, 151.79, 151.97, 164.67, 165.04, 165.22, 165.29.

Nonamethyl [7,8,9,10,11,22,23,28,29,42,43,46,47,57,58-pentadecafluoro-8,9,10,11,22,23,28,29,42,43,46,47,57,58-tetradecahydro(C_{60}-I_h)[5,6]fullerene-1,41,48(7*H*)-triyl]trimethanetricarboxylate (17). The yield was 95%. ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 3.84 (s, 9 H); 4.00 (s, 18 H). ^{19}F NMR ($CDCl_3$), δ: −137.40 (d, 6 F); −143.60 (d, 3 F); −144.09 (s, 6 F). ^{13}C NMR ($CDCl_3$, 150 MHz), δ: 29.62 (<u>C</u>(COOMe)$_3$), 54.26 (OMe), 127.61, 128.17, 128.98, 130.51, 130.81, 132.66, 135.37, 135.46, 141.78, 144.78, 145.40, 148.61, 149.47, 151.72, 164.75 (C=O), 165.32 (C=O).

Hexamethyl {1,9-([1.9]epi(C_{60}-I_h)[5,6]fullereno)[2,5,6,12,13,14,19,20,33,34,35,36,37,38-tetradecafluoro-2,5,6,12,13,14,19,20,33,34,35,36,37,38-tetradecahydro(C_{60}-I_h)[5,6]fullerene-32,39-diyl]}dimethanetricarboxylate (19). A solution of trannulene **5** (45 mg, 0.03 mmol) and fullerene C_{60} (41 mg, 0.06 mmol) in anhydrous 1,2-dichlorobenzene (60 mL) was degassed and then refluxed for 5 h under argon. After the reaction completion, the mixture was cooled down and applied on a chromatographic column with silica gel. The reaction product was eluted with toluene—ethyl acetate (98 : 2 vol/vol). The dry residue obtained after distillation of the solvent was washed with hexane and dried in air. Compound **19** was obtained as a yellow-brown powder in a yield of 37.5 mg (60%). ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 3.90 (s, 3 H); 3.93 (s, 3 H); 4.05 (m, 3 H); 4.07 (m, 6 H); 4.24 (m, 3 H). ^{19}F NMR ($CDCl_3$), δ: −129.98 (d, 2 F, J = 22.0 Hz); −135.42 (dd, 2 F, J_1 = 33.1 Hz, J_2 = 23.3 Hz); −136.36 (m, 2 F); −136.90 (m, 2 F); −142.69 (t, 2 F, J = 18.1 Hz); −143.55 (d, 2 F, J = 3.24 Hz); −145.08 (dd, 2 F, J_1 = 33.1 Hz, J_2 = 5.83 Hz). ^{13}C NMR ($CDCl_3$), δ: 33.49 (<u>C</u>(COOMe)$_3$); 54.04 (OMe); 54.56 (OMe); 65.58 (sp^3-C of cage); 66.86 (sp^3-C of cage); 68.16 (sp^3-C of cage), 128.82, 130.89, 132.47, 139.30, 140.35, 140.86, 141.37, 141.68, 141.97, 142.55, 142.59, 142.77, 142.80, 142.94, 142.97, 143.08, 143.10, 144.38, 144.78, 145.27, 145.35, 145.46, 145.54, 145.84, 145.89, 145.98, 146.17, 146.22, 146.29, 146.37, 147.32, 147.51, 148.33, 148.45, 148.87, 148.95, 149.14, 149.18, 149.20, 149.46, 149.76, 150.65, 150.67, 151.20, 151.53, 152.51, 162.72, 164.88, 164.94, 165.38, 167.78.

Hexamethyl {1,9-([9,25](C_{70}-$D_{5h(6)}$)[5,6]fullereno)[2,5,6,12,13,14,19,20,33,34,35,36,37,38-tetradecafluoro-2,5,6,12,13,14,19,20,33,34,35,36,37,38-tetradecahydro(C_{60}-I_h)[5,6]fullerene-32,39-diyl]}dimethanetricarboxylate (20). A solution of trannulene **5** (100 mg, 0.06 mmol) and fullerene C_{70} (120 mg, 0.14 mmol) in anhydrous 1,2-dichlorobenzene (60 mL) was degassed and then refluxed for 5 h under argon. After reaction completion, the mixture was cooled down and applied on a chromatographic column with silica gel. The reaction product was eluted with toluene—ethyl acetate (98 : 2 vol/vol). After the solvent was distilled off, the dry residue was washed with hexane and dried in air. Compound **20** was obtained as a yellow powder in a yield of 72.8 mg (55%). ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 4.03 (m, 6 H); 4.05 (s, 6 H); 4.07 (s, 3 H); 4.08 (s, 3 H). ^{19}F NMR ($CDCl_3$), δ: −126.14 (t, 2 F, J = 23.7 Hz); −132.54 (dd, 1 F, J_1 = 33.6 Hz, J_2 = 22.4 Hz); −134.77 (dd, 1 F, J_1 = 33.6 Hz, J_2 = 22.4 Hz); −135.53 (m, 2 F); −136.06 (m, 2 F); −141.79 (q, 2 F, J = 19.1 Hz); −142.79 (d, 2 F, J = 13.8 Hz); −144.3 (dt, 2 F, J_1 = 33.5 Hz, J_2 = 6.2) Hz.

We failed to obtain the ^{13}C NMR spectrum of compound **20** because of its low solubility in organic solvents.

Hexamethyl {9´,10´-dihydro[9,10]ethanoanthra[11´,12´:1,9]-(2,5,6,12,13,14,19,20,33,34,35,36,37,38-tetradecafluoro-2,5,6,12,13,14,19,20,33,34,35,36,37,38-tetradecahydro(C_{60}-I_h)-[5,6]fullerene-32,39-diyl)}dimethanetricarboxylate (21). A solution of trannulene **5** (50 mg, 0.03 mmol) and anthracene (113 mg, 0.6 mmol) in anhydrous 1,2-dichlorobenzene (60 mL) was degassed and then refluxed for 5 h under argon. After reaction completion, the mixture was cooled down and applied on a chromatographic column with silica gel. The reaction product was eluted with toluene—ethyl acetate (98 : 2 vol/vol). After the solvent was distilled off, the dry residue was washed with hexane and dried in air. Compound **21** was obtained as a yellow powder in a yield of 20.8 mg (45%). ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 3.85 (s, 6 H); 3.95 (s, 6 H); 4.00 (s, 6 H); 5.36 (s, 1 H); 5.39 (s, 1 H); 7.30 (t, 2 H, J = 7.6 Hz); 7.35 (t, 2 H, J = 7.6 Hz); 7.47 (d, 2 H, J = 7.1 Hz); 7.68 (d, 2 H, J = 7.3 Hz). ^{19}F NMR ($CDCl_3$), δ: −136.15 (m, 4 F); −136.80 (m, 2 F); −140.52 (dd, 2 F, J_1 = 33.4 Hz, J_2 = 16.2 Hz); −142.51 (t, 2 F, J = 16.8 Hz); −143.01 (s, 2 F); −145.58 (dd, 2 F, J_1 = 33.4 Hz, J_2 = 7.1 Hz). ^{13}C NMR ($CDCl_3$), δ: 31.6 (<u>C</u>(COOMe)$_3$); 45.74 (C—H); 46.97 (C—H); 54.34 (OMe); 54.37 (OMe); 54.41 (OMe); 61.63 (sp^3-C of cage); 61.94 (sp^3-C of cage); 124.28, 127.08, 127.31, 127.73, 127.86, 128.51, 129.88, 131.74, 138.2, 140.72, 142.77, 144.34, 145.09, 145.30, 148.15, 148.42, 148.65, 148.87, 149.30, 149.43, 151.11, 151.38, 152.09, 152.96, 164.81 (COO), 164.87 (COO), 165.34 (COO).

Hexamethyl {6´,13´-dihydro[6,13]ethanopentaceno-[15´,16´:1,9] (2,5,6,12,13,14,19,20,33,34,35,36,37,38-tetradecafluoro-2,5,6,12,13,14,19,20,33,34,35,36,37,38-tetradecahydro(C_{60}-I_h)[5,6]fullerene-32,39-diyl)}dimethanetricarboxylate (22). A solution of trannulene **5** (55 mg, 0.03 mmol) and

pentacene (48 mg, 0.17 mmol) in anhydrous 1,2-dichlorobenzene (60 mL) was degassed and then refluxed for 5 h under argon. After reaction completion, the mixture was cooled down and applied on a chromatographic column with silica gel. The reaction product was eluted with toluene—ethyl acetate (98 : 2 vol/vol). After the solvent was distilled off, the dry residue was washed with hexane and dried in air. Compound **22** was obtained as a yellow powder in a yield of 19.6 mg (40%). ^{1}H NMR ($CDCl_3$, 600 MHz), δ: 3.52 (s, 6 H); 3.88 (m, 12 H); 5.55 (m, 1 H); 5.80 (s, 1 H); 7.53 (dt, 2 H, J_1 = 14.8 Hz, J_2 = 1.4 Hz); 7.58 (dt, 2 H, J_1 = 7.4 Hz, J_2 = 1.4 Hz); 7.88 (d, 2 H, J = 8.6 Hz); 7.99 (d, 2 H, J = 8.0 Hz); 8.20 (s, 2 H); 8.74 (s, 2 H). ^{19}F NMR ($CDCl_3$), δ: −136.17 (m, 4 F); −136.76 (m, 2 F); −140.01 (dd, 2 F, J_1 = 30.9 Hz, J_2 = 15.1 Hz); −142.51 (t, 2 F, J = 15.8 Hz); −143.00 (s, 2 F); −145.45 (dd, 2 F, J_1 = 33.4 Hz, J_2 = 5.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 29.71(C(COOMe)$_3$); 46.43 (C—H); 46.51 (C—H); 52.99 (OMe); 54.34 (OMe); 54.39 (OMe); 61.31 (sp^3-C of cage); 61.58 (sp^3-C of cage); 127.09 (Ar); 127.87 (Ar); 128.5 (Ar); 128.63 (Ar); 129.62 (Ar); 129.67 (Ar); 132.24 (Ar); 132.42 (Ar); 133.25 (Ar); 134.64 (Ar); 142.70, 144.32, 144.82, 145.09, 145.24, 146.30, 146.84, 146.97, 148.17, 148.39, 148.68, 148.83, 149.29, 149.38, 151.10, 151.34, 152.06, 152.83, 164.17 (COO), 164.86 (COO), 165.33 (COO), 165.79 (COO). MS (ESI), *m/z*: 1606.175 $[M - 2F + H]^+$, 1644.182 $[M + H]^+$; calculated, *m/z*: 1606.181 $[M - 2F + H]^+$, 1644.178 $[M + H]^+$.

X-ray diffraction analysis of single crystals of the adduct of triumphene 17 with chlorobenzene. Single crystals were grown by slow concentrating of a solution of compound **17** in dichlorobenzene in air at ambient temperature. The data for a crystal 0.07×0.03×0.01 mm in size were collected at 100 K using synchronous radiation on an accumulation ring of a BESSY synchrotron (λ = 0.9050 Å, BL 14.2, Free University of Berlin, Germany). Structure **17**·2C_6H_5Cl was solved using the SHELXS-97 program[21] and refined using the SHELXL-97 program.[22] The crystals of compound **17**, $C_{93}H_{42}Cl_2F_{15}O_{18}$, are triclinic; space group $P\bar{1}$; cell parameters a = 16.2890(1) Å, b = 18.9588(1) Å, c = 22.6521(2) Å, α = 90.9596(4)°, β = = 94.0701(4)°, γ = 93.3589(5)°; V = 6936.5(2) Å^3; Z = 4; R-factors: wR_2 = 0.251 (for 25 816 reflections and 2409 prameters), R_1 = 0.094 (for 18779 reflections with $I \geq 2\sigma(I)$). Two crystallographically independent fullerene molecules and four chlorobenzene molecules were found in the structure. Some methoxy groups of the C(COOMe)$_3$ substituents and two chlorobenzene molecules were orientationally disordered in the crystal packing. The crystallographic data for the structure of the adduct of **17** with chlorobenzene were deposited with the Cambridge Crystallographic Data Centre (CCDC 715951) and are available free of charge at www.ccdc.cam.ac.uk/data_request/cif.

The authors are grateful to N. V. Polyakova (Research Institute of Electrocarbon Products, Elektrougli, Moscow Region, Russia) for help in the synthesis of the starting fluorofullerene $C_{60}F_{18}$.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 10-03-00443a), the Federal Agency on Science and Innovations (Contract No. 02.740.11.0749), and the Council on Grants at the President of the Russian Federation (Program for State Support of Young Scientists, Candidates of Science, MK-4916.2011.3).

References

1. X. W. Wei, A. D. Darwish, O. Boltalina, P. B. Hitchcock, J. M. Street, R. Taylor, *Angew. Chem., Int. Ed.*, 2001, **40**, 2989.
2. G. A. Burley, *Angew. Chem., Int. Ed.*, 2005, **44**, 3176.
3. P. A. Troshin, R. N. Lyubovskaya, I. N. Ioffe, N. B. Shustova, E. Kemnitz, S. I. Troyanov, *Angew. Chem., Int. Ed.*, 2005, **44**, 235.
4. T. Canteenwala, P. A. Padmawar, L. Y. Chiang, *J. Am. Chem. Soc.*, 2005, 127, 26.
5. P. A. Troshin, O. A. Troshina, S. M. Peregudova, E. I. Yudanova, A. G. Buyanovskaya, D. V. Konarev, A. S. Peregudov, A. N. Lapshin, R. N. Lyubovskaya, *Mendeleev Commun.*, 2006, 206.
6. P. A. Troshin, E. A. Khakina, A. V. Zhilenkov, A. S. Peregudov, O. A. Troshina, V. I. Kozlovskii, N. V. Polyakova, R. N. Lyubovskaya, *Eur. J. Org. Chem.*, 2010, 1037.
7. E. A. Khakina, S. I. Troyanov, A. S. Peregudov, N. V. Polyakova, P. A. Troshin, *Chem. Eur. J.*, 2010, **16**, 12947.
8. J. W. Aborgast, C. S. Foote, *J. Am. Chem. Soc.*, 1991, **113**, 8886.
9. Y. Tabata, Y. Murakami, Y. Ikada, *Fullerene Sci. Technol.*, 1997, **5**, 989.
10. Y. Tabata, T. Ishii, T. Aoyama, R. Oki, Y. Hirano, O. Ogawa, Y. Ikada, in *Perspectives of Fullerene Nanotechnology*, Ed. E. Osawa, Kluwer Acad. Publ., New York—Dordrecht—Boston—London—Moscow, 2002, 375 pp.
11. Pat. RF 2005140680; *Byul. Izobr.* [*Invention Bulletin*], 2007, No. 20; http://www.fips.ru (in Russian).
12. P. Pitt, H. Berry, *Postgrad. Med. J.*, 1991, **67**, 323.
13. G. A. Burley, A. G. Avent, O. V. Boltalina, T. Drewello, I. V. Goldt, M. Marcaccio, F. Paolucci, D. Paolucci, J. M. Street, R. Taylor, *Org. Biomol. Chem.*, 2003, **1**, 2015.
14. G. A. Burley, A. G. Avent, I. V. Gol´dt, P. B. Hitchcock, H. Al-Matar, D. Paolucci, F. Paolucci, P. W. Fowler, A. Soncini, J. M. Street, R. Taylor, *Org. Biomol. Chem.*, 2004, **2**, 319.
15. O. V. Boltalina, J. M. Street, R. Taylor, *J. Chem. Soc. Chem. Commun.*, 1998, 1827.
16. A. D. Darwish, A. G. Avent, A. K. Abdul-Sada, I. V. Gol´dt, P. B. Hitchcock, I. V. Kuvytchko, R. Taylor, *Chem. Eur. J.*, 2004, **10**, 4523.
17. *Organic Syntheses*, *Collective Volume I*, Ed. H. Gilman, Flushing, New York, 1949, 541 pp.
18. *Organic Syntheses*, *Collective Volume II*, Ed. A. Blatt, Flushing, New York, 1949, 471 pp.
19. *Metody polucheniya khimicheskikh reaktivov i preparatov* [*Synthesis Methods of Chemical Reagents and Preparations*], Ed. R. P. Lastovskii, IREA, Moscow, 1969, Issue 18, 234 pp. (in Russian).
20. A. B. Kornev, P. A. Troshin, A. S. Peregudov, Z. E. Klinkina, N. V. Polyakova, R. N. Lyubovskaya, *Mendeleev Commun.*, 2006, **16**, 157.
21. G. M. Sheldrick, *SHELXS-97*, *Program for the Solution of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.
22. G. M. Sheldrick, *SHELXL-97*, *Program for the Refinement of Crystal Structures*, University of Göttingen, Göttingen (Germany), 1997.

Received May 20, 2011;
in revised form September 4, 2011