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# Polyadducts of fullerene $C_{60}$ with *tert*-butyl groups

**E. A. Rychagova, L. V. Kalakutskaya, S. N. Titova, G. A. Domrachev, and S. Yu. Ketkov★**

G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences,
49 ul. Tropinina, 603950 Nizhny Novgorod, Russian Federation.
Fax: +7 (831) 462 7497. E-mail: sketkov@iomc.ras.ru

New soluble fullerene derivatives $Bu^t{}_nC_{60}$ were synthesized by the reaction of $C_{60}M_n(THF)_x$ (M = Li, Na; $n$ = 4, 6, 8, 10, 12) with *tert*-butyl bromide $Bu^tBr$. The thus obtained compounds were characterized by spectroscopic methods (IR and NMR spectroscopy), mass spectrometry (MALDI), elemental analysis, and quantum chemical calculations. HPLC was used for chromatographic separation of the products of the reaction of $C_{60}Na_n(THF)_x$ ($n$ = 4, 6, 8, 12) with $Bu^tBr$. It was found that $Bu^t{}_4C_{60}$ and $Bu^t{}_6C_{60}$ decompose on the column. A complex of physicochemical methods of analysis was used for establishing compositions of individual fractions of chromatographic separation of $Bu^t{}_4C_{60}$. The structure of one of the components was determined as 1-*tert*-butyl-1,2-dihydrofullerene 1,2-$Bu^tC_{60}H$.

**Key words:** fullerene $C_{60}$, metal fullerides, fullerene *tert*-butyl derivatives, quantum chemical calculations, synthesis, MALDI mass spectrometry, HPLC.

After experimental discovery of fullerenes,[1] studies of these very interesting forms of carbon rapidly became a wide, dynamically developing direction lying on the borderlines of very different fields of modern science. It was shown that fullerene $C_{60}$ and its numerous derivatives, due to their unique properties, are promising objects for the use in chemistry (fragment for construction of new molecules),[2—4] biology and medicine (inhibition of enzymes, controlled cleavage of DNA, treatment of cancer and nervous system diseases),[5—7] physics and electronics (nanosized photoconducting and superconducting devices, solar cells, electric batteries of increased capacity).[8—10] Various fullerene polyadducts are of great interest for researches, since they can serve as "building blocks" for the development of different constructions of nanometer sizes. Specific role is assigned to the development of new efficient approaches to functionalization of fullerene with different organic groups, which provide high yields of target products and ready addition of required addends to the carbon cage. Here, an important aspect is an ability to control composition of the products obtained.

Earlier,[11] we have suggested a new approach to the preparation of fullerene trimethylsilyl derivatives in solution by the reaction of sodium fullerides $C_{60}Na_n(THF)_x$ ($n$ = 4, 6, 8, 10, 12) with trimethylsilyl chloride. The interest to functionalization of fullerene with *tert*-butyl groups is caused by a dual nature of the effect of bulky alkyl fragments. On the one hand, they shield the cage $C_{60}$, on the other hand, increase reactivity of the adducts $Bu^t{}_nC_{60}$ because of steric strains of the fullerene framework and decrease in ionization energy. The data on the fullerene *tert*-butyl derivatives shown in the literature are limited to the description of several compounds. For instance, 1-*tert*-butyl-1,2-dihydrofullerene-60 was obtained[12] by nucleophilic addition of $Bu^tLi$ (1.2 equiv.) to $C_{60}$ in benzene. Introduction of even higher excess of organolithium compound (>1.2 equiv.) into the reaction mixture leads to further addition of *tert*-butyl groups to the fullerene cage, However, attempted isolation and characterization of the formed polyadducts failed.[12] As it was shown in the serial works[13—15] on alkylation of electrochemically reduced dianion $C_{60}{}^{2-}$, the $Bu^tC_{60}{}^{-}$ emerging in the first step of the electron transfer does not further react with $Bu^tI$ to form a bisadduct, which can be attributed to the susceptibility of the second step of the reaction ($S_N2$) to the steric effects of alkyl groups. Obtaining fullerene anions by the Olah and Barbier procedures leads to a different extent of reduction of $C_{60}$ and, therefore, to a mixture of adducts $C_{60}H_n(Bu^t)_qO_x(THF)_y$ ($n \le 8$, $q + y \le 18$, $x$ = 0, 1, 2).[16] To sum up, it seems very relevant to develop methods for obtaining fullerene adducts $Bu^t{}_nC_{60}$ of controlled composition.

The present work deals with the systematic studies of "functionalization" processes of fullerene $C_{60}$ with *tert*-butyl groups. A procedure used by us for the synthesis of fullerene *tert*-butyl derivatives is similar to the method for obtaining trimethylsilyl adducts.[11] The use of alkali metal fullerides as precursor has the advantage that the changes in the distribution of electron density in the fullerene anion determine direction of further addition of the groups. This leads to a predominant formation of a monoproduct and a higher yield. Metal fullerides, which,

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in contrast to the neutral $C_{60}$, display nucleophilic properties, readily react with electrophilic reactants to yield the corresponding fullerene derivatives. In the present work, taking reactions of $C_{60}M_n(THF)_x$ (M = Li, Na; $n$ = 4, 6, 8, 10, 12) with $Bu^tBr$ in the mixture of toluene with THF as examples, we for the first time systematically studied the process of formation of soluble *tert*-butyl fullerenes $Bu^t{}_nC_{60}$ ($n$ = 4, 6, 8, 10, 12). The advantage of this synthetic method consists in a possibility to control the content of $Bu^t$ groups in the product $Bu^t{}_nC_{60}$ on deeper "functionalization", which takes place under mild conditions. The thus obtained compounds were characterized by spectroscopic methods (IR and NMR spectroscopy), mass spectrometry (MALDI), elemental analysis data, and HPLC. Because of problems with isolation of individual fullerene polyadducts and difficulties with preparation of monocrystals suitable for X-ray crystallography, quantum chemical calculations of geometric and energy parameters of the molecule become very important, which are also reported in the framework of the presents work.

## Results and Discussion

When R groups are incorporated into the fullerene molecule, some carbon atoms (in $C_{60}$) are transformed from the $sp^2$- to the $sp^3$-hybridized state, which leads to deformation of the strained carbon cage. For dihydro[60]fullerenes $C_{60}RR'$, the number of possible geometric isomers is 23. However, theoretical studies showed that only three isomers $C_{60}RR'$, whose groups are at positions 1,2, 1,4, and 1,16, are the most energetically favorable.[17] These isomers were found experimentally.[17] The type of addition depends on the addend sizes. Thus, for two small (not bulky) groups (R, R′ = Me, Et) or when hydrogen is one of the groups, 1,2-addition occurs at the [6,6] bond of the fullerene cage. Our PBE/TZ2P quantum chemical calculations for different isomers of the $Me_2C_{60}$ molecule showed that 1,2-$Me_2C_{60}$ is more stable in energy than 1,4-$Me_2C_{60}$ by 1.34 kcal mol$^{-1}$ and more stable than 1,16-$Me_2C_{60}$ by 11 kcal mol$^{-1}$. For more bulky groups (R, R′ = $OOBu^t$, Ph, Flu (9-fluorenyl), $CH_2Ph$, $CH_2CO_2Et$, $Bu^t$), formation of 1,4-isomers or their mixtures with 1,16-adducts are observed.[17] These isomers are close in energy due to the partial compensation of favorable 1,4-addition of the addends by steric repulsion of the groups. The DFT calculation of isomers $Bu^t{}_2C_{60}$ (PBE/TZ2P) showed that 1,4- and 1,16-adducts are energetically equivalent (Table 1) and are more favorable than 1,2-$Bu^t{}_2C_{60}$ by 26.8 kcal mol$^{-1}$. The 1,16 type of addition occurs for R = $Si(SiMe_3)_3$, $SiBu^tPh_2$.[17] Table 1 shows the calculated geometric and energy parameters for fullerene *tert*-butyl derivatives.

**Table 1.** Geometric and energy parameters of the $Bu^t{}_nC_{60}$ ($n$ = 2, 4, 8, 12) molecules calculated by the density functional method (B3LYP/3-21 G) (for $Bu^t{}_nC_{60}$ ($n$ = 2, 4, 8), the relative energies of isomers are given)

| Compound[a] | $E_{rel}$ /kcal mol$^{-1}$ | Bond length $C(\underline{C}Me)-C_{60}{}^b$/Å | $-E$/eV | |
|---|---|---|---|---|
| | | | HOMO | LUMO |
| $C_{60}$ | — | — | 6.51 | 3.57 |
| 1,4-$\underline{\mathrm{Bu}}^t{}_2\underline{\mathrm{C}}_{60}$ | 0 | 1) 1.633$^c$<br>4) 1.598$^d$ | 6.03 | 3.33 |
| 1,16-$Bu^t{}_2C_{60}$ | 0.38 | 1) 1.595$^d$<br>16) 1.595$^d$ | 5.69 | 3.55 |
| 1,4,11,15-$Bu^t{}_4C_{60}$ | 0.95 | 1.60 (2)$^d$<br>1.63 (2)$^c$ | 5.84 | 3.19 |
| 1,16,11,36-$\underline{\mathrm{Bu}}^t{}_4\underline{\mathrm{C}}_{60}$ | 0 | 1.60 (2)$^d$<br>1.63 (2)$^c$ | 5.58 | 3.15 |
| 1,4,11,15,42,53,57,60-$\underline{\mathrm{Bu}}^t{}_8\underline{\mathrm{C}}_{60}$ | 0 | 1.60 (4)<br>1.63 (4) | 5.34 | 2.73 |
| 1,16,11,36,39,42,47,59-$Bu^t{}_8C_{60}$ | 3.09 | 1.60 (4)<br>1.63 (4) | 4.73 | 2.72 |
| 1,4,11,15,42,53,57,60,<br>21,24,33,48-$Bu^t{}_{12}C_{60}$ | — | 1.60 (4);<br>1.63 (4);<br>1.64 (2);<br>1.66 (2) | 4.85 | 2.52 |

[a] The most energetically favorable isomers are underlined; the atoms numeration is given according to the nomenclature.[18]

[b] The bond distance is preceded by the position at which the fragment is bound to the fullerene cage, the amount of bonds of such a type is given in parentheses.

[c] The eclipsed conformation.

[d] The staggered conformation.

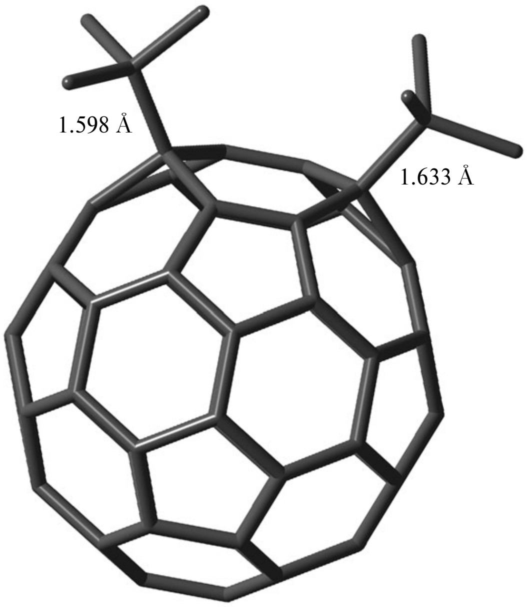

**Fig. 1.** The structure of 1,4-$Bu^t{}_2C_{60}$ optimized at the B3LYP/3-21 G level.

As it is seen from Table 1, formation of 1,4-$Bu^t{}_2C_{60}$ is somewhat more favorable than formation of its 1,16-isomer. However, steric repulsion of $Bu^t$ groups in the 1,4-addition at the [6,6] bond of the fullerenes cage leads to nonequivalence of the *tert*-butyl fragments: one of the C($\underline{C}$Me)—$C_{60}$ bonds becomes elongated (1.633 Å, see Table 1) and the group becomes oriented over the cage $C_{60}$ in the unfavorable eclipsed conformation (Fig. 1). Thus, one can expect that elimination of a $Bu^t$ group from the 1,4-$Bu^t{}_2C_{60}$ will occur readily, and this derivative will be characterized by increased reactivity.

Another interesting conclusion can be drawn upon comparison of isosurfaces of the highest occupied MO (HOMO) of fullerene *tert*-butyl derivatives with different amount of groups. Figure 2 shows such surfaces of HOMO for the $Bu^t{}_4C_{60}$ and $Bu^t{}_{12}C_{60}$ molecules. Only those occupied orbitals, whose energies were less than $E_{HOMO}$ by no more than 1 eV, were considered. It is seen from Fig. 2 that electron density becomes less diffuse with the increase in *n*. This, together with the steric shielding of the fullerene cage, leads to the increase in stability of derivatives with larger amount of added groups.

New fullerene derivatives can be obtained based on fullerene compounds with alkali metals due to the high reactivity of the latter. The choice of alkali metal used in the synthesis of metal fullerenes is not occasional, since formation of dodecaadduct $R_{12}C_{60}$ is possible only with lithium and sodium fullerides. This is related to the degree of the charge transfer from the metal to fullerene. As it is known, $C_{60}$ on chemical reduction can accept no more than six electrons. It was shown[19] that fullerene reacts with only 6 equiv. of potassium naphthalenide to give $K_6C_{60}$, the reaction does not proceed further, since the charge transfer for potassium is close to 1. In contrast to this, lithium ion donates only ~0.5 charge to $C_{60}$ (see Refs 20 and 21) and can form $Li_{12}C_{60}$. In addition, some extent of covalent binding Li—C, leading to localization of the metal ions on the surface of fullerene to form stable molecule $Li_{12}C_{60}$ of icosahedral symmetry, promote formation of lower number of isomers. It was shown theoretically that similar pattern is observed for sodium.[22,23]

Earlier,[24] we have reported on stoichiometric synthesis of fullerene compounds with alkali metals. In the present work, *tert*-butyl derivatives of fullerene were synthesized by the reaction of lithium or sodium fullerides of a given composition $C_{60}M_n(THF)_x$ ($n = 4, 6, 8, 10, 12$) with a ten-fold excess of *tert*-butyl bromide. These

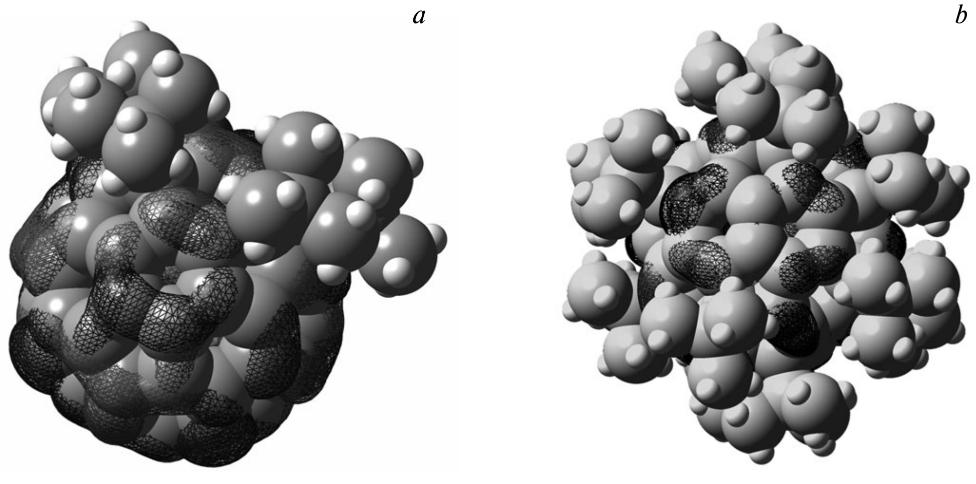

**Fig. 2.** The isosurfaces of the highest occupied MO for $Bu^t{}_4C_{60}$ (*a*) and $Bu^t{}_{12}C_{60}$ (*b*) calculated by the B3LYP/3-21 G method. The atoms are shown as spheres of the Van der Waals radii.

reactions lead to the formation of fullerene adducts (Scheme 1).

**Scheme 1**

$$C_{60}M_n(THF)_x + Bu^tBr \xrightarrow[-n\ MBr,\ -x\ THF]{PhCH_3—THF\ (20\ :\ 1),\ \Delta}$$

$$\longrightarrow Bu^t{}_nC_{60}$$

$$\eta = 60—80\%$$

M = Li, Na; $n$ = 4, 6, 8, 10, 12

The optimum reaction conditions were found in the course of numerous experiments. It turned out that preliminary isolated lithium and sodium fullerides are inert to the alkyl halides in toluene solution, which is attributed to the polymerization of $C_{60}M_n$ in the process of their isolation. The use of more polar reaction medium (PhMe—PhCN (3 : 1), PhMe—THF (4 : 1)), which promotes electron transfer in the first step of the reaction, leads to the formation of organofullerenes with a low amount of addends due to the small number of reaction centers in the polymeric phases of fullerides. Introduction of $Bu^tBr$ into the reaction system in the process of formation of $C_{60}M_n(THF)_x$ results in obtaining desired fullerene adducts. This method for the synthesis of $Bu^t{}_nC_{60}$ is applicable to the preparation of polyorganofullerenes with $n \geq 4$. Difficulties in proceeding the reaction of $C_{60}M_2(THF)_x$ with $Bu^tBr$ are attributed to the low nucleophilicity of the $RC_{60}{}^{\delta-}$ particle formed in the initial step of the process because of incomplete charge transfer from metal to fullerene in $C_{60}M_2(THF)_x$ (as compared to the fullerene dianion generated electrochemically[13]). The found optimum temperatures for the synthesis of $Bu^t{}_nC_{60}$ facilitate the most complete substitution for the metal atoms by *tert*-butyl groups (see Experimental).

The procedure described was used for the synthesis of compounds $Bu^t{}_nC_{60}$ ($n$ = 4 (**1**), 6 (**2**), 8 (**3**), 10 (**4**), 12 (**5**)). They are black solid compounds, susceptible to air oxygen, however, stable on prolonged storage *in vacuo* or under inert atmosphere at room temperature. The fullerene adducts obtained are moderately soluble, and the solubility increases with the increase in the amount of $Bu^t$ groups on the fullerene cage. The solubility of $Bu^t{}_nC_{60}$ increases in the following order of solvents: $MeCN < Et_2O < C_5H_{12} < PhCH_3 < CH_2Cl_2$. It was shown that the reaction products obtained from lithium and sodium fullerides are identical. The derivatives $Bu^t{}_nC_{60}$ synthesized are characterized by spectroscopic methods (IR and NMR spectroscopy), mass spectrometry (MALDI), elemental analysis, and quantum chemical calculations. HPLC was used for chromatographic separation of the products of reaction of $C_{60}Na_n(THF)_x$ ($n$ = 4, 6, 8, 12) with $Bu^tBr$. For $n$ = 4, the individual fraction compositions were studied in detail using a combination of spectroscopic methods (electron absorption spectroscopy, $^1H$ NMR spectroscopy, mass spectrometric analysis (MALDI)).

The mass spectra of adducts $Bu^t{}_nC_{60}$ ($n$ = 4, 6, 8) exhibit peaks corresponding to the molecular ions. Examples are shown in Figure 3, *a*, *b*. Mass spectra were recorded in both the negative and the positive modes. The positive ion spectra were the most informative, since addition of electron-donating $Bu^t$ groups to the fullerene cage results in the decrease in the ionization energy of the molecule. Despite the mild conditions of ionization, fragmentation of the fullerene *tert*-butyl derivatives was observed. Usually, the mass spectra show the presence of a molecular ion peak and peaks of fragment ions differing from each other by the mass of a $Bu^t$ group (57 au). The maximum intensity of signals is shifted toward fragments of higher weights with the increase in the number of groups in $Bu^t{}_nC_{60}$ (see Fig. 3, *c*, *e*).

An increase in the amount of addends in $Bu^t{}_nC_{60}$ leads to the internal strains in the molecule and weakening the $Bu^t—C_{60}$ bond, that facilitates the fragmentation process resulting in the fact that in a number of cases it is impossible to record a molecular ion peak. For example, in the mass spectrum of $Bu^t{}_{12}C_{60}$ obtained in the reflectron mode (see Fig. 3, *e*), only a fragment peak $[M - 3\ Bu^t]^+$ ($m/z$ = 1234) was recorded. Attempts in the work[16] to detect molecular ions of $Bu^t{}_nC_{60}H_m$ ($n$ = 5, 6) also failed. However, we found that the change in configuration of the time-of-flight analyzer from reflectron to the linear mode, allowing one to intensify signals of ions with shorter lifetimes, leads to the appearance of a fragment ion peak with higher amount of $Bu^t$ groups ($[Bu^t{}_{12}C_{60}]^+$, $m/z$ = 1291) in the spectrum, which also confirms the presence of fragmentation of the starting ionized molecules. In the reflectron mass spectra of $Bu^t{}_nC_{60}$, there are present signals of ions, which are formed by the laser desorption/ionization (when $n$ = 0, 1, 2, ..., 8, see Fig. 3, *c*, *e*) and which are obtained as a result of the post-source fragmentation (marked with (*), differ from the stable peaks by $m/z \approx 11$). The nature of the marked ions was established based on the recording the mass spectra in the linear mode, where such peaks were completely absent (see Fig. 3, *d*).

In addition to mass spectrometric analysis, we used IR and NMR spectroscopy for characterization of the compounds obtained. Figure 4 shows the fragments of the IR spectra of $Bu^t{}_nC_{60}$ in the most informative regions of frequencies (600—500 $cm^{-1}$ is the region of $T_{1u}(1)$ and $T_{1u}(2)$ radial vibrational modes of $C_{60}$ (*c*, *d*), 1420—1090 $cm^{-1}$ is the region characteristic of the skeletal vibrations of $Bu^t$ groups (*a*, *b*)). In the spectra of $Bu^t{}_nC_{60}$, there are bands of the fullerene fragment and addends, with intensities of the corresponding bands becoming higher with the increase in the amount of $Bu^t$ groups (see Fig. 4, *b*). Comparative analysis of the IR spectra of products **1**—**5** with the spectra of $C_{60}$ and $Bu^tBr$ allows one to find out how function-

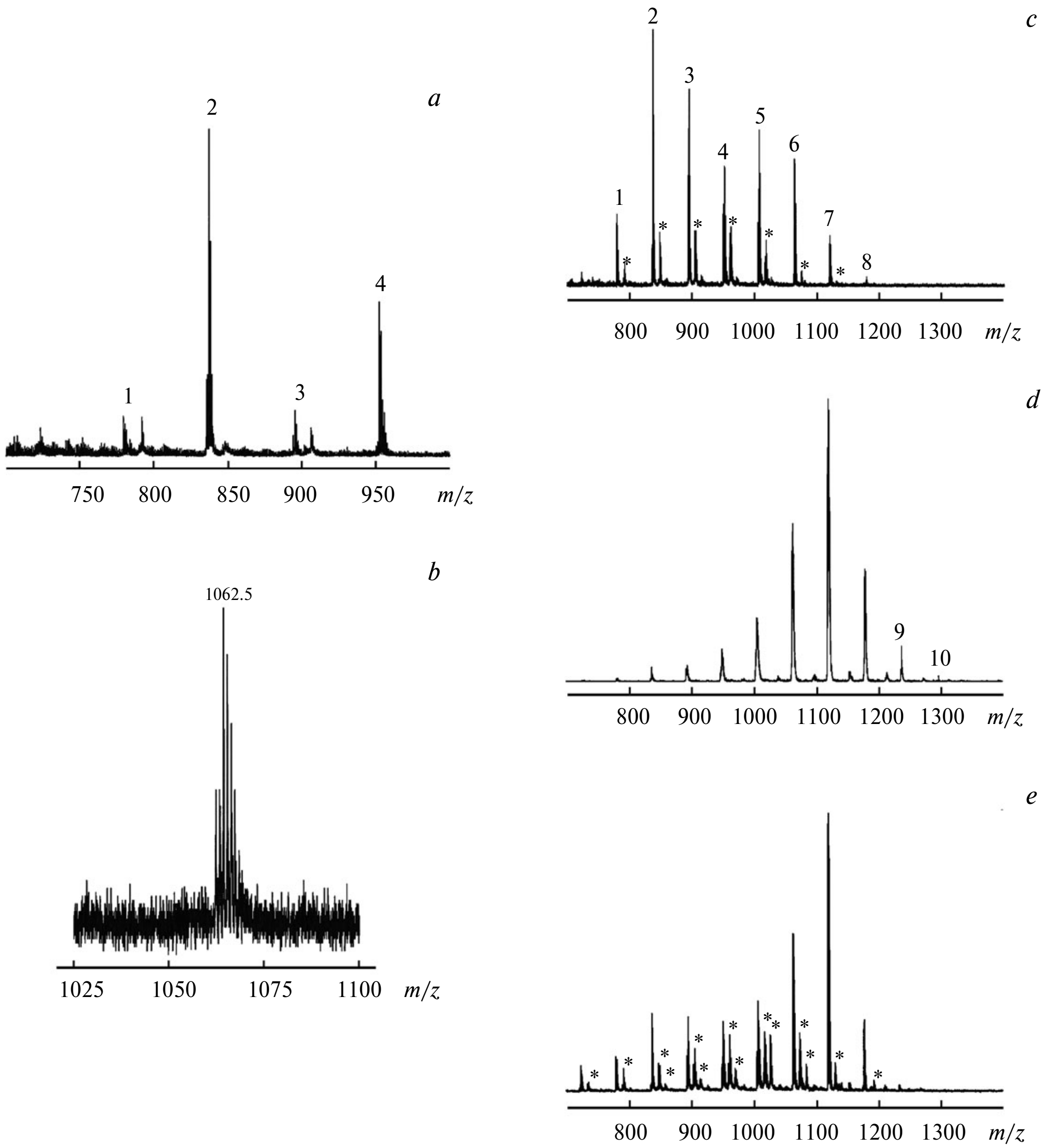

**Fig. 3.** The positive ion MALDI mass spectrum for $Bu^t_4C_{60}$ (the reflectron mode) (*a*); the fragment of the positive ion MALDI mass spectrum (in the region of molecular ion) for the product $Bu^t_6C_{60}$, $n = 6$ (the range of molecular weights 1025—1100, the reflectron mode) (*b*); the positive ion MALDI mass spectra (the range of molecular weights 700—1400) for the samples of $Bu^t_8C_{60}$ (the reflectron mode) (*c*), $Bu^t_{12}C_{60}$ (linear mode) (*d*), $Bu^t_{12}C_{60}$ (the reflectron mode) (*e*). The DCTB matrix, the numbers near the peaks show the number of $Bu^t$ groups at the fragment ions $[Bu^t_nC_{60}]^+$ (*n*), the signals of the post-source fragment ions are marked (*).

alization affects vibrations $T_{1u}(1)$ and $T_{1u}(2)$ of the fullerene cage and follow the changes in the spectral characteristics of addends. Studies of the changes in the character of vibrations in the spectra of $Bu^t_nC_{60}$ were also carried out based on the DFT-calculations (PBE/TZ2P) of IR spectra for $Bu^t_4C_{60}$, $C_{60}$, and $Bu^tBr$ (see Fig. 4, *a*). An increase in *n* causes regular decrease in the relative intensities of the $C_{60}$ peaks in the IR spectra of $Bu^t_nC_{60}$ (see Fig. 4, *d*). Splitting of the $T_{1u}(2)$ band in the spectra of tetra- and hexaadducts to several components ($Bu^t_4C_{60}$: 556 w, 563 m, 577 m; $Bu^t_6C_{60}$: 562, 580 w) agrees with the calculated data (see Fig. 4, *c*) and corresponds to the IR spectra of fullerene derivatives with small amount of addends described in the literature.[12] In addition, changes in the spectral characteristics of addends in comparison with the starting $Bu^tBr$ are also observed. For instance, the bands of skeletal vibrations of $Bu^tBr$ at 1144 and 1236 $cm^{-1}$ are transformed to a broad strong band at 1201—1204 $cm^{-1}$, whereas the band at 1370 $cm^{-1}$ ($\delta_s$ $CH_3$, $Bu^tBr$) splits to two components at 1364—1366 and 1392—1395 $cm^{-1}$ ($Bu^t_nC_{60}$) (see Fig. 4, *b*). All these changes were confirmed by the DFT-calculations (see Fig. 4, *a*) and

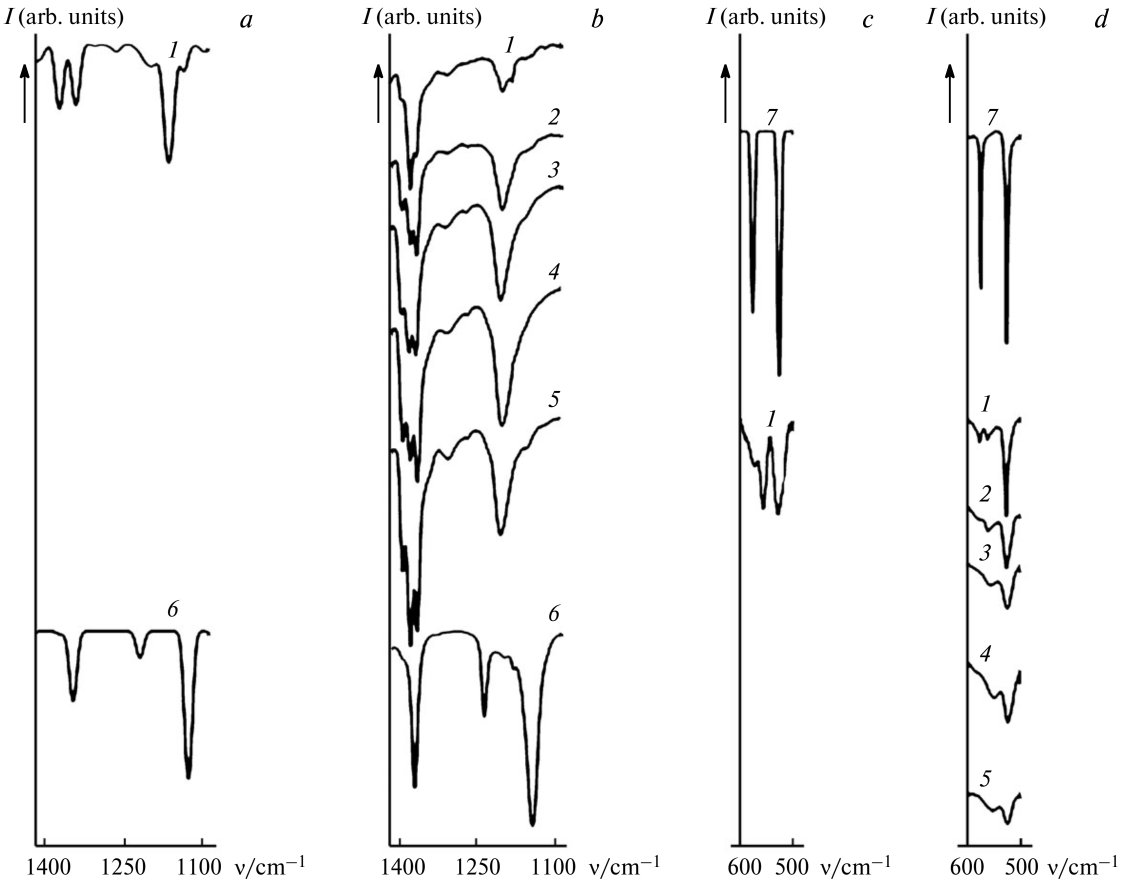

**Fig. 4.** The fragments of the IR spectra of $Bu^t_nC_{60}$ in the regions 1420—1090 (*a*, *b*) and 600—500 cm$^{-1}$ (*c*, *d*): calculated (*a*, *c*, PBE/TZ2P) and experimental (*b*, *d*), Nujol, the signal for the latter is marked (*): *n* = 4 (*1*), 6 (*2*), 8 (*3*), 10 (*4*), 12 (*5*). The calculated and experimental spectra of $Bu^tBr$ (*6*) and $C_{60}$ (*7*) are given for comparison, as well.

indicate addition of the $Bu^t$ groups to the fullerene fragment.

In the $^1H$ NMR spectra of adducts **1—5** ($C_6D_6$), the protons of the $Bu^t$ groups are found as broad multiplets at δ 0.40—2.30. Figure 5 shows $^1H$ and $^{13}C$ NMR spectra of the $Bu^t_{12}C_{60}$ sample as examples. In the $^{13}C$ NMR spectra of the product **1—5** ($C_6D_6$), signals for the C (sp$^3$) atoms of the $Bu^t$ groups are found at δ 26—30 ($CH_3$) and 39—40 ($\underline{C}(CH_3)_3$). The C (sp$^3$) atoms from $C_{60}$ are found in the region δ 58—70, the C (sp$^2$) atoms from $C_{60}$ resonate as broad signals at δ 135—160. Going from $Bu^t_4C_{60}$ to $Bu^t_{12}C_{60}$, the ratio of integral intensities of the signals for the sp$^2$- and sp$^3$-hybridized carbon atoms in the $^{13}C$ NMR spectra decreases by 3.5 times as is theoretically predicted.

HPLC was used for chromatographic separation of the product of the reaction of $C_{60}Na_n(THF)_x$ ($n$ = 4, 6, 8, 12) with $Bu^tBr$. Comparative analysis of chromatographic patterns (Fig. 6, Table 2) showed that the fraction with shorter retention times correspond to the derivatives with greater amount of added groups due to their better solubility and weaker interaction with the stationary phase. The chromatographic set of peaks for the hexaadduct **2** is very close to the results for $n$ = 4 except that a new fraction with the shorter retention time (~22%) is present, which corresponds to the fullerene derivative with six $Bu^t$ groups.

Chemical transformations of $Bu^t_nC_{60}$ are observed under chromatographic conditions: elimination of the addend and addition of hydrogen takes place (Fig. 7), and the more the fullerene surface is shielded with the $Bu^t$ groups, the more the compound is stable to decomposition. Thus, the chromatographic patterns for $Bu^t_{12}C_{60}$ and $Bu^t_8C_{60}$ show the presence of one major peak (see Fig. 6), while analysis of the $Bu^t_4C_{60}$ adduct shows the presence of a whole spectrum of derivatives with $n \leq 4$, including unmodified $C_{60}$, which were absent in the starting sample. At the same time, the chromatographic analysis performed for each isolated fraction showed their purity (95+%, see Fig. 7, *a*), that indicates the absence of further decomposition of the individual compounds. It is obvious that unstable isomers of $Bu^t_nC_{60}$ undergo decomposition. Our quantum chemical calculations of geometric and energy parameters for the molecules $Bu^t_nC_{60}$ also indicate kinetic instability of adducts with the small amount of groups.

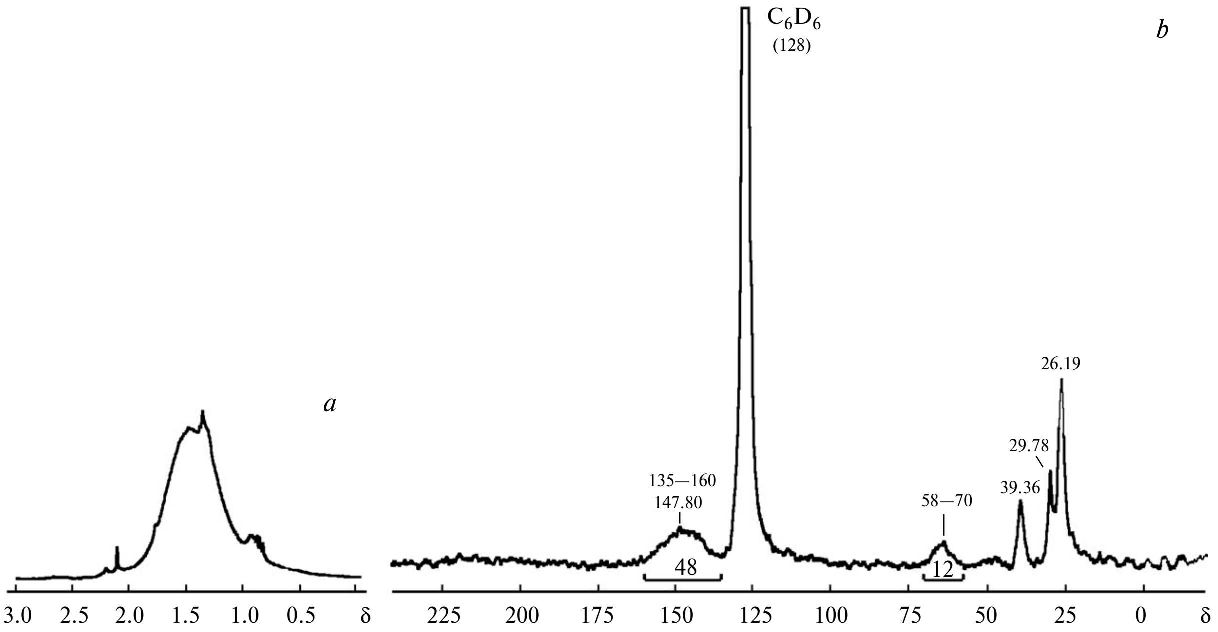

**Fig. 5.** The $^1$H (*a*) and $^{13}$C (*b*) NMR spectra of $Bu^t{}_{12}C_{60}$ ($C_6D_6$).

Composition of chromatographic fractions of the product of the reaction $C_{60}Na_4(THF)_x$ + $Bu^tBr$ was studied by us

**Table 2.** The results of chromatographic separation of the products $Bu^t{}_nC_{60}$ ($n$ = 4, 6, 8, 12): retention times ($R_T$/min) and relative content of individual fractions P1—P8 and $C_{60}$

| Product | $R_T$ /min | Content[a] (%) |
|---|---|---|
| $Bu^t{}_{12}C_{60}$ | 2.83 | 91.03 |
| | 2.93 | 91.03 |
| | 3.11 | 91.03 |
| | 3.40 | 91.03 |
| | 3.57 | 5.45 |
| | 3.94 | 2.27 |
| | 4.26 | [b] |
| | 4.58 | [b] |
| | 5.27 | [b] |
| $Bu^t{}_8C_{60}$ | 2.88 | 95.64 |
| | 3.12 | 95.64 |
| | 3.44 | 95.64 |
| | 3.57 | 95.64 |
| | 3.94 | 2.33 |
| | 4.07 | [b] |
| | 4.27 | [b] |
| | 4.60 | [b] |
| | 5.28 | [b] |
| $Bu^t{}_6C_{60}$ | 2.92 | 26.80 |
| | 2.98 | 26.80 |
| | 3.16 | 26.80 |
| | 3.46 | 15.84 |
| | 3.56 | 18.08 |
| | 3.94 | 10.76 |
| | 4.06 | 5.34 |
| | 4.26 | 10.25 |
| | 4.58 | 7.57 |
| | 5.26 | 3.81 |
| | 7.32 | [b] |
| $Bu^t{}_4C_{60}$ | 3.16 | 5.44 (P1) |
| | 3.47 | 19.03 |
| | 3.57 | 19.03 (P2) |
| | 3.95 | 11.73 (P3) |
| | 4.06 | 5.51 (P4) |
| | 4.26 | 16.51 (P5) |
| | 4.58 | 11.13 (P6) |
| | 5.26 | 11.41 (P7) |
| | 7.28 | 10.68 ($C_{60}$) |
| | 7.60 | 5.12 (P8) |

[a] The fraction is given in parentheses.

[b] The content was <1%.

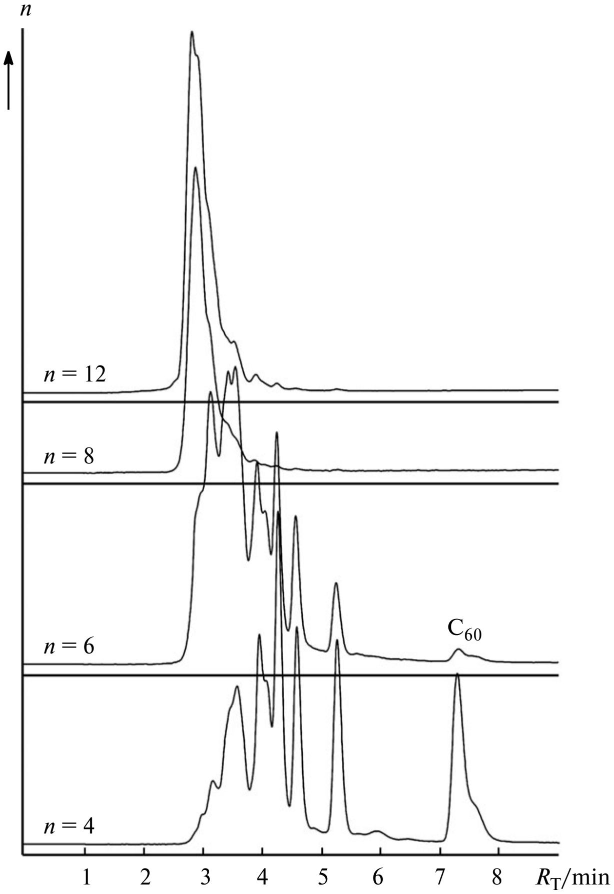

**Fig. 6.** Chromatographic patterns of the product upon obtaining $Bu^t{}_nC_{60}$ ($n$ = 12, 8, 6, 4) (a Cosmosil Buckyprep column, 4.6×250 mm, toluene, 1 mL min$^{-1}$).

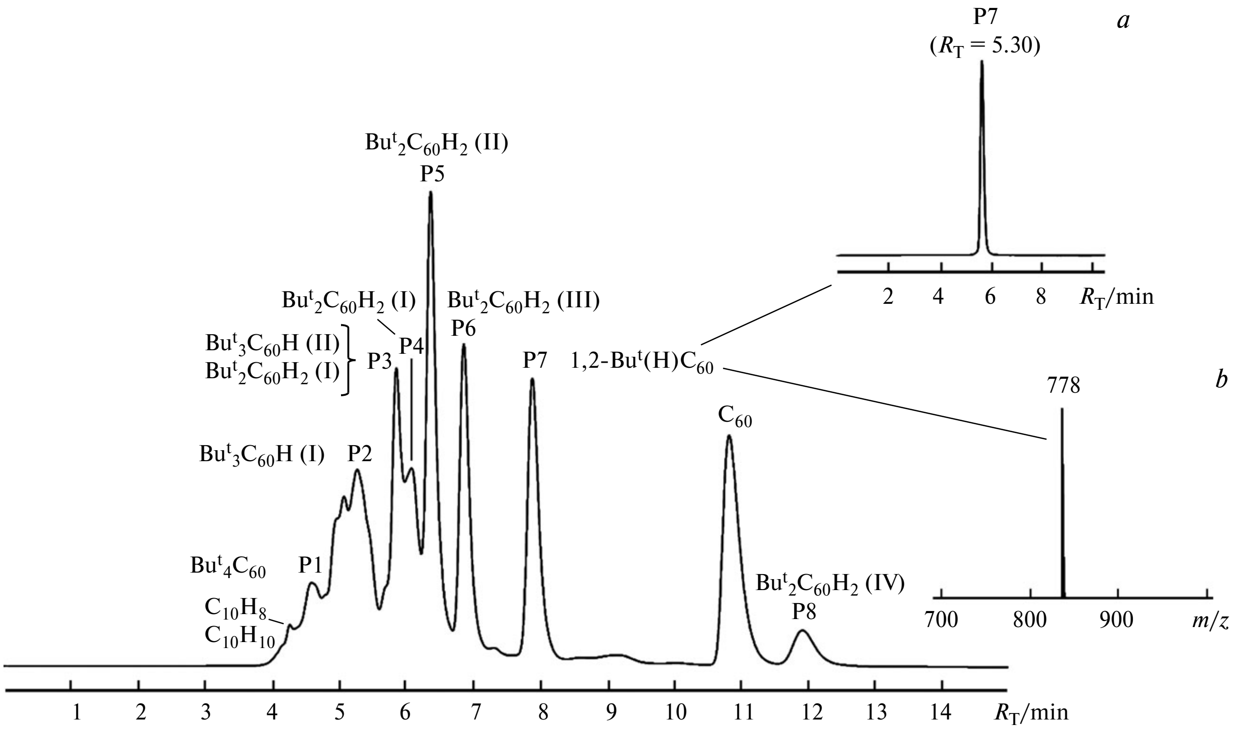

**Fig. 7.** Chromatographic patterns of the product of the reaction of $C_{60}Na_4(THF)_x$ with $Bu^tBr$ in excess amount (a Cosmosil Buckyprep column, 10×250 mm, toluene, 4.6 mL $min^{-1}$, $\lambda$ = 290 nm), the isomer number is given in parentheses. The insertion *a*: chromatographic pattern of the isolated fraction P7 (a Cosmosil Buckyprep column, 4.6×250 mm, toluene, 1 mL $min^{-1}$, $\lambda$ = 290 nm), The insertion *b*: the MALDI mass spectrum of the fraction P7 (DCTB (+), the reflectron mode).

in detail. The isolated fractions were analyzed by MALDI mass spectrometry, $^1H$ NMR spectroscopy, and electron absorption spectroscopy. The chromatographic pattern of the product **1** is shown in Figure 7. Eight major fractions were isolated: P1—P8. The unmodified $C_{60}$ has the retention time $R_T$ = 10.83 min. Chromatographic pattern of each isolated fraction (except P3) is a single sharp peak of a regular shape (95+%, see Fig. 7, *a*). The isolated fractions P1—P8 were identified using MALDI mass spectrometry (the corresponding molecular ions are present in the spectra, see Experimental): P1 is the $Bu^t_4C_{60}$, P2 is the $Bu^t_3C_{60}H$ (isomer I), P3 is the $Bu^t_3C_{60}H$ (isomer II) + + $Bu^t_2C_{60}H_2$ (isomer I), P4 is the $Bu^t_2C_{60}H_2$ (isomer I), P5 is the $Bu^t_2C_{60}H_2$ (isomer II), P6 is the $Bu^t_2C_{60}H_2$ (isomer III), P7 is the $Bu^tC_{60}H$ (see Fig. 7, *b*), P8 is the $Bu^t_2C_{60}H_2$ (isomer IV). As an example, Figure 8 shows the mass spectrum of the chromatographic fraction P2 identified as $Bu^t_3C_{60}H$.

Each fraction was characterized by electron absorption spectroscopy and $^1H$ NMR spectroscopy. The electron absorption spectrum of the fraction P7 is identical to the spectrum of 1,2-$Bu^tC_{60}H$ reported in the work.[12] The band observed at $\lambda_{max}$ = 435 nm is characteristic of the 1,2-addition product.[25] In the case of 1,4-addition of the addends to $C_{60}$, the absorption spectrum of $RR'C_{60}$ exhibits electron transition at $\lambda_{max}$ = 450 nm.[25] To sum up, the presence of the absorption bands with $\lambda_{max}$ = = 425—430 nm or $\lambda_{max}$ = 450 nm in the spectra of fullerene diadducts allows one to conclude on the character of addition of the R group to the fullerene cage. Interpretation of the electron spectra for derivatives $R_nC_{60}$ ($n > 2$) is more difficult because of both a possible combination of 1,2- and 1,4-additions and exhibiting of a large amount of electron transitions (the detailed description of the absorption spectra for the isolated fractions is given in Experimental).

Unlike the starting adduct **1**, the $^1H$ NMR spectra of chromatographic fractions show signals for the $Bu^t$ protons as separate peaks and resonance for the protons bound to the fullerene cage in correspondence with the molecular formulas of each fraction (see Experimental). This agrees with the data of MALDI mass spectrometry indicating addition of hydrogen to the fullerene cage. Shift of the peaks for the fullerene protons ($\delta$ 5.60—6.61, $CDCl_3$) toward the low-field region as compared to the protons of the $sp^3$-hybridized carbon atoms of the aliphatic groups ($(CH_3)_2C\underline{H}C_2H_5$, $\delta$ 1.45, $CDCl_3$; $PhC\underline{H}(CH_3)_2$, $\delta$ 2.88, $CDCl_3$) is due to the electron-withdrawing character of the $C_{60}$ cage. Protons of *tert*-butyl groups (9 H from each $Bu^t$ group) are found as separate singlets in the region $\delta$ 1.64—2.15. Chemical shifts for the protons $Bu^tC_{60}H$ ($\delta$ 2.09, 9 H, 1 $Bu^t$ group; 6.67, 1 H, $C_{60}H$) correspond to 1-*tert*-butyl-1,2-dihydrofullerene-60 described in the literature.[26]

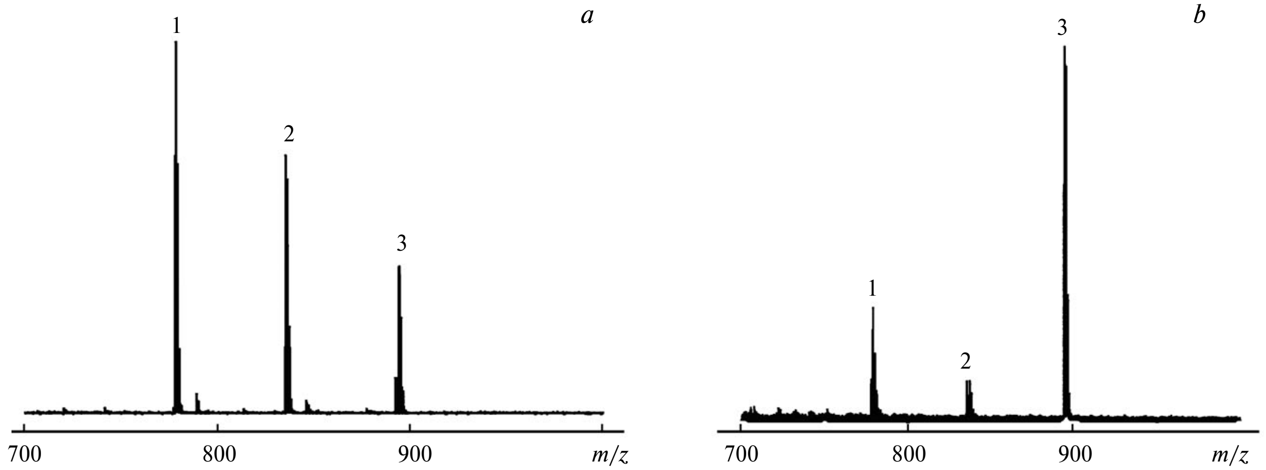

**Fig. 8.** The negative (*a*) and positive (*b*) ion mass spectra for the chromatographic fraction P2, ($Bu^t_3C_{60}H$); the numbers near he peaks mean the *n* values.

In conclusion, the following fullerene derivatives, obtained by the reaction of $C_{60}Na_4(THF)_x$ with $Bu^tBr$, were for the first time chromatographically isolated and identified: P1 as $Bu^t_4C_{60}$; P2 as $Bu^t_3C_{60}H$ (isomer I); P3 (isomer II, $Bu^t_3C_{60}H$, 1,4- and 1,2-addition of the addends); P4 as $Bu^t_2C_{60}H_2$ (isomer I, 1,4-addition of the addends); P5 as $Bu^t_2C_{60}H_2$ (isomer II; 1,4-addition of the addends); P6 as $Bu^t_2C_{60}H_2$ (isomer III, 1,4-addition of the addends); P7 as 1,2-$Bu^tC_{60}(H)$, P8 as $Bu^t_2C_{60}H_2$ (isomer IV, 1,2-addition of the addends).

## Experimental

All the synthetic and isolation operations were carried out either *in vacuo* or under inert atmosphere. Solvents were purified and dried according to the standard procedures.[27] Samples of $C_{60}$ and $C_{10}H_8$ were subjected to additional purification by gradient sublimation *in high vacuo* ($P = 10^{-4}$ Torr). *tert*-Butyl bromide (Fluka) was dried with $CaCl_2$ and distilled at the boiling point. Solvents and $Bu^tBr$ were collected directly before use by condensation *in vacuo*.

**IR spectra** of fullerene derivatives **1**—**5** were recorded on a FSM 1201 FTIR Fourier-spectrometer in Nujol and fluorinated Nujol (in the region 4000—400 $cm^{-1}$).

**$^1H$ and $^{13}C$ NMR spectra** were recorded on a Bruker Avance DPX-200 Fourier-NMR-spectrometer (200.14 and 50.0 MHz, respectively). A Bruker ARX 400 spectrometer (400 MHz) was used for recording $^1H$ NMR spectra of chromatographic fractions. Spectra were obtained at ~20 °C and correlated with the signals for the residual isotopes $^1H$ and $^{13}C$ of deuterated solvents, tetramethylsilane was an internal standard.

**MALDI mass spectra** were recorded on a Bruker AutoFlex II reflectron time-of-flight mass spectrometer. Peaks in the experimental mass spectra were identified based on theoretically calculated isotope distribution and mass defects for each separate ion (the IsoPro 3.0 program).

**Elemental analysis** was carried out on a Carlo Erba 1106 automatic analyzer.

**Electron absorption spectra** were recorded on a Perkin—Elmer Lambda 25 UV—Vis spectrometer (the region 220—1100 nm) at ~20 °C in air, using hexane as a solvent.

**Quantum chemical calculation procedures.** Optimization of geometry was carried out using the HyperChem,[28] GAUSSIAN 03,[29] and PRIRODA[30] program packages. The AM1 method was used for semi-empirical calculations, the DFT calculations were performed at B3LYP/3-21G, B3LYP/6-31G, and PBE/TZ2P levels. For the DFT studies, the most stable isomers found by the semi-empirical calculations were chosen. Interpretation of the IR spectra of fullerene *tert*-butyl adducts was carried out on the PBE/TZ2P level.

**Synthesis and characterization of obtained compounds.** Fullerene *tert*-butyl derivatives were synthesized by the reaction of lithium and sodium fullerides (without their isolation from the reaction mixtures) with the ten-fold excess of the corresponding alkyl halide. The optimum reaction temperatures were found experimentally.

**Synthesis of $Bu^t_4C_{60}$ (1).** A solution of $Bu^tBr$ (1.0 mL, 1.25 g, 9.15 mmol) in toluene (10 mL) was added over 30 min to a cooled (–70 °C) reaction mixture containing $C_{60}Li_4(THF)_x$ ($C_{60}Na_4(THF)_x$), which was obtained according to the procedure described earlier,[24] with vigorous stirring. The temperature of the reaction mixture was gradually elevated to ~20 °C, then the mixture was heated to 70—85 °C for 1.5 h and kept for 20 h. The reaction progress was accompanied by the change of the solution color (from black to claret). Then the reaction mixture was filtered in the evacuated system, the solvent from the filtrate was evaporated *in vacuo*, the residual solid product was 4—5 times washed with cold hexane, dried, and isolated. The other fullerene compounds with *tert*-butyl groups were synthesized similarly. The yields of $Bu^t_nC_{60}$ were 60—80% calculated on the fullerene weight. IR (KBr), ν/$cm^{-1}$: 527 s ($T_{1u}(1)$), 556 w, 563 m, 577 m ($T_{1u}(2)$), 1182 m ($T_{1u}(3)$), 1201 m (skeletal vibrations of $Bu^t$ group), 1366 s, 1395 m ($\delta_s(CH_3)$), 1440 w, 1461 w ($\delta_{as}(CH_3)$), 2858 w, 2901 w ($\nu_s(CH_3)$), 2924 w, 2956 w ($\nu_s(CH_3)$). $^1H$ NMR ($C_6D_6$), δ: 0.80—1.90 (m, 36 H, 12 $CH_3$ groups from 4 $Bu^t$). $^{13}C$ NMR ($C_6D_6$), δ: 27.12, 30.25 ($C(\underline{C}H_3)_3$); 40.13 ($\underline{C}(CH_3)_3$); 67—68 (~67.77, $sp^3$-C from $C_{60}$); 142—152 (145.52, $sp^2$-C from $C_{60}$). MALDI MS (DCTB (+), *m/z*): 952 $[Bu^t_4C_{60} + 4 H]^+$, 894

$[Bu^t{}_4C_{60} - Bu^t + 3\ H]^+$, 836 $[Bu^t{}_4C_{60} - 2\ Bu^t + 2\ H]^+$, 779 $[Bu^t{}_4C_{60} - 3\ Bu^t + 2\ H]^+$, 721 $[Bu^t{}_4C_{60} - 4\ Bu^t + H]^+$.

**Compound $Bu^t{}_6C_{60}$ (2).** IR (KBr), ν/cm$^{-1}$: 526 m ($T_{1u}(1)$), 562 w, 580 w ($T_{1u}(2)$), 1201 s (skeletal vibrations of $Bu^t$ group), 1366 s, 1392 m ($\delta_s(CH_3)$), 1440 w, 1461 w ($\delta_{as}(CH_3)$), 2858 w, 2901 w ($\nu_s(CH_3)$), 2924 w, 2956 w ($\nu_s(CH_3)$). $^1H$ NMR ($C_6D_6$), δ: 0.60—2.00 (m, 54 H, 18 $CH_3$ groups from 6 $Bu^t$). $^{13}C$ NMR ($C_6D_6$), δ: 27.07, 29.98 ($C(\underline{C}H_3)_3$); 40.11 ($\underline{C}(CH_3)_3$); 64—69 (~67.55, sp$^3$-C from $C_{60}$); 138—157 (~146.40, sp$^2$-C from $C_{60}$). MALDI MS (DCTB (+), *m/z*): 1064 $[Bu^t{}_6C_{60} + 2\ H]^+$, 1007 $[Bu^t{}_6C_{60} - Bu^t + 2\ H]^+$, 952 $[Bu^t{}_6C_{60} - 2\ Bu^t + 4\ H]^+$, 895 $[Bu^t{}_6C_{60} - 3\ Bu^t + 4\ H]^+$, 837 $[Bu^t{}_6C_{60} - 4\ Bu^t + 3\ H]^+$, 779 $[Bu^t{}_6C_{60} - 5\ Bu^t + 2\ H]^+$, 721 $[Bu^t{}_6C_{60} - 6\ Bu^t + H]^+$. Found (%): C, 92.42; H, 4.02. $C_{84}H_{54}$. Calculated (%): C, 94.88; H, 5.12.

**Compound $Bu^t{}_8C_{60}$ (3).** IR (KBr), ν/cm$^{-1}$: 524 m ($T_{1u}(1)$), 555 w ($T_{1u}(2)$), 1201 s (skeletal vibrations of $Bu^t$ group), 1365 s, 1392 s ($\sigma_s(CH_3)$), 1440 w, 1461 w ($\delta_{as}(CH_3)$), 2858 w, 2901 w ($\nu_s(CH_3)$), 2924 w, 2956 m ($\nu_s(CH_3)$). $^1H$ NMR ($C_6D_6$), δ: 0.50—2.10 (m, 72 H, 24 $CH_3$ groups from 8 $Bu^t$). $^{13}C$ NMR ($C_6D_6$), δ: 26.78, 29.96 ($C(\underline{C}H_3)_3$); 39.87 ($\underline{C}(CH_3)_3$); 62—70 (~66.77, sp$^3$-C from $C_{60}$); 137—159 (~147.01, sP2-C from $C_{60}$). MALDI MS (DCTB (+), *m/z*): 1178 $[Bu^t{}_8C_{60} + H]^+$, 1120 $[Bu^t{}_8C_{60} - Bu^t + H]^+$, 1063 $[Bu^t{}_8C_{60} - 2\ Bu^t + H]^+$, 1007 $[Bu^t{}_8C_{60} - 3\ Bu^t + 2\ H]^+$, 951 $[Bu^t{}_8C_{60} - 4\ Bu^t + 3\ H]^+$, 895 $[Bu^t{}_8C_{60} - 5\ Bu^t + 4\ H]^+$, 837 $[Bu^t{}_8C_{60} - 6\ Bu^t + 3\ H]^+$, 779 $[Bu^t{}_8C_{60} - 7\ Bu^t + 2\ H]^+$, 723 $[Bu^t{}_8C_{60} - 8\ Bu^t + 3\ H]^+$. Found (%): C, 91.40; H, 5.21. $C_{92}H_{72}$. Calculated (%): C, 93.84; H, 6.16. Considerable disagreements of the elemental composition of compounds **2** and **3** found experimentally with the theoretical values are due to the incomplete combustion of the samples and are typical of the fullerene derivatives.[31]

**Compound $Bu^t{}_{10}C_{60}$ (4).** IR (KBr), ν/cm$^{-1}$: 524 m ($T_{1u}(1)$), 551 w ($T_{1u}(2)$), 1202 s (skeletal vibrations of $Bu^t$ group), 1364 s, 1392 s ($\delta_s(CH_3)$), 1440 w, 1461 m ($\delta_{as}(CH_3)$), 2858 w, 2901 w ($\nu_s(CH_3)$), 2924 w, 2956 m ($\nu_s(CH_3)$). $^1H$ NMR ($C_6D_6$), δ: 0.50—2.30 (m, 90 H, 30 $CH_3$ groups from 10 $Bu^t$). $^{13}C$ NMR ($C_6D_6$), δ: 26.40, 29.94 ($C(\underline{C}H_3)_3$); 39.70 ($\underline{C}(CH_3)_3$); 61—70 (~66.00, sp$^3$-C from $C_{60}$); 137—160 (~147.21, sP2-C from $C_{60}$). MALDI MS (DCTB (+), *m/z*): 1234 $[Bu^t{}_{10}C_{60} - Bu^t]^+$, 1178 $[Bu^t{}_{10}C_{60} - 2\ Bu^t + H]^+$, 1120 $[Bu^t{}_{10}C_{60} - 3\ Bu^t + H]^+$, 1063 $[Bu^t{}_{10}C_{60} - 4\ Bu^t + H]^+$, 1007 $[Bu^t{}_{10}C_{60} - 5\ Bu^t + 2\ H]^+$, 951 $[Bu^t{}_{10}C_{60} - 6\ Bu^t + 3\ H]^+$, 895 $[Bu^t{}_{10}C_{60} - 7\ Bu^t + 4\ H]^+$, 837 $[Bu^t{}_{10}C_{60} - 8\ Bu^t + 3\ H]^+$.

**Compound $Bu^t{}_{12}C_{60}$ (5).** IR (KBr), ν/cm$^{-1}$: 523 w ($T_{1u}(1)$), 1204 s (skeletal vibrations of $Bu^t$ group), 1364 s, 1392 s ($\delta_s(CH_3)$), 1440 w, 1461 m ($\delta_{as}(CH_3)$), 2858 w, 2901 w ($\nu_s(CH_3)$), 2924 w, 2956 m ($\nu_s(CH_3)$). $^1H$ NMR ($C_6D_6$), δ: 0.40—2.22 (m, 108 H, 36 $CH_3$ groups from 12 $Bu^t$). $^{13}C$ NMR ($C_6D_6$), δ: 26.19, 29.78 ($C(\underline{C}H_3)_3$); 39.36 ($\underline{C}(CH_3)_3$); 58—70 (~64.81, sp$^3$-C from $C_{60}$); 135—160 (~147.80, sp$^2$-C from $C_{60}$). MALDI MS (DCTB (+), *m/z*): 1291 $[Bu^t{}_{12}C_{60} - 2\ Bu^t]^+$ (linear mode), 1234 $[Bu^t{}_{12}C_{60} + 3\ Bu^t]^+$, 1178 $[Bu^t{}_{12}C_{60} - 4\ Bu^t + H]^+$, 1120 $[Bu^t{}_{12}C_{60} - 5\ Bu^t + H]^+$, 1063 $[Bu^t{}_{12}C_{60} - 6\ Bu^t + H]^+$, 1007 $[Bu^t{}_{12}C_{60} - 7\ Bu^t + 2\ H]^+$, 951 $[Bu^t{}_{12}C_{60} - 8\ Bu^t + 3\ H]^+$, 895 $[Bu^t{}_{12}C_{60} - 9\ Bu^t + 4\ H]^+$, 837 $[Bu^t{}_{12}C_{60} - 10\ Bu^t + 3\ H]^+$, 779 $[Bu^t{}_{12}C_{60} - 11\ Bu^t + 2\ H]^+$. Found (%): C, 92.29; H, 6.75. $C_{108}H_{108}$. Calculated (%): C, 92.26; H, 7.74.

**HPLC of $Bu^t{}_4C_{60}$ and analysis of individual fractions.** A Waters 2487 chromatographic system was used with Cosmosil Buckyprep (Nacalai Tesque, Japan) analytical (4.6×250 mm) and semipreparative (10×250 mm) columns (the stationary phase was silica gel modified with pyrenylpropyl groups). Toluene was an eluent. Detection was performed spectrophotometrically at 290 nm.

**Characteristics of the individual fractions** obtained by separation of the $Bu^t{}_4C_{60}$ product (a Cosmosil Buckyprep column, 10×250 mm, toluene, 4.6 mL min$^{-1}$) (see Fig. 6).

<u>Fraction P1.</u> MALDI MS (DCTB (–), *m/z*): 948 $[\underline{Bu}^t{}_4\underline{C}_{60}]^-$, 891 $[Bu^t{}_4C_{60} - Bu^t]^-$, 834 $[Bu^t{}_4C_{60} - 2\ Bu^t]^-$, 777 $[Bu^t{}_4C_{60} - 3\ Bu^t]^-$. MALDI MS (DCTB (+), *m/z*): 950 $[\underline{Bu}^t{}_4\underline{C}_{60} + 2\ H]^+$, 893 $[Bu^t{}_4C_{60} - Bu^t + 2\ H]^+$, 835 $[Bu^t{}_4C_{60} - 2\ Bu^t + H]^+$, 777 $[Bu^t{}_4C_{60} - 3\ Bu^t]^+$.

<u>Fraction P2.</u> EAS ($CH_2Cl_2$, $\lambda_{max}$/nm): 320, 345, 382, 385, 428, 492. $^1H$ NMR ($CDCl_3$), δ: 1.64 (s, 9 H, $Bu^t$); 2.08 (s, 9 H, $Bu^t$); 2.15 (s, 9 H, $Bu^t$); 6.19 (s, 1 H, $C_{60}H$). MALDI MS (DCTB (–), *m/z*): 892 $[\underline{Bu}^t{}_3\underline{C}_{60}\underline{H}]^-$, 835 $[Bu^t{}_3C_{60}H - Bu^t]^-$, 778 $[Bu^t{}_3C_{60}H - 2\ Bu^t]^-$. MALDI MS (DCTB (+), *m/z*): 894 $[\underline{Bu}^t{}_3\underline{C}_{60}\underline{H} + 2\ H]^+$, 835 $[Bu^t{}_3C_{60}H - Bu^t]^+$, 778 $[Bu^t{}_3C_{60}H - 2\ Bu^t]^+$.

<u>Fraction P3.</u> EAS ($CH_2Cl_2$, $\lambda_{max}$/nm): 248, 317, 385, 430, 450, 494, 620, 715, 819, 915. $^1H$ NMR ($CDCl_3$), δ: 1.84 (s, 9 H, $Bu^t$); 2.10 (s, 9 H, $Bu^t$); 2.15 (s, 9 H, $Bu^t$); 6.57 (s, 1 H, $C_{60}H$). MALDI MS (DCTB (–), *m/z*): 892 $[\underline{Bu}^t{}_3\underline{C}_{60}\underline{H}]^-$, 835 $[Bu^t{}_3C_{60}H - Bu^t]^-$, 777 $[Bu^t{}_3C_{60}H - 2\ Bu^t - H]^-$, 720 $[Bu^t{}_3C_{60}H - 3\ Bu^t - H]^-$. MALDI MS (DCTB (+), *m/z*): 894 $[\underline{Bu}^t{}_3\underline{C}_{60}\underline{H} + 2\ H]^+$, 836 $[Bu^t{}_3C_{60}H - Bu^t + H]^+$, 779 $[Bu^t{}_3C_{60}H - 2\ Bu^t + H]^+$, 721 $[Bu^t{}_3C_{60}H - 3\ Bu^t]^+$.

<u>Fraction P4.</u> EAS ($CH_2Cl_2$, $\lambda_{max}$/nm): 325, 340, 388, 450, 500, 625, 654, 687, 720. $^1H$ NMR ($CDCl_3$), δ: 2.06 (s, 9 H, $Bu^t$); 2.07 (s, 9 H, $Bu^t$); 6.48 (s, 1 H, $C_{60}H$); 6.61 (s, 1 H, $C_{60}H$). MALDI MS (DCTB (–), *m/z*): 836 $[\underline{Bu}^t{}_2\underline{C}_{60}\underline{H}_2]^-$. MALDI MS (DCTB (+), *m/z*): 836 $[\underline{Bu}^t{}_2\underline{C}_{60}\underline{H}_2]^+$.

<u>Fraction P5.</u> EAS ($CH_2Cl_2$, $\lambda_{max}$/nm): 255, 325, 450, 530, 610, 685. $^1H$ NMR ($CDCl_3$), δ: 1.73 (s, 9 H, $Bu^t$); 1.76 (s, 9 H, $Bu^t$); 5.83 (s, 1 H, $C_{60}H$); 5.98 (s, 1 H, $C_{60}H$). MALDI MS (DCTB (–), *m/z*): 836 $[\underline{Bu}^t{}_2\underline{C}_{60}\underline{H}_2]^-$, 777 $[Bu^t{}_2C_{60}H_2 - Bu^t - 2\ H]^-$, 720 $[Bu^t{}_2C_{60}H_2 - 2\ Bu^t - 2\ H]^-$. MALDI MS (DCTB (+), *m/z*): 836 $[\underline{Bu}^t{}_2\underline{C}_{60}\underline{H}_2]^+$, 779 $[Bu^t{}_2C_{60}H_2 - Bu^t]^+$, 720 $[Bu^t{}_2C_{60}H_2 - 2\ Bu^t - 2\ H]^+$.

<u>Fraction P6.</u> EAS ($CH_2Cl_2$, $\lambda_{max}$/nm): 325, 450, 520, 615, 685. $^1H$ NMR ($CDCl_3$), δ: 1.79 (s, 18 H, 2 equiv. of $Bu^t$); 6.09 (s, 2 equiv. of fullerene protons). MALDI MS (DCTB (–), *m/z*): 836 $[\underline{Bu}^t{}_2\underline{C}_{60}\underline{H}_2]^-$. MALDI MS (DCTB (+), *m/z*): 836 $[\underline{Bu}^t{}_2\underline{C}_{60}\underline{H}_2]^+$.

<u>Fraction P7.</u> EAS (hexane, $\lambda_{max}$/nm): 213, 248, 257, 308, 326, 408, 425, 464, 484, 640. $^1H$ NMR ($CDCl_3$), δ: 2.09 (s, 9 H, $Bu^t$); 6.67 (s, 1 H, $C_{60}H$). MALDI MS (DCTB (–), *m/z*): 778 $[\underline{Bu}^t\underline{C}_{60}\underline{H}]^-$. MALDI MS (DCTB (+), *m/z*): 778 $[\underline{Bu}^t\underline{C}_{60}H]^+$.

<u>Fraction P8.</u> EAS ($CH_2Cl_2$, $\lambda_{max}$/nm): 325, 373, 404, 430, 500, 530, 615, 680, 930. $^1H$ NMR ($CDCl_3$), δ: 1.83 (s, 9 H, $Bu^t$); 1.93 (s, 9 H, $Bu^t$); 5.60 (s, 1 H, $C_{60}\underline{H}$); 6.02 (s, 1 H, $C_{60}\underline{H}$). MALDI MS (DCTB (–), *m/z*): 777 $[\underline{Bu}^t{}_2\underline{C}_{60}\underline{H}_2 - Bu^t - 2\ H]^-$, 720 $[Bu^t{}_2C_{60}H_2 - 2\ Bu^t - 2\ H]^-$. MALDI MS (DCTB (+), *m/z*): 836 $[\underline{Bu}^t{}_2\underline{C}_{60}\underline{H}_2]^+$, 720 $[Bu^t{}_2C_{60}H_2 - 2\ Bu^t - 2\ H]^+$.

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