Preparation and study of hydrides of fullerenes C_{60} and C_{70}

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Fullerene hydrides were prepared by hydrogenation of fullerenes C_{60} and C_{70} using proton transfer from 9,10-dihydroanthracene to fullerene and were studied by mass spectrometry (electron impact, field desorption), IR, UV, and ^1H and ^{13}C NMR spectroscopy. The main product of the hydrogenation of C_{60} is $C_{60}H_{36}$, which is sufficiently stable. Hydrogenation of fullerene C_{70} gives a series of polyhydrides $C_{70}H_n$ (n = 36—46), and the main product is $C_{70}H_{36}$. The dehydrogenation of $C_{60}H_{36}$ by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone is not quantitative and results in the formation of fullerene derivatives along with C_{60}. The comparison of the IR and ^1H and ^{13}C NMR spectral data for solid $C_{60}H_{36}$ with the theoretical calculations suggests that the fullerene hydride has a *T*-symmetric structure and contains four isolated benzenoid rings located at tetrahedral positions on the surface of the closed skeleton of the molecule.

Key words: fullerene, C_{60}, C_{70}, fullerene hydrides, $C_{60}H_{36}$, $C_{60}H_{18}$, $C_{70}H_{36}$; mass spectrometry, IR spectroscopy, UV spectroscopy, ^1H and ^{13}C NMR.

Interest in fullerene hydrides (FH) with high content of hydrogen stems from the possibility of using them as materials for the development of hydrogen accumulators. Presently, FH of the composition $C_{60}H_x$ (x = 2, 4, 18, 32, 36, 36—50, 42—44) and $C_{70}H_x$ (x = 2, 4, 12, 34—36, 36—38, 36—44)[1—15] are known. Fullerene hydrides with a low (x = 2 and 4) hydrogen content were isolated as individual compounds and studied in detail, while the synthesis of higher FH results in the formation of mixtures of hydrides of different compositions. Therefore, the search for the methods of preparation and isolation of individual FH with high hydrogen content, especially $C_{60}H_{36}$ and $C_{70}H_{36}$, whose stability was theoretically predicted, is being carried out. The structure of these compounds has not been yet established. In theoretical works, the structures of four $C_{60}H_{36}$ isomers with the symmetry T, T_h, D_{3d} and S_6 were considered. The structure with the T symmetry contains four isolated benzenoid rings located in the tetrahedral positions on the surface of the closed skeleton of the molecule. The structure of the T_h symmetry contains 12 isolated double bonds in five-membered rings. Fullerene hydrides with the structures of the D_{3d} and S_6 symmetry have one benzenoid ring at each pole of the molecule and isolated double bonds along and parallel (D_{3d}) as well as perpendicular (S_6) to the equator of the molecule. According to the calculations, the $C_{60}H_{36}$ structure with the T symmetry is the most stable. For $C_{70}H_{36}$, three isomers of aromatic character have been considered in which two phenanthrenoid rings and one benzenoid ring (two isomers) or one phenanthrenoid ring and two naphthalenoid rings are arranged along the equator of the molecule.[16—18]

$C_{60}H_{36}$ and $C_{60}H_{18}$ were observed for the first time by electron impact (EI) mass spectrometry in the products of the Birch reduction[1] of C_{60}. More detailed studies using different methods of mass spectral analysis showed[2] that the Birch reduction gives a mixture of polyhydrofullerenes $C_{60}H_{18}$—$C_{60}H_{36}$, the main components being $C_{60}H_{30}$ and $C_{60}H_{32}$.

The hydrogenation of C_{60} using the hydrogen transfer from 9,10-dihydroanthracene (DHA) to fullerene results in the formation of $C_{60}H_{18}$ or $C_{60}H_{36}$ depending on the experimental conditions,[3] while the reaction of fullerenes C_{60} and C_{70} with DHA in the presence of [7]benzanthrene as the catalyst gives a mixture of hydrides $C_{60}H_x$ (x = 0—36, 42—44) and $C_{70}H_x$ (x = 0—36).[4]

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The composition of a mixture of FH obtained on a 5% Ru/C catalyst depends on the temperature and hydrogen pressure: $C_{60}H_{18}$, $C_{60}H_{36-50}$ (p = 110—160 atm, T = 100—280 °C),[5,6] and $C_{70}H_{34-38}$ (p = 2—100 atm, T = 100—180 °C).[7]

The reduction of fullerenes C_{60} and C_{70} as solutions in benzene or toluene with a Zn—HCl (conc.) system results in the formation of $C_{60}H_{36-40}$ and $C_{70}H_{36-38}$. When DCl is used, fullerene deuterides with a higher maximum content of hydrogen $C_{60}D_{44}$ and $C_{70}D_{48}$ are obtained.[8]

The dehydrogenation of FH is poorly studied. Quantitative data on the composition of the products of this reaction are absent. According to the results of mass spectral analysis, C_{60} was observed in the products of the reaction of $C_{60}H_{36}$ with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), which indicates that the hydrogenation reaction is reversible.[1,3]

Thus, hydrogenation of fullerenes by several methods results in the formation of a mixture of FH of different composition, and the results of quantitative analysis of these mixtures often depend on the methods used. Several variants of spectroscopic characteristics (IR, UV, and NMR) of FH are published,[1,3,8] which are also evidence that hydrides differing in composition and isomerism are obtained. In the present work, hydrides of fullerenes C_{60} and C_{70} were synthesized using the hydrogen transfer from 9,10-dihydroanthracene to fullerene. The results of their study by mass spectrometry (electron impact and field desorption), IR and UV spectroscopy, and ^1H and ^{13}C NMR are presented. The experimental and calculated data for different isomers of $C_{60}H_{36}$ are compared.

Results and Discussion

Mass spectra of hydrogenated fullerenes. a. Derivatives of fullerene C_{60}. The results of the study of the products of the reaction of C_{60} with DHA by electron impact (EI) and field desorption (FD) mass spectrometry are presented in Figs. 1 and 2: immediately after the reaction (see Figs. 1, *a* and 2, *a*), 3 months after storage of the hydride in air (see Fig. 1, *b*), and after heating of the hydride at 300 °C for 3 h (see Figs. 1, *c* and 2, *b*).

In the EI mass spectrum of the freshly prepared sample (see Fig. 1, *a*), a peak with m/z 756 corresponding to $C_{60}H_{36}$ is the most abundant. The ratio of the experimental intensities of peaks of ions [m/z (I_{rel} (%)): 756 (100), 757 (55), 758 (18), 759 (4.5), 760 (0.8)] agrees well with the calculated isotopic spectrum of the $C_{60}H_{36}$ ion: 756 (100), 757 (67.8), 758 (22.6), 759 (4.9), 760 (0.8). This indicates to the absence of hydrides with more than 36 hydrogen atoms. The presence of the peaks of ions with a lower content of hydrogen (m/z 721—755) and of the initial C_{60} (m/z 720) in the spectrum can be explained by a partial thermal decomposition of FH during evaporation and by fragmentation of the molecular ion $C_{60}H_{36}$ with the hydrogen loss upon EI. This is confirmed by the mass spectra of the sample after long storage in air (see Fig. 1, *b*) and of the sample heated for 3 h at 300 °C (see Fig. 1, *c*). In both cases, the intensities of the peaks of ions with m/z 720 (C_{60}) and 738 ($C_{60}H_{18}$) increase, which is evidence of a partial decomposition of $C_{60}H_{36}$ to form the second stable hydride $C_{60}H_{18}$ and the initial C_{60} during storage and upon heating of FH. The presence of the peak of the initial C_{60}

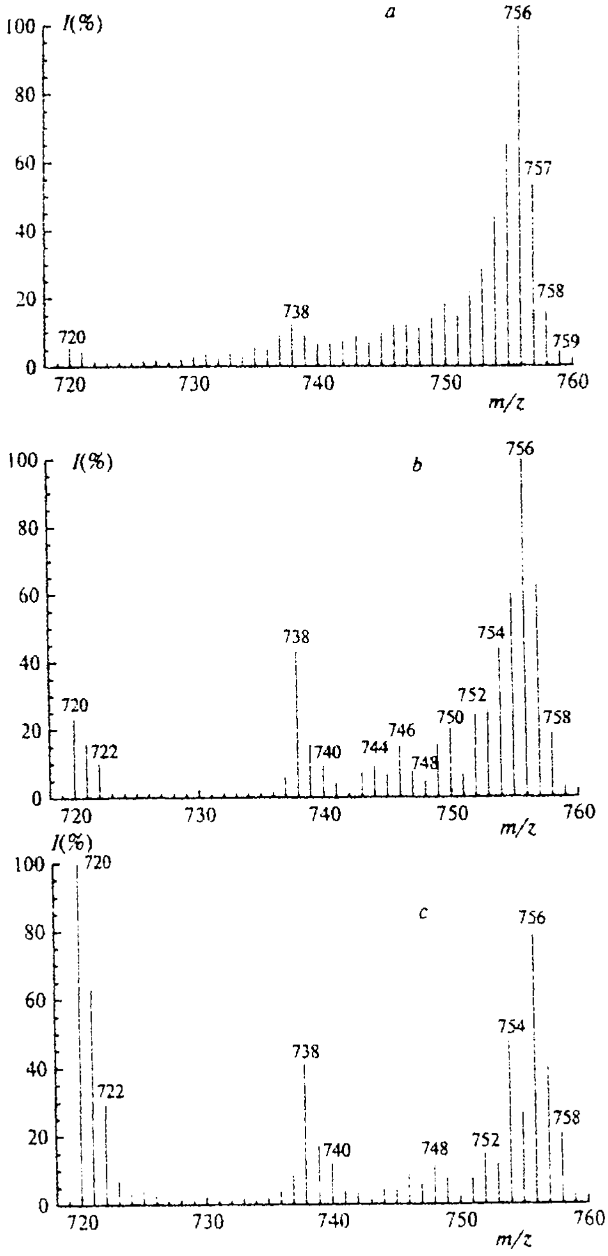

Fig. 1. Mass spectra (EI) of products of hydrogenation of C_{60} by DHA for 20—30 min recorded: *a*, immediately after the reaction; *b*, 3 months after storage of the hydride in air; *c*, after heating hydride at 300 °C for 3 h.

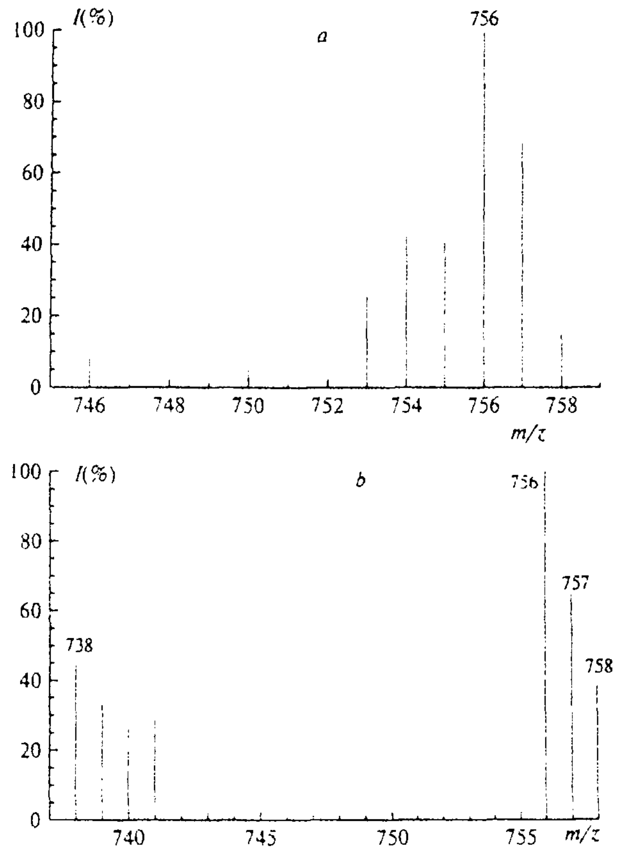

Fig. 2. Mass spectra (FD) of products of hydrogenation of C_{60} by DHA for 20—30 min recorded: *a*, immediately after the reaction; *b*, after heating hydride at 300 °C for 3 h.

in the EI mass spectra (see Fig. 1) indicates that the addition of hydrogen to fullerene is reversible. The EI mass spectra also exhibit abundant peaks of ions with *m/z* 378, 378.5, and 379 (not shown in Fig. 1), which are assigned to double charged ions of FH, indicating a rather stable skeleton of the $C_{60}H_{36}$ molecule.

Since the degree of fragmentation of the molecular ion in FD is substantially lower than that in EI, FD mass spectra of the products of the reaction of C_{60} with DHA were recorded immediately after the reaction (see Fig. 2, *a*) and after heating of the hydride at 300 °C for 3 h (see Fig. 2, *b*). In the spectrum of the freshly prepared sample (see Fig. 2, *a*), the peak of the $C_{60}H_{36}$ ion (*m/z* 756) is the most abundant, and the number of the fragments with a lower hydrogen content (*m/z* 753—755) and their intensity are substantially smaller than those in the EI spectra. The comparison of the experimental intensities of the peaks of ions [*m/z* (I_{rel} (%)): 756 (100), 757 (69) and 758 (16)] with the calculated isotopic spectrum of the $C_{60}H_{36}$ ion (see above) shows good coincidence, which is evidence of the absence of hydrides with more than 36 hydrogen atoms. The FD mass spectrum contains no peaks of ions with *m/z* 738 ($C_{60}H_{18}$) or of the initial fullerene with *m/z* 720, unlike the EI mass spectrum (see Fig. 1, *a*) of this sample that contains these peaks. The FD mass spectrum of the sample heated for 3 h at 300 °C (see Fig. 2, *b*) contains two main peaks with *m/z* 756 ($C_{60}H_{36}$) and 738 ($C_{60}H_{18}$), and peaks of ions with *m/z* 720 (C_{60}), 753 ($C_{60}H_{33}$), 754 ($C_{60}H_{34}$), and 755 ($C_{60}H_{35}$) are absent. It thus follows that $C_{60}H_{18}$ is the primary product of the thermal decomposition of $C_{60}H_{36}$, and lower hydrides $C_{60}H_n$ (n = 33—35) are considerably less stable than $C_{60}H_{36}$.

The FD mass spectra of $C_{60}H_{36}$ obtained after the first sublimation (see Experimental) contain the peaks of ions with *m/z* 928, 930, 934, and 935 corresponding to the products of the addition of the 9-hydroanthryl radical $C_{14}H_{11}{}^{\cdot}$ (*m/z* 179) to FH. The mechanism of hydrogenation involving DHA includes the first stage of the transfer of an H atom to fullerene and the formation of the $C_{14}H_{11}{}^{\cdot}$ radical (see Ref. 19) that can add to C_{60} yielding adducts of the composition $C_{60}H_{36}-C_{14}H_{11}{}^{\cdot}$ (935) and $C_{60}H_{35}-C_{14}H_{11}{}^{\cdot}$ (934). The latter are thermally unstable and decompose at $T \approx 300$ °C during the second sublimation of FH.

It can be concluded from the comparison of the EI and FD mass spectra that $C_{60}H_{36}$ is the main product of the reaction of C_{60} with DHA. Our data do not give an unambigous answer on whether the reaction product contains a hydride of the composition $C_{60}H_{34}$ or this results from fragmentation or thermal decomposition of $C_{60}H_{36}$ during mass spectrometric analysis. The appearance of the peaks of ions $C_{60}H_{18}$ and C_{60} in the EI mass spectra (see Fig. 1, *a*) can be explained by partial decomposition of FH during evaporation and by fragmentation of the molecular ion $C_{60}H_{36}$. A sharp increase in the peak of the ion C_{60} in the EI mass spectrum (see Fig. 1, *c*) shows that $C_{60}H_{18}$ is less stable to EI than $C_{60}H_{36}$. Thus, FD mass spectra are more reliable for the determination of the composition of FH.

The FD mass spectrum of the products of the hydrogenation of C_{60} by DHA after heating the reaction mixture for more than 12 h is presented in Fig. 3. It can be seen that $C_{60}H_{18}$ is the main reaction product. The comparison of the experimental intensities of the peaks of ions [*m/z* (I_{rel} (%)): 738 (100), 739 (64), 740 (33), 741 (29), 742 (8)] with the calculated data [738 (100), 739 (67.9), 740 (22.4), 741 (4.9), 742 (0.8)] shows that the intensities of the peaks of ions with *m/z* 740—742 are greater than the calculated values. This testifies to the presence of hydrides $C_{60}H_{20}$ and $C_{60}H_{22}$ (10 and 3%, respectively). A group of the peaks in the range of *m/z* 690—713 and two groups with *m/z* 916 and 929 are also observed in the spectrum. The first group can be assigned to the products of condensation of four anthracene molecules or of the intermediate product of the hydrogenation 9-hydroanthryl radical $C_{14}H_{11}{}^{\cdot}$. The second two groups can be assigned to the adducts of FH with anthracene or 9-hydroanthryl radical $C_{14}H_{11}{}^{\cdot}$. For example, an abundant peak of the ion with *m/z* 916 can

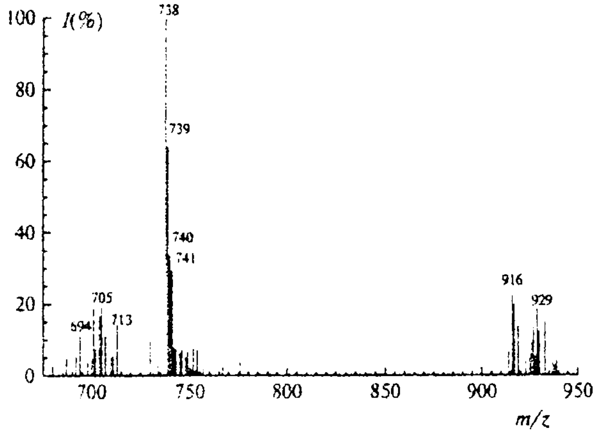

Fig. 3. Mass spectrum (FD) of products of hydrogenation of C_{60} by DHA for 12 h.

be considered as belonging to the adduct $C_{60}H_{18}{}^{\cdot}$—anthracene.

The EI mass spectrum of $C_{60}H_{18}$ contains two main peaks with m/z (I_{rel} (%)) 720 (100), and 738 (11), which indicates the instability of this FH toward EI.

b. Derivatives of fullerene C_{70}. It can be seen from the EI mass spectrum of $C_{70}H_{36}$ (Fig. 4, *a*) that $C_{70}H_{36}$ is unstable under these conditions and decomposes to the initial fullerene C_{70} and hydrides with a low content of hydrogen. The comparison of the experimental intensities of the peaks of ions [m/z (I_{rel} (%)): 840 (100), 841 (80), 842 (99), 843 (66), 844 (30), 845 (23), 846 (15)] with the calculated intensities of the isotopic peaks for C_{70} [840 (100), 841 (78.4), 842 (30.3), 843 (7.7), 844 (1.4), and 845 (0.2)] gave the following content of hydrides relative to C_{70}: $C_{70}H_2$ (69), $C_{70}H_4$ (8), $C_{70}H_6$ (11), and $C_{70}H_8$ (11). Hydrides with a high content of hydrogen are also present: $C_{70}H_{24}$ (6.9), $C_{70}H_{32}$ (7.3), $C_{70}H_{36}$ (1.7), and $C_{70}H_{38}$ (3.6) (in a lesser amount), and $C_{70}H_{36}$ is less stable under these conditions. The degree of dehydrogenation of $C_{70}H_{36}$ in EI is higher than that of $C_{60}H_{36}$, which indicates its lower stability.

It can be seen from the FD mass spectrum of the product of the reaction of C_{70} with DHA (see Fig. 4, *b*) that it is a mixture of hydrides $C_{70}H_{36}$ (100), $C_{70}H_{38}$ (40), $C_{70}H_{40}$ (8), $C_{70}H_{44}$ (27), and $C_{70}H_{46}$ (30), the major one being $C_{70}H_{36}$. The formation of fullerene polyhydrides was also observed in the hydrogenation of C_{70} in a Zn—HCl (conc.) system (see Ref. 8) and in the catalytic hydrogenation.[5,6]

The mass spectrum (see Fig. 4, *b*) contains intense peaks of ions with m/z 889, 891, 896, 940, and 968, which can be assigned to the products of the reactions of hydrides with oxygen or of the hydrogenation of oxidized C_{70}: $C_{70}H_{33}O$ (889), $C_{70}H_{35}O$ (891), $C_{70}H_{40}O$ (896), $C_{70}H_{36}O_4$ (940), and $C_{70}H_{48}O_5$ (968). The products of oxidation of FH in air have been previously observed in the mass spectra as well (see Ref. 8). The mass spectra contain no peaks of the ions with m/z > 1019 corresponding to the products of the addition of the anthryl radical (m/z 179) to the initial fullerene C_{70} or its hydrides.

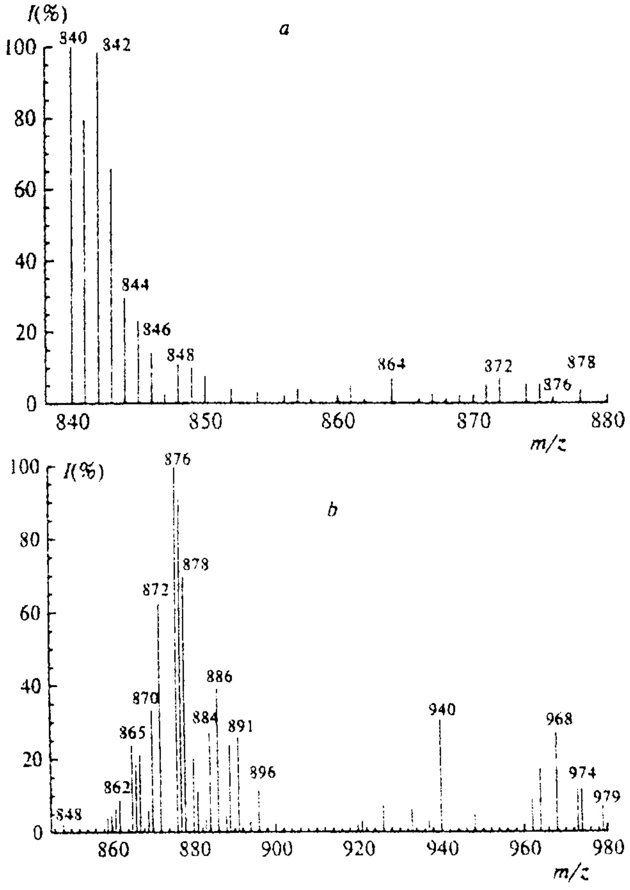

Fig. 4. Mass spectra of products of hydrogenation of C_{70} by DHA for 45 min: *a*, EI; *b*, FD.

^1H NMR spectrum of the solid sample and a solution of $C_{60}H_{36}$. The ^1H NMR spectrum of a solution of $C_{60}H_{36}$ in $CDCl_3$ (Fig. 5, *a*) is a group of signals in the region of 2.5—4.5 ppm with the maxima of the peaks at δ 2.97, 3.36, 3.80, 3.95, 4.05, and 4.43. The spectrum is similar in shape to those published previously,[8] but differs in positions of the maxima and their intensities. The most intense peak at δ 3.36 can be compared with the peak of protons (δ 3.38) in dodecahedrane ($C_{20}H_{20}$) containing 20 equivalent protons at 20 tertiary carbon atoms.[20] The unusual shape of the spectrum is due to both the existence of a mixture of the isomers and the instability of FH in solution, which results in the formation of new compounds during recording of the spectrum. The ^1H NMR spectrum of solid $C_{60}H_{36}$, which represents a broad signal with several peaks, is shown in Fig. 5, *b*. The sharp signals at δ 6.55 and 3.04 can be assigned to two nonequivalent groups of protons of FH: 24 protons with the sp^2-hybridized C atoms in the nearest surrounding and the remaining 12 protons without this surrounding. This agrees with the theoretical calculations,[16,17] according to which the $C_{60}H_{36}$ structure with the T and T_h symmetry contains two types of equivalent H atoms: 24 H atoms have C atoms with the sp^2-hybridization and 12 H atoms have the sp^3-hybridized C atoms in the nearest surrounding. The third broad signal at 1.3 ppm cannot be explained in terms of these concepts. Our calculations of the theoretical ^{1}H NMR spectra of $C_{60}H_{36}$ with the T and T_h symmetry (program ACD/Labs., Ver. 2.0.) showed that these spectra contained three groups of peaks, which agrees well with the experimental spectrum (see Fig. 5, *b*). The signals at −1.9 and 15 ppm are side signals that appear when the sample is rotated at a magic angle due to incomplete averaging of the anisotropy tensor of the chemical shift if the rotation rate of the sample is insufficient.

^{13}C NMR spectrum of solid $C_{60}H_{36}$. The ^{13}C NMR spectrum of the solid sample of $C_{60}H_{36}$ (Fig. 6) contains at least three resolved signals assigned to three types of the C atoms with the sp^3-hybridization (δ 31.1, 37.2, and 44.1) and three signals assigned to three types of the C atoms with the sp^2-hybridization (δ 124.9, 134.7, and 137.3). The ratio of the integral intensities of these peaks gives a ratio of the sp^3- and sp^2-C atoms equal to 36 : 24, which corresponds to the $C_{60}H_{36}$ composition. The calculated chemical shifts of ^{13}C NMR for the $C_{60}H_{36}$ isomers are the following:[21] for the isomer with the T symmetry (δ, relative to SiMe$_4$ (*I*)), 25.7 (12), 37.1 (12), 43.8 (12), 132.5 (12), and 136.5 (12); for T_h, 27.6 (12), 39.7 (12), and 129.6 (24); for D_{3d}, 28.5 (6), 35.3 (6), 36.1 (12), 37.9 (12), 135.1 (12), and 148.8 (12); for S_6, 30.3 (6), 33.7 (6), 34.2 (6), 36.2 (6), 37.6 (6), 39.2 (6), 127.8 (6), 134.9 (6), 142.7 (6), and 142.8 (6). The spectrum of the $C_{60}H_{36}$ isomer with the T symmetry is the closest to the experimental one: it contains the same number of peaks and the chemical shifts for the sp^3-hybridized C atoms almost coincide, and for the sp^2-hybridized C atoms, the differences (2.6 and 4 ppm) between the chemical shifts of the benzenoid C atoms are close (δ 134.7 and 137.3 (experiment) and δ 132.5 (12), 136.5 (12) (calculation)). There probably are admixtures of other isomers as well, for example, a peak at δ 124.9 and the partially resolved peak at δ 46.7 (shoulder), which correspond to the isomer with the D_{3d}' symmetry (see Ref. 21). Thus, the comparison of the experimental ^{1}H and ^{13}C NMR spectra of solid $C_{60}H_{36}$ with the theoretical ones suggests that $C_{60}H_{36}$ has a structure with the T symmetry containing four isolated benzenoid rings localized at the tetrahedral positions on the surface of the closed skeleton of the molecule. This hypothesis should be experimentally checked, for example, by chemical reactions or η^6-coordination of $C_{60}H_{36}$ with metal complexes.

IR spectra of hydrogenated fullerenes. The IR spectra of FH contain three absorption bands (AB) each in the region of 3100—2700 cm^{-1} (Fig. 7). These AB of high intensity are assigned to C—H stretching vibrations, and the intensity of the bands for $C_{60}H_{18}$ is lower than that for $C_{60}H_{36}$ and $C_{70}H_{36}$. It follows from the spectra that the FH have three types of sp^3-hybridized C atoms with the C—H bond, which agrees with the ^{13}C NMR spectral data and additionally favors the structure with the T symmetry for $C_{60}H_{36}$. Since the symmetry of the initial fullerene changed, the vibrational modes were split into numerous vibrations: sets of low-intensity bands appeared in the region of stretching C—C, bending, and skeletal C—C—C vibrations. The spectra of $C_{60}H_{36}$, $C_{70}H_{36}$, and $C_{60}H_{18}$ contain AB of

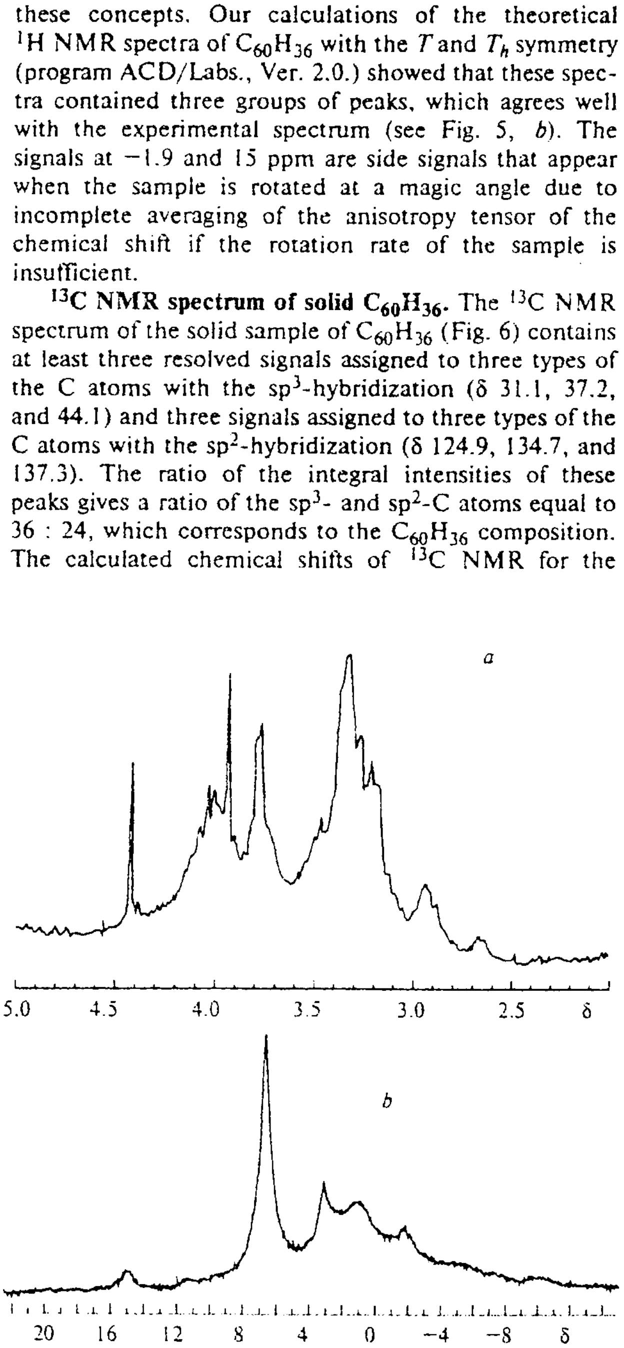

Fig. 5. ^{1}H NMR spectrum of $C_{60}H_{36}$: *a*, solution in CDCl$_3$ (250 MHz, 25 °C, SiMe$_4$ as the internal standard); *b*, solid sample (300 MHz, 25 °C, SiMe$_4$ as the internal standard).

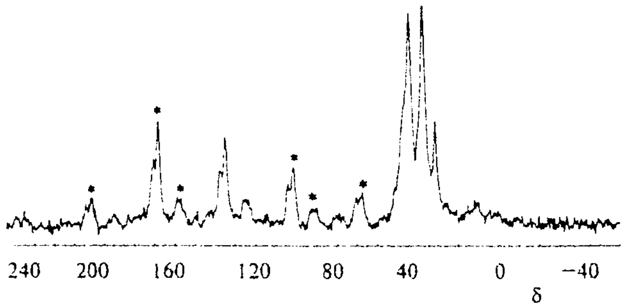

Fig. 6. ^{13}C NMR of solid $C_{60}H_{36}$ (300 MHz, 25 °C, SiMe$_4$ as the internal standard). Asterisk designates side signals that appeared during rotation of the sample due to incomplete averaging of the anisotropy tensor of the chemical shift.

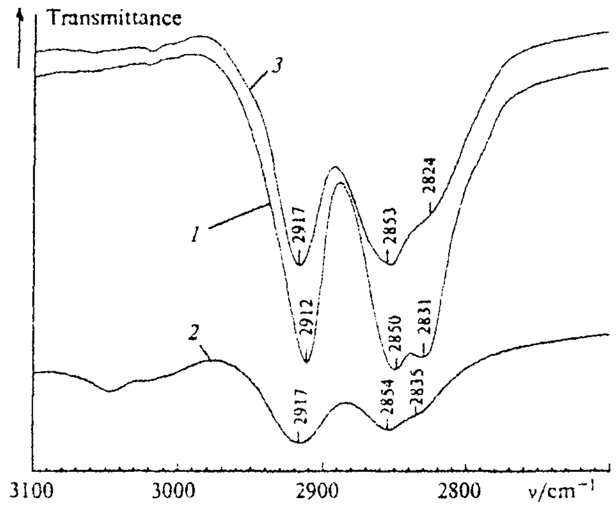

Fig. 7. IR spectra of fullerene hydrides $C_{60}H_{36}$ (*1*), $C_{60}H_{18}$ (*2*), and $C_{70}H_{36}$ (*3*).

medium intensity of the stretching C=C vibrations at 1492, 1452, and 1438 cm^{-1} and AB of the bending C—H vibrations at 729, 729, and 735 cm^{-1}, respectively.

UV spectra of hydrogenated fullerenes. Fullerene hydrides $C_{60}H_{36}$ and $C_{70}H_{36}$ are well soluble in carbon disulfide and trichloroethylene and are little soluble in cyclohexane, toluene, $CHCl_3$, and CH_2Cl_2. The initially transparent solutions become turbid with time (in air and in an inert atmosphere) and form precipitates that cannot be entirely dissolved in CS_2. The spectrum of a saturated solution of $C_{60}H_{36}$ in cyclohexane (Fig. 8) contains absorption bands at 212 (max), 222 (sh), 241 (max), and 250 (sh) nm.

Dehydrogenation of $C_{60}H_{36}$. A brown solution and a precipitate are formed upon the dehydrogenation of $C_{60}H_{36}$ by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in toluene. The spectrum of the toluene solution in the visible region contains AB at 336, 405, 434, and 595 nm, broad AB at 455—575 nm, and, behind the absorption region of C_{60}, AB with a flattened maximum at 700—750 nm. This spectrum corresponds to a mixture of pure C_{60} (λ = 336, 405, and 595 nm), fullerene derivatives (λ = 434, 455—575 nm) (see, *e.g.*, Ref. 22), and complexes of fullerenes with the donor molecules (λ = 700—750 nm).[23,24] In our case, the π-donor-acceptor type interaction can occur between C_{60} and the product of hydrogenation of DDQ, 2,3-dichloro-5,6-dicyano-1,4-dihydrobenzoquinone (H_2DDQ), followed by the formation of molecular complexes when the solution is concentrated. Extraction by hexane and a hexane—toluene mixture from the precipitate obtained upon concentration of the toluene solution results in a very slow isolation of C_{60}. The IR spectrum of the precipitate consists of AB at 1425, 1183, 578, and 528 cm^{-1} of the vibrational modes of C_{60} (initial C_{60}: 1429, 1183, 576, and 528 cm^{-1}) and AB at 2253, 2230, 1453, 1377, 1335, 1276, 1207, 1082, 1001, 946, 919, 888, 795, 775, 743, 740, and 699 cm^{-1} of H_2DDQ incorporated in the complex (individual H_2DDQ: 2255, 1575, 1453, 1362, 1277, 1194, 1076, 887, 776, 746, 689, 623 cm^{-1}). The shift of AB of C_{60} and redistribution of the intensities, and the shift and splitting of AB of H_2DDQ are evidence of the formation of a C_{60}—H_2DDQ molecular complex in which the interaction of π-electrons of the components and, likely, distortion of the initial configuration of H_2DDQ occur. Rather stable molecular complexes of C_{60} and C_{70} with hydroquinone are known.[25,26]

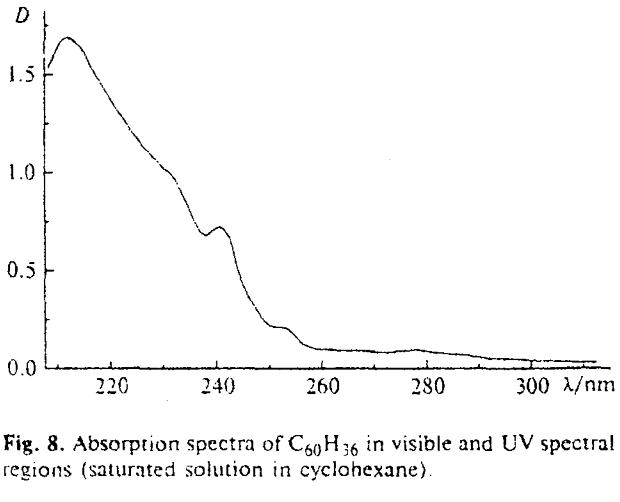

Fig. 8. Absorption spectra of $C_{60}H_{36}$ in visible and UV spectral regions (saturated solution in cyclohexane).

The FD mass spectra (the emitter current is 25 mA) of the toluene solution and toluene extract of the precipitate contain three groups of peaks of ions with *m/z* 224—241, 720—728, and 880—980. The first group is related to the presence of H_2DDQ, the second group to C_{60} and hydrides containing 2—8 H atoms, and the third group to fullerene derivatives containing H atoms, an H_2DDQ molecule, or a fragment of an H_2DDQ molecule.

Thus, the dehydrogenation of $C_{60}H_{36}$ under the action of DDQ is not quantitative (according to our estimations based on the spectrophotometric analysis data, the yield of C_{60} is less than 50%), because side reactions occur along with the dehydrogenation reaction. The products of the dehydrogenation are C_{60} and H_2DDQ. They give rather stable molecular complexes as the solvent is evaporated. Other products are formed due to the chemical interaction of FH in the FH—C_{60}—DDQ—H_2DDQ system. The nature of the latter is presently under study.

Experimental

The starting fullerenes C_{60} (99.5%) and C_{70} (≥99.0 %) (from the data of UV spectroscopy and HPLC) were obtained by a known procedure.[27]

Dihydroanthracene (Reakhim) was additionally purified by double sublimation. The final product contained 99% of the main substance and 1% of anthracene (from the spectrophotometric analysis data). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (Fluka) was used without additional purification. Toluene, cyclohexane, and carbon disulfide were purified by known procedures and prior were distilled in an atmosphere of Ar prior to use.

Fullerenes were hydrogenated by DHA in glass evacuated tubes. The typical experimental procedure is the following: fullerene C_{60} (100 mg, $1.39 \cdot 10^{-4}$ mol) and DHA (2.5—3.0 g, 100—120-fold excess) were placed in an tube that was then evacuated to a residual pressure of 10^{-3} Torr. Then the tube was filled with argon to a pressure of 300—400 Torr and sealed. The tube was placed in an air thermostat at 350±5 °C. The hydrogenation of C_{60} to $C_{60}H_{36}$ was performed for 20—30 min: the initial melt (a solution of C_{60} in a DHA melt) was violet and changed its color with time to reddish-brown, bright-red, orange, and yellow, and the final product was pale yellow. The reaction mixture was cooled to room temperature, and non-consumed DHA, anthracene, and other reaction products were sublimed *in vacuo* at 100—120 °C for 8—10 h. The yield of the amorphous product (**1**) obtained after sublimation was 2—5% greater (in different experiments) than the theoretical one calculated per $C_{60}H_{36}$. After short (10 min) sublimation of this product at 300 °C, the yield of fullerene hydride was 98%. Found (%): C, 95.0; H, 5.1. $C_{60}H_{36}$. Calculated (%): C, 95.2; H, 4.8. IR (pellet with KBr), ν/cm^{-1}: 2912, 2850, 2831, 1492, 1448, 1422, 1333, 1317, 1240, 1180, 1156, 939, 922, 816, 791, 776, 746, 729, 668, 503, 483. The absorption spectrum of **1** (cyclohexane), λ/nm: 212, 231, 241, 252, 273, 286, 296, 308, 323, 339, 356, 375, 388. The absorption spectrum of the product of the second sublimation (λ/nm: 231, 252, 273, 286, 296, 308, 323, 339, 356, 375, 388) is close to the spectrum of anthracene (251.5, 308, 323, 338, 354.5, 374.5) (see Ref. 28), but differs in the ratio of intensities and in the presence of additional AB at 231, 273, 286, 296, and 388 nm. The spectrum of fullerene hydride after the second sublimation, presented in Fig. 8, is the difference between the spectrum of the initial product (**1**) and the product of the second sublimation. The FD mass spectra of this second product contained intense peaks of ions with *m/z* 178, 179, 180, 356, 358, 360, 534, 539, and 547, which can be assigned to anthracene, DHA, and products of condensation of 2—3 anthracene molecules or a dimer of the 9-hydroanthryl radical $C_{14}H_{11}{}^{\cdot}$, which is an intermediate species of the hydrogenation reaction.

Hydrogenation of C_{60} to $C_{60}H_{18}$ was performed similarly to the procedure presented above; the reaction time was 10—20 h, and the final product was brown. The reaction products (FH, excess DHA, anthracene formed, *etc.*) were separated by sublimation *in vacuo* at 100—120 °C for 8—10 h. The yield of the amorphous product (**2**) obtained after sublimation under these conditions was 1.5—2 times greater (in different experiments) than the theoretical one calculated per $C_{60}H_{18}$. The yield of FH after the second sublimation (250 °C, 8 h) was less than 80%. IR of **2** (pellet with KBr), ν/cm^{-1}: 3046, 2917, 2854, 2835, 1502, 1438, 1272, 1152, 1015, 951, 735, 468.

Fullerene C_{70} was hydrogenated similarly to the procedure of preparation of $C_{60}H_{36}$, but the reaction time was ~1.5-fold longer. IR (pellet with KBr), ν/cm^{-1}: 2917, 2853, 2824, 1452, 1282, 1116, 1039, 950, 746, 729, 468.

Dehydrogenation of $C_{60}H_{36}$ was performed as follows: an 18—19-fold excess of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was added to a suspension of $C_{60}H_{36}$ in toluene, and the mixture was refluxed for 8 h in an atmosphere of Ar. The initial bright-red solution was decolorized with time and became brown. A brown precipitate was formed. After cooling to room temperature, the precipitate and solution were separated by filtration. The IR spectrum of the precipitate corresponds to pure H_2DDQ. AB of DDQ were absent in the IR spectrum of the precipitate obtained when the toluene solution was concentrated.

Mass spectra were recorded on a Varian MAT-731 mass spectrometer with double focusing of a resolution of ~2000. In the case of FD, samples were dissolved in toluene or CS_2 and applied onto the emitter followed by evaporation of excess solvent. The analysis was performed by consecutive scans of the mass spectrum with a gradual increase in the heating current of the emitter. Emitters were activated on a special setup by growing carbon nibs by the Beckey method.[29] In the case of electron impact analysis, a substance was placed in a golden crucible, and consecutive scans of the mass spectrum were performed as the temperature of the crucible increased (energy of ionizing electrons 70 eV, temperature of evaporation of the sample 350—420 °C).

^{13}C NMR spectra of solid samples were recorded on a Bruker MSL-300 instrument with rotation at a magic angle with a rate of 3 kHz in a 7-mm rotor (100 mg of $C_{60}H_{36}$), polarization transfer from ^{1}H to ^{13}C, contact time 1 μs, length of the 90°-pulse 6 μs, time of repeating experiments 3 s, and time of the signal acquisition 35 μs with 6000 scans. ^{1}H NMR spectra in the liquid phase were recorded on a Bruker instrument (250 MHz, $CDCl_3$) using $SiMe_4$ as the internal standard.

IR spectra were recorded on a Perkin—Elmer 1600 IR spectrophotometer, resolution 2 cm^{-1}, pellets with KBr.

Electronic absorption spectra were recorded on a Specord M-40 spectrophotometer (resolution 1 nm) with reference cells filled with the corresponding solvent (l = 1.0 cm).

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