Reduction of C_{60} and C_{70} by primary amines: optical and ESR studies

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Radical anions C_{70}^- and C_{70}^{2-} were obtained *in vacuo* by the reaction of 1-amino-3-propanol (AP) and 1,5-diaminopentane (DAP) with fullerene C_{70}. The radical anions were identified by visible/near IR (λ = 1372 and 1172 nm, respectively) and ESR spectroscopies. The temperature dependences of the ESR spectra were studied for the C_{60}—AP, C_{70}—AP, and C_{70}—DAP systems. At low temperatures (15—45 K), the ESR spectrum for C_{60}^- is close to that for species with axial symmetry of the g-factor ($g_\parallel$ = 2.000 and $g_\perp$ = 1.995). The anisotropy of the g-factor is averaged, when the temperature increases. At $T > 148$ K the averaged line is broadened, and the sharp signal with $g = 2.0001$ overlaps this broad line. The intensity of the narrow line increases, when the temperature increases. The ESR spectrum observed in the C_{70}—AP system at 12.5 K may be tentatively described as a superposition of two ESR spectra, namely, the ESR spectra of a radical with $g_\parallel$ = 2.0042 and $g_\perp$ = 2.0015 (presumably a radical cation) and of C_{70}^- with $g_\parallel$ = 2.000 and $g_\perp$ = 1.994. The spectra of the sample in which C_{70} is present mainly as C_{70}^{2-} exhibit only a line with g = 2.0004.

Key words: fullerene, C_{70}, C_{60}, anion; 1-amino-3-propanol, 1,5-diaminopentane; near IR; ESR spectra.

We have recently reported that 1-amino-3-propanol (AP) in an inert atmosphere reduces C_{60} fullerene to the C_{60}^- monoanion, which is characterized by the absorption spectra in the near IR range (λ = 1076 nm) and by the appearance of an ESR signal.[1,2] At the present time, several works that confirm the possibility of reducing C_{60} with various amines have been published.[3,4] For example, the reduction of C_{60} to a radical monoanion (λ = 1073 nm, the ESR signal with ΔH = 0.14 mT) with ternary amine, 1,8-diazabicyclo[5.4.0]undec-7-ene, in benzonitrile was studied.[3] The formation of the C_{60}^- anion was also observed in reductive quenching of the triplet state of fullerene by an electron donor, diazabicyclooctene, in an aqueous solution of the complex of C_{60} with γ-cyclodextrin, an aqueous micellar solution of Triton X-100, and aliphatic alcohols. The C_{60}^- anion was identified by the appearance of an absorption band (AB) at λ = 1080 nm.[4]

Only a few works are devoted to the preparation of C_{70} radical anions and their study by various methods, which can be explained by the fact that fullerene-70 is less easily accessible. The literature data on the reduction of C_{70} by various methods and the optical parameters of its anions are collected in Table 1. It is seen that the spectra of C_{70}^{n-} anions (n = 1—4) contain AB in the near IR range, and the position of the maximum for C_{70}^- is independent of the polarity of a solvent and the type of a counterion[5,6] and is the parameter inherent only in the C_{70}^- anion. Examples of the reduction of C_{70} by chemical reagents are scarce in the literature. In this work, the reduction of fullerene C_{70} by 1-amino-3-propanol (AP) and 1,5-diaminopentane (DAP) has been studied by optical and ESR spectroscopies, and the temperature dependences of the form of the line in the ESR spectrum have been studied for the C_{60}—AP, C_{70}—AP, and C_{70}—DAP systems.

Results and Discussion

Optical spectra of C_{70}—AP and C_{70}—DAP systems. The addition of crystalline C_{70} to a solution of AP or DAP *in vacuo* at room temperature results in slow dissolution of fullerene that is completed in 8—10 h, when the solution becomes brown. In the spectra of the solutions (Figs. 1 and 2) the absorption bands appear in UV, visible, and near IR ranges: two broad bands with smooth maxima at ~320 and ~405 nm (they are not shown in Figs. 1 and 2), a shoulder at 625 nm, a broad AB in the range of ~700—1000 nm, and bands at 1076* (1078), 1172 (1176), and 1372 (1370) nm. These spectra differ from those of C_{70} and pure amines, which testifies that new compounds are formed. The form of the spectra of the solutions obtained change slowly in time (see Figs. 1 and 2); the intensity of the peak at λ = 1372 (1370) nm at first increases, reaching a maximum, and

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* The values of λ_{max} in the spectrum of the C_{70}—AP system. The corresponding wavelengths for C_{70}—DAP are given in parentheses.

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Table 1. Data of optical spectroscopy in the visible and near IR ranges for anions of fullerene-70 obtained by various methods

Anion	Solvent (electrolyte)	*T*/K	Method of preparation	λ/nm	ε /L mol^{-1} cm^{-1}	Reference
C_{70}^-	Benzonitrile (0.1 *M* Bu_4NPF_6)	293	Electrochemical reduction	1368	4000	5
C_{70}^{2-}				670 1170	2600 7200	5
C_{70}^{3-}				670 1170	4600 5800	5
C_{70}^{4-}				670 1170	6000 3000	5
C_{70}^-	Ne matrix	5	Ne—I radiation	1363		6
C_{70}^-	Methylcyclohexane	77	γ-Radiation	1386		7
C_{70}^{2-}	Methyltetrahydrofurane	77	γ-Radiation	1377 1184		7
C_{70}^-	CH_2Cl_2 (0.05 *M* Bu_4NPF_6)	293	Electrochemical reduction		340 386 483	8
C_{70}^{2-}					609	8
C_{70}^-	AP DAP	293	Chemical reaction		1372 1370	*
C_{70}^{2-}	AP DAP				1172 1176	*

* Data of this work.

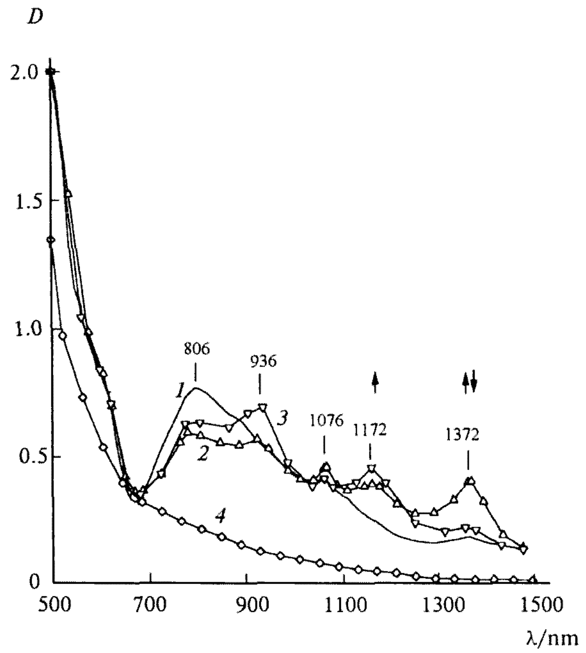

Fig. 1. Electronic absorption spectra in the visible and near IR ranges of the C_{70}—AP system *in vacuo* after 8 h (*1*), 6 days (*2*), and 21 days (*3*) from the beginning of the reaction and after exposure in air (*4*).

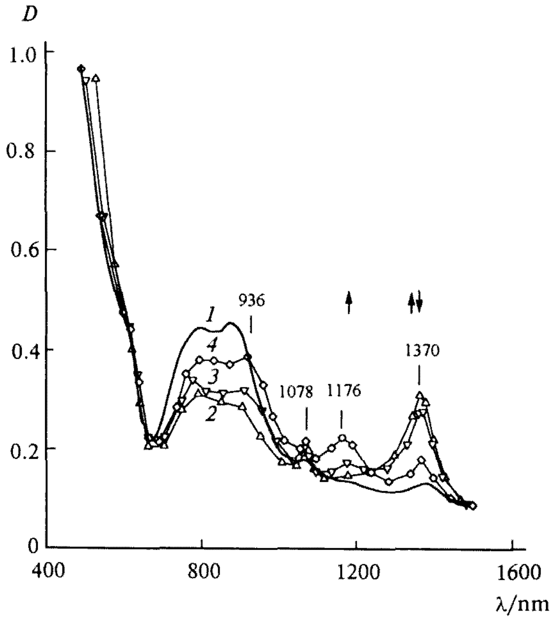

Fig. 2. Electronic absorption spectra in the visible and near IR ranges of the C_{70}—DAP system *in vacuo* after 8 h (*1*), 51 h (*2*), 8 days (*3*), and 24 days (*4*) from the beginning of the reaction.

then decreases. The intensity of the peak at λ = 1172 (1176) nm increases in parallel with a decrease in the intensity of the peak at λ = 1372 (1370) nm, and an isobestic point is observed at λ = 1220 (1240) nm.

The absorption bands at λ = 1372 (1370) nm can be assigned to the C_{70}^- anion, because they coincide with the known AB of the monoanion (see Table 1) and are independent of the type of amine. By analogy, AB at λ = 1172 (1176) nm can be assigned to the C_{70}^{2-} dianion. The absence of AB at 670 nm observed previously[5] for C_{70}^{2-} is probably associated with its overlapping by a broad band in the range of 700—1000 nm. This is confirmed by the fact that exposure of the solutions studied in air results in the disappearance of AB in the near IR range, and the spectrum takes the form of the smooth descending curve (see Fig. 1, spectrum *4*).

Both the form and the intensity of the broad AB at λ = 700—1000 nm change in time, and when AP is used as a reducing agent, the intensity of the peak at λ = 806 nm decreases and that at λ = 936 nm increases. The latter band is absent in the spectra of the C_{70}^- and C_{70}^{2-} anions in other solutions and can be assigned to the products of the reaction of fullerene with amines. The form of this AB, unlike the bands corresponding to anions of fullerene-70, depends on the type of amine.

The intensity and the form of AB at λ = 1076 (1078) nm remain almost unchanged in time. It can be supposed that this AB is related to C_{60}, which is present as an admixture (~1 %) in C_{70} (see Ref. 9).

Using extinction coefficients presented in Table 1, the content of mono- and dianions of fullerene-70 in a DAP solution can be estimated. The maximum concentration of C_{70}^- (see Fig. 2, spectrum *2*) is $\sim 4 \cdot 10^{-4}$ mol L^{-1} that is equal to ~70 % of the initial concentration of C_{70} ($[C_{70}]_0 = 5.5 \cdot 10^{-4}$ mol L^{-1}). After 24 days (see Fig. 2, spectrum *4*), the ratio is the following: $[C_{70}^-]/[C_{70}^{2-}]$ = 1.5 : 1.0.

ESR spectra of the C_{60}—AP system. Fullerene-60 is dissolved slowly in freshly distilled AP *in vacuo* at room temperature to form a red-brown solution. A signal[1,2] consisting of two singlets with g = 2.0004 (ΔH = 0.022 mT) and 2.0000 (ΔH = 0.1 mT) (Fig. 3, spectrum *9*) is observed in the ESR spectrum of this solution and increases with time. The line with g = 2.0004 is easily saturated, and virtually one line with g = 2.0000 and ΔH = 0.1 mT is observed at 100 mW. In the 15—350 K temperature range, the temperature dependences of the ESR spectra of two C_{60} samples in AP have been studied: at early (5 h at room temperature, sample **1**) and late (at 70 °C, sample **2**) stages of the reaction. The ESR spectra of sample **1** are presented in Fig. 3. At low temperatures (15—45 K), the spectrum is close to the ESR spectrum of the species with axial symmetry of the g-factor ($g_{\parallel}$ = 2.000 and $g_{\perp}$ = 1.995). A weak line in the low-frequency field is also seen at 15 K. The anisotropy of the g-factor is averaged as the temperature increases.

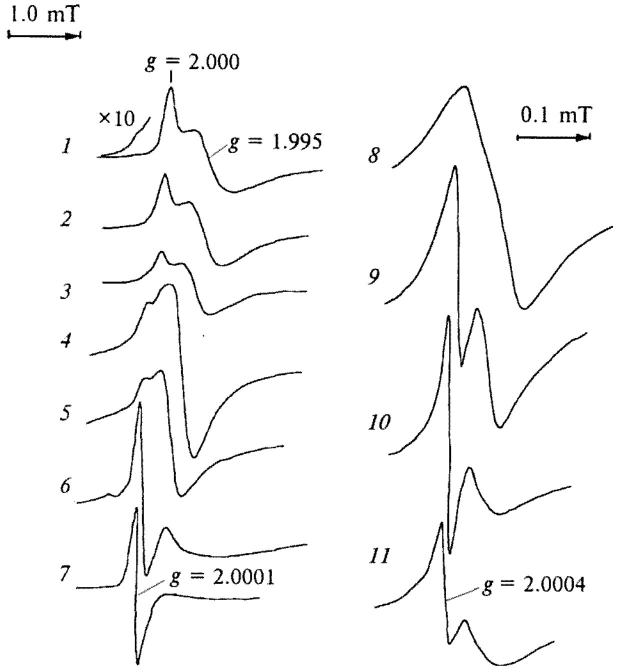

Fig. 3. Temperature dependence of the ESR spectra of the products of the reaction of C_{60} with AP *in vacuo* after 5 h from the beginning of the reaction, T/K. *1*, 15.6; *2*, 30; *3*, 45; *4*, 75; *5*, 109; *6*, 148; *7*, 250; *8*, 275; *9*, 290; *10*, 320; *11*, 350.

Further increase in temperature results in broadening of this averaged line, and a narrow signal with g = 2.0001 begins to overlap it. The intensity of the narrow line increases as the temperature increases, and at 250 K only a narrow line about 0.1 mT in width is observed, while the main line has broadened so much that it is not observed at all. The double integration of the spectrum recorded at room temperature shows that the narrow line corresponds to 25 % of the total amount of C_{60}, while the remaining 75 % likely corresponds with the main broad line that is not observed. Further increase in temperature results in splitting of the narrow line into two components: with g = 2.0004 and a width of about 0.015 mT and with $g \approx 2.0001$ and a width of about 0.1 mT (see Fig. 3, spectrum *11*).

The spectra of sample **2** (Fig. 4) resemble much the spectra of sample **1**, although they contain new lines. At low temperatures (15.1—30 K), an additional line with g = 1.998 is observed, whose intensity decreases rapidly as the temperature increases, and it disappears at 45 K. The shoulder with g = 2.0000 (the spectrum is shown by the dotted curve) disappears at 15.1 K and high microwave powers. As in the spectrum of sample **1**, when the temperature increases to 45—74 K, the anisotropy of g-factor is averaged, the main line is broadened and overlapped with the narrow line with g = 2.0000, whose intensity increases as the temperature increases. Almost

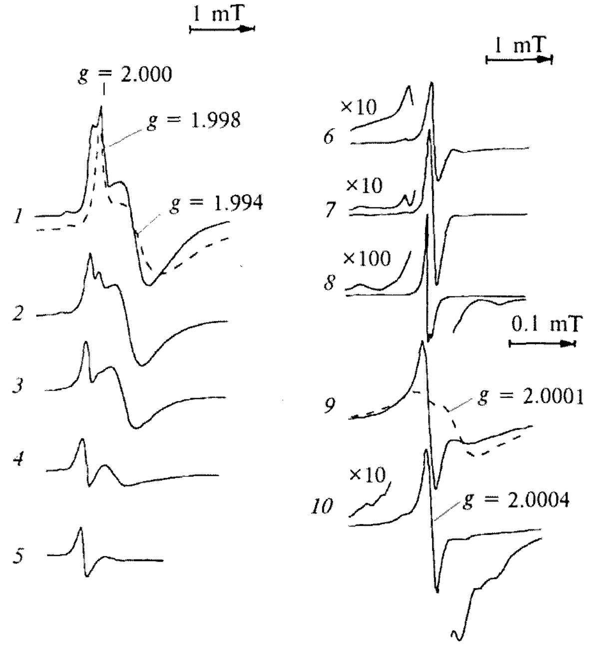

Fig. 4. Temperature dependence of the ESR spectrum of the products of the reaction of C_{60} with AP *in vacuo* after heating the mixture for 5 h at 70 °C. *T*/K: *1*, 15.1; *2*, 30; *3*, 45; *4*, 74; *5*, 104; *6*, 150; *7*, 240; *8*, 280; *9*, 293; *10*, 330.

only the narrow line is observed at 104 K, and the main line is broadened so much that it is not observed. As compared to the ESR spectrum of sample **1**, at 150—280 K the spectrum of sample **2** contains four additional satellites with splitting of about 1 mT, which are most intense at 240 K and hardly detectable at 280 K. At 293 K, the ESR line, as in the case of sample **1**, is a superposition of the narrow and broad lines with approximately the same widths and *g*-factors. The satellites appear again with the further increase in the temperature to 330 K.

In the present time, it is difficult to explain unambiguously all peculiarities of the ESR spectra recorded. The appearance of the axial anisotropy of *g*-factor at low temperatures and its averaging when the temperature increases seem most clear. Similar averaging has also been described in numerous works (see, *e.g.*, Refs. 10—15 and references cited herein) and is explained by so-called Jahn—Teller distortions of symmetry of the C_{60} molecule, which can be presented as vibration of the sphere of the C_{60} molecule, and these distortions increase as the temperature increases. The anisotropy of *g*-factor is caused[11] by distortion of symmetry of C_{60} due to the interaction between C_{60}^- and the counterion. No anisotropy is observed for some counterions at low temperatures.[11] Our attempts to record the ESR spectrum of the aminopropanol radical cation failed, although the radical cation formed due to the electron transfer to the C_{60}—amine system is observed in some case (see, *e.g.*, Ref. 16). The broadening of the main line as the temperature increases is likely explained by the appearance of a wide set of structures[15] at high temperatures rather than by the dynamic broadening of the ESR lines.

It is more difficult to understand the nature of the narrow line appeared at $T > 70$ K. According to the data published previously,[11] this line is caused by the excited states, whose population increase as the temperature increases. Several authors[15] believe that the intensity of the narrow line was measured in Ref. 11 incorrectly at high microwave frequencies and, as a consequence, the conclusion about an increase in the intensity of this line as the temperature increases was invalid. However, our measurements performed taking into account these circumstances, also have shown that the intensity of the narrow line increases as the temperature increases. The authors of Ref. 15 supposed that the narrow line is caused by fullerene derivatives with low symmetry and a higher barrier of molecular rotation than that of C_{60}. The splitting of this line into the narrower and broad components also is not quite clear. According to the literature data,[17] the narrow line corresponds to the free C_{60}^- anion, while the broad one corresponds to the complex of C_{60}^- with a counterion.

In principle, the appearance of the satellites[18] could be explained by the existence of the admixture of C_{60}^{2-}, but the same authors[15] consider that the C_{60}^{2-} dianion is diamagnetic, and these satellites are caused by species of the other, yet unknown nature. The disappearance of the shoulder with $g = 2.0000$ in the ESR spectrum of sample **2** at 15.1 K and high microwave power can be related to the fact that the rates of spin-lattice and spin-spin relaxation of C_{60} depend strongly on the magnetic field and increase as its strength increases[15]; therefore, the line with $g = 2.0000$ should be saturated faster in a weak field.

ESR spectra of the C_{70}—AP system. The temperature dependences of the ESR spectra of solutions of C_{70} in AP have been studied at the early stage of the reaction (sample **3**), when, according to the optical spectra, mainly C_{70}^- anions are present in the system, and at the late stage of the reaction (sample **4**), when mainly C_{70}^{2-} anions are present in the solution.

The ESR spectrum of sample **3** at 12.5 K (Fig. 5) is considerably more complex than the ESR spectrum of the C_{60}^- anion at 15 K (see Fig. 3) and can be preliminarily described as a superposition of two spectra: a spectrum of some radical with $g_{\parallel} = 2.0042$ and $g_{\perp} = 2.0015$ and that of the C_{70}^- anion with $g_{\parallel} = 2.000$ and $g_{\perp} = 1.994$, which are close to the *g*-factors of C_{60}^-. Previously,[18] the ESR spectrum of the C_{70}^- anion has been interpreted as the spectrum with the triaxial anisotropy of *g*-factor. When the temperature increases to 196 K, it is transformed into the spectrum containing two lines: one line of a radical with $g = 2.0028$ and that of the C_{70}^- dianion with $g = 2.0003$. According to the literature data,[18] the ESR spectra of the C_{70}^- anion are characterized by a weaker temperature dependence com-

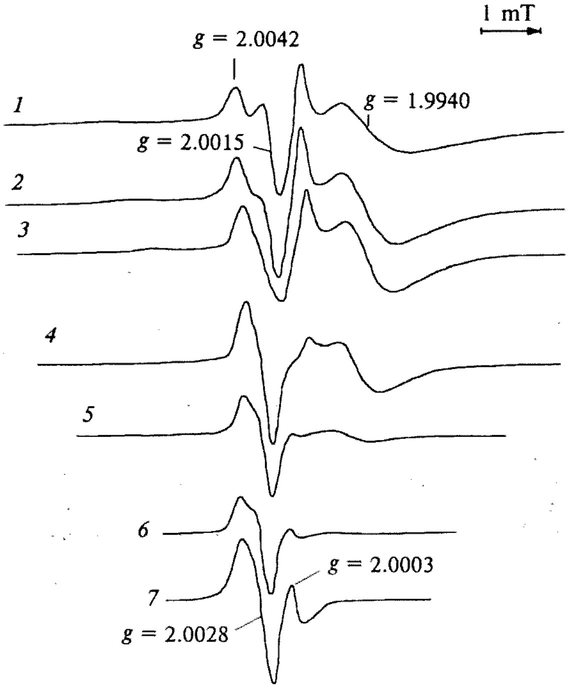

Fig. 5. Temperature dependence of the ESR spectrum of the products of the reaction of C_{70} with AP *in vacuo* after 6 days from the beginning of the reaction. *T*/K: *1*, 12.5; *2*, 19.2; *3*, 27.8; *4*, 49.5; *5*, 72; *6*, 102; *7*, 196.

pared to the spectra of C_{60}^- (smaller broadening of the lines with g = 2.0000, the anisotropy of g-factor is averaged at higher temperatures), which can be explained by greater Jahn—Teller distortions of the geometry of the C_{70} molecule, and, hence, by slower thermally induced transitions between these distorted structures.

The spectra of sample **4** (Fig. 6), in which C_{70} is mainly present in the C_{70}^{2-} form, only the line with g = 2.0004 is observed, and two satellites appear at 20 and 40 °C, which are probably caused by splitting on ^{13}C nuclei. The ESR spectrum of sample **1** contains no signals of the radical observed in the case of sample **3**; it is likely that this radical (presumably, the radical cation) is reduced to the diamagnetic form in sample **4**.

ESR spectra of the C_{70}—DAP system. The ESR spectra of a solution of C_{70} in DAP (Fig. 7) resemble the spectra of sample **3** (see Fig. 5) and are characterized by the existence of paramagnetic species of two types: radicals and C_{70}^- anions. At 60 °C, the spectrum consists of a line of the radical with g = 2.0021 and two lines of C_{70}^- with g = 2.0004 and 2.0001. In this case, the ESR spectrum of the C_{70}^- anion is very close to the spectrum of C_{60}^- (*cf.* Figs. 3 and 7).

Thus, the reactions of C_{70} with 1-amino-3-propanol and 1,5-diaminopentane *in vacuo* result in the reduction of fullerene to mono- and dianions. The temperature dependences of the ESR spectra in the C_{60}—AP, C_{70}—AP, and C_{70}—DAP systems are explained by the

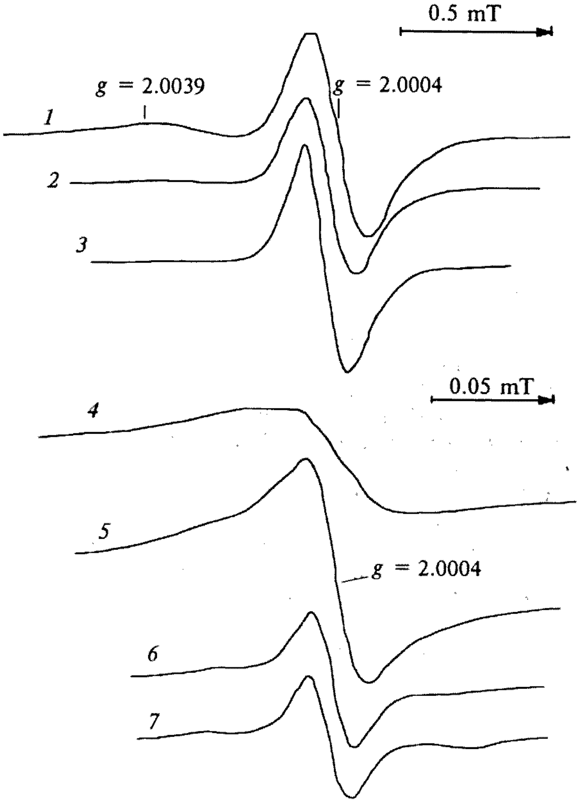

Fig. 6. Temperature dependence of the ESR spectrum of the products of the reaction of C_{70} with AP *in vacuo* after 21 days from the beginning of the reaction. *T*/°C: *1*, −100; *2*, −50; *3* and *4*, −20; *5*, 0; *6*, 20; *7*, 40.

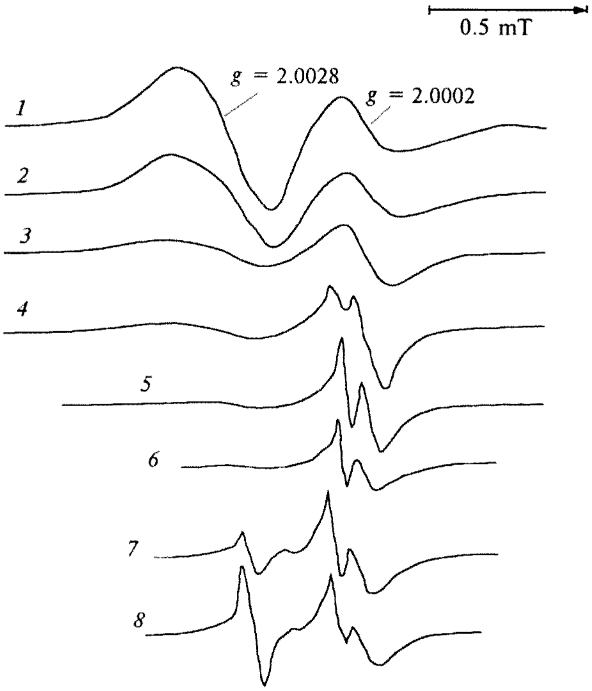

Fig. 7. Temperature dependence of the ESR spectrum of the products of the reaction of C_{70} with DAP *in vacuo* after 51 h from the beginning of the reaction. *T*/°C: *1*, −196; *2*, −140; *3*, −60; *4*, −40; *5*, −10; *6*, 20; *7*, 40; *8*, 60.

distortion of symmetry of the anions due to their reaction with amine radical cations and, hence, by the formation of fullerene derivatives with lower symmetry than initial fullerenes.

Experimental

Initial fullerenes C_{70} and C_{60} were obtained by the procedure described previously.[19] High purity of C_{70} was achieved by multiple chromatography of a mixture of fullerenes and was $\geq$99.0 % according to the data of UV and electronic spectroscopies and HPLC.

1-Amino-3-propanol (Reakhim, high-purity grade) and 1,5-diaminopentane (Fluka) were distilled prior to use.

Experiments were carried out in evacuated quartz spectrometric cells attached to a quartz ESR-tube provided with an additional vessel for freezing a solvent. The typical experimental procedure is the following: 0.7 mg ($8.2 \cdot 10^{-7}$ mol) of C_{70} and 1.5 mL of amine were placed into the cell and the additional vessel, respectively. The cell was evacuated, oxygen from the solution was removed by the triple freezing—thawing out procedure accompanied by evacuation, and the components were mixed *in vacuo*. When fullerene was completely dissolved, ESR and electronic absorption spectra were recorded.

Absorption spectra were recorded on a SF-8 spectrophotometer with 1-nm resolution, using a reference cell filled with the corresponding amine (l = 0.2 cm). ESR spectra were recorded on a Radiopan SE/X-2544 radiospectrometer (modulation 0.01 mT, power 10 mW).

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