The reaction of ethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate with fullerene C_{60}

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Heating (100 °C, toluene) or photolysis (Nd^{3+} : YAG laser, $\lambda = 532$ nm, benzonitrile) of a mixture of ethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantsch ester) (**1**) and fullerene C_{60} under anaerobic conditions results in the formation of fullerene hydrogenation products and ethyl 2,6-dimethylpyridine-3,5-dicarboxylate, which is the product of dehydrogenation of **1**, identified by IR spectroscopy and mass spectrometry. The triplet state of C_{60} is quenched by the Hantsch ester.

Key words: fullerene C_{60}; 1,4-dihydropyridines; Hantsch ester; dehydrogenation; laser photolysis, ^{1}H NMR spectroscopy.

The coenzymes nicotinamide adenine dinucleotide (NAD) and nicotinamide adenine dinucleotide phosphate (NADP) participate in enzymatic processes of hydrogen transfer. The role of NAD and NADP as coenzymes, mainly manifested in redox reactions, is due to their ability for mutual transformations of the pyridinium (in the oxidized form) and dihydropyridine (in the reduced form) rings. The oxidized form has strong electron affinity, and the reduced form possesses strong electron-donor properties. It has been shown that under nonenzymatic conditions dihydronicotinamide adenine dinucleotide ($NADH_2$) and various 1,4-dihydropyridines modeling its action are capable of reducing organic molecules, including carbonyl compounds, maleic acid, and others.[1,2] Organic catalysts of the π-acceptor type for reduction of substrates by ethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (Hantsch ester **1**) have been found.[3]

In the present work, the reaction of the Hantsch ester with fullerene C_{60}, a new allotropic carbon modification with acceptor properties, was studied.

Results and Discussion

Heating of solutions of the Hantsch ester and fullerene C_{60} in toluene or CH_2Cl_2 at 100 °C with exclusion of oxygen results in a change in the color and absorption spectrum in the visible region. The bands characteristic of free fullerene at 24570 and 20000—16600 cm^{-1} (407 and 500—600 nm) almost disappear, and bands at 23044 and 14124 cm^{-1} (434 and 708 nm) appear in the spectrum (Fig. 1), which shows that dihydrofullerene* is present in the solution.[4] The character of the spectrum obtained depends on the **1** : C_{60} ratio, which agrees with different degrees of reduction of C_{60} by the Hantsch ester. Thin layer chromatography (TLC) also showed the appearance of a new compound and the almost total absence of C_{60} in the reaction mixture. It was shown by spectrophotometry (see Experimental) that unconsumed compound **1** (ν = 26660 cm^{-1}) and ethyl 2,6-dimethylpyridine-3,5-dicarboxylate (**2**) (ν = 36364 cm^{-1}), the product of dehydrogenation of compound **1**, are present in the ethanolic extract. Under the conditions studied, ~50% Hantsch ester was consumed; no radical particles were observed in the reaction mixture.

The IR spectrum of the brown precipitate **3** isolated from the reaction mixture (see Experimental) is not the superposition of the spectra of C_{60}, **1**, and **2**. In this spectrum, the vibrational modes are split and shifted to the low-frequency region relative to the vibrations of individual C_{60}: 1424 (1425), 1175 (1177), 855, 575, 564, 550, 545, 542 (574) and 524, 520, 516 (526) cm^{-1} (the frequencies of the corresponding vibrations of C_{60} are given in parentheses). A similar change in the spectrum of C_{60} was observed for $C_{60}H_2$.[5] The IR spectrum of compound **3** also contains bands due to vibrations of C—O and C=O bonds (1020 and 1720 cm^{-1}), which could indicate oxidation of the product. Oxidation of fullerene hydride was also described in Ref. 6.

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* The IUPAC (A-23.1) rules recommend using the prefixes "dihydro," "tetrahydro," *etc.* for fullerene derivatives obtained in addition reactions.

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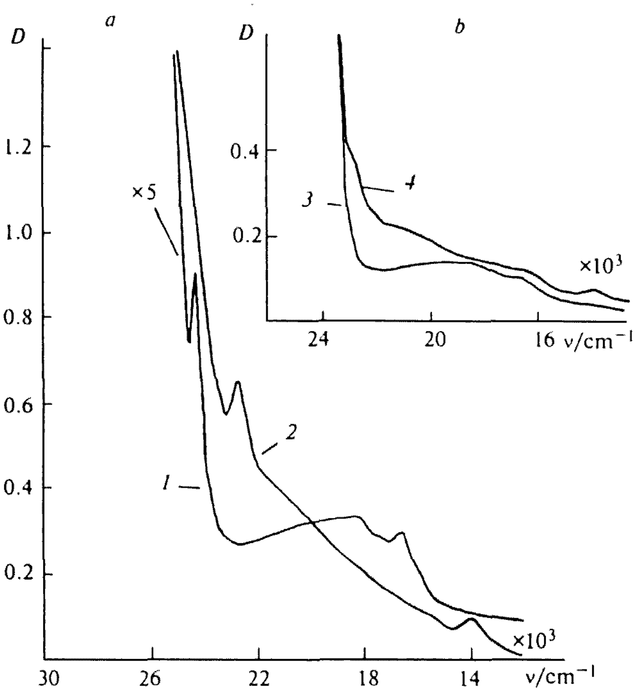


Fig. 1. *a*, Absorption spectra of C_{60} (*1*) and reaction mixture (C_{60} : **1** = 1 : 3) after heating for 2 h at 100 °C (*2*) (toluene as solvent); *b*, absorption spectra of C_{60} (*3*) and reaction mixture (C_{60} : **1** = 1 : 10) after pulsed photolysis (*4*) (benzonitrile as solvent).

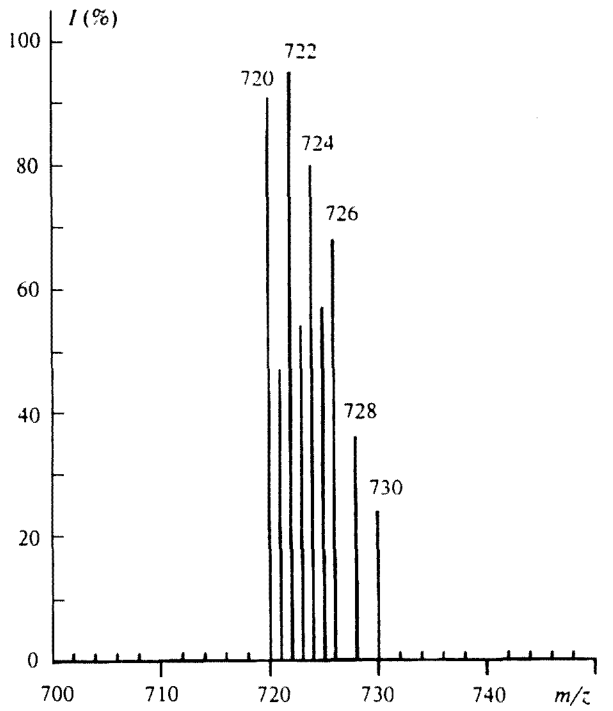


Fig. 2. Mass spectrum (field desorption) of the reaction products of C_{60} with ethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate.

The X-ray photoelectron spectra of compound **3** and C_{60} differ: the half-width of the peak of C1s in the spectrum of compound **3** (3.1 eV) is substantially larger than that in the spectrum of C_{60} (1.8 eV). In the case of compound **3**, the satellite peaks in the range of higher bond energies relative to the basic C1s peak are shifted to the main photoelectron peak. For the lines corresponding to plasma oscillations of all valence electrons, this shift is rather noticeable: for solid C_{60}, $\hbar\omega_p = 26.1\pm0.3$ eV, while for compound **3**, $\hbar\omega_p = 23.7\pm0.3$ eV. Thus, the product formed in the reaction of compound **1** with C_{60} differs substantially from the initial substances and is probably not an individual compound.

Product **3** was also analyzed by field-desorption mass spectrometry. Unlike the electron-impact mass spectra of fullerene hydrides, the mass spectrum consisted almost entirely of single-charged molecular ions.[7] The mass spectrum of compound **3** contained the peaks corresponding to the addition of two, four, and six hydrogen atoms to fullerene C_{60} (Fig. 2).

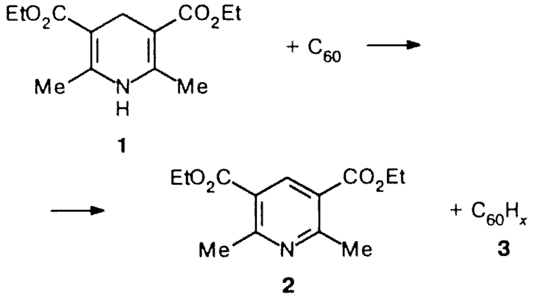
The **1**—C_{60} system was also studied by ^{1}H NMR. The quantitative composition of the reaction mixture was determined by comparing the integral intensities of the signals of the Me and CH_2 groups in the spectra of samples *A* (**1**—C_{60}—toluene-d_8) and *B* (**1**—toluene-d_8) after their heating at 100 °C in a sealed tube for 2 h. Compounds **1** and **2** were identified in sample *A*.

The molar ratio **1** : **2** ≈ 1.4 in sample *A* was determined from the ratio of the areas of the signals of the Me groups. This ratio points to the dehydrogenation of compound **1** with the participation of C_{60}. The ^{1}H NMR spectrum of sample *B* mainly contained the lines assigned to compound **1**, but weak signals of compound **2** were also present (<10%, as determined from the ratio of the intensities of singlets of Me groups with δ 3.124 and 2.090).

The kinetic behavior of the Hantsch ester—C_{60} system in benzonitrile was studied by laser photolysis. Excitation was performed by the second harmonic of an Nd^{3+} : YAG laser (λ = 532 nm). The changes in the signal of the optical density at the wavelength of 750 nm (the absorption maximum of the triplet state of C_{60} {$^3C_{60}$}) indicate the quenching of $^3C_{60}$ (the oxidation potential is +1.14 V) by the Hantsch ester. The signal itself has a pronounced biphase nature with a fast stage with $k_q = 5.9 \cdot 10^7$ L mol^{-1} s^{-1} and slow decay with a time constant of τ = 10 μs. An increase in the optical density at 950 nm (one of the maxima of C_{60}^{-}) is observed simultaneously in this time range. Thus, the typical kinetic curves of the change in the optical density at λ = 750 and 950 nm in the system after a laser pulse indicate that the decay of $^3C_{60}$ is accompanied by accumulation of the products. It is noteworthy that the reaction occurs efficiently in polar solvents (benzonitrile, chlorobenzene). The changes in the absorption spectrum of the solution after photolysis are similar to those observed for a thermal action (see Fig. 1).

According to the known data[4,8] on the sensitizing effect of C_{60}, the Hantsch ester can be completely transformed into the oxidized state, *viz.* compound **2**, in the presence of fullerene on irradiation with soft light under aerobic conditions at room temperature. The concentration and spectrum of C_{60} remain almost unchanged (spectrophotometry). Product **2** was isolated from the reaction mixture in a high yield.

Thus, dihydropyridines are dehydrogenated in the presence of fullerenes. The data obtained under anaerobic conditions are evidence of the formation of fullerene hydrides of $C_{60}H_x$ composition (x = 2, 4, and 6). The mechanism of the formation of the reduction products of C_{60} is the subject of further study.



Experimental

Fullerene C_{60} was obtained by the known procedure.[9] Ethyl 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate was prepared by the procedure described previously,[10] m.p. 175 °C (*cf.* Ref. 10: 175—180 °C), IR (nujol), ν(N—H) 3350 cm^{-1}. UV, (EtOH) λ: 375 nm (ε 6500). Toluene, CH_2Cl_2, and benzonitrile were purified by the known methods.[11]

IR spectra were recorded on Specord 75 IR and UR-20 spectrophotometers in pellets with KBr and in nujol. Absorption spectra were recorded on a Specord UV-VIS instrument. X-ray photoelectron spectra were recorded on a Varian-IEE-15 spectrometer with a magnesium anode (*hν* 1253.6 eV). Mass spectra were recorded on a MAT-731 mass spectrometer with double focusing in the field descrption regime (the emitter heating current was 30 mA). ^{1}H NMR spectra were recorded at 22 °C on a Tesla BC-575 A spectrometer (80 MHz) with stabilization over the NMR signal from deuterium of the solvent. The chemical shifts were measured relative to residual protons of the solvent (toluene-d_8) and recalculated relative to Me_4Si. The reaction products were analyzed taking into account the reference data on the chemical shifts of the functional groups and by comparison with the spectra of the individual compounds obtained under similar conditions.

Reaction of ester 1 with fullerene. The Hantsch ester (**1**) (2.50 mg, 0.96 · 10^{-2} mmol), C_{60} (2.20 mg, 0.3 · 10^{-2} mmol), and toluene (4 mL) were placed in a 8-mL tube, which was sealed after evacuation and heated for 1.5 h at 100 °C. The solvent was distilled off into a cooled trap, and the residue was dried and extracted with EtOH in an inert atmosphere. The concentrations of compounds **1** and **2** were determined in the extract from the intensity of the peaks at 375 and 275 nm, respectively. The brown compound remaining after extraction with EtOH was evacuated for 5 h at 60 °C. IR (KBr), ν/cm^{-1}: 516, 520, 524, 542, 545, 550, 564, 575, 690, 855, 1020, 1175, 1424, 1465, and 1720. TLC, R_f = 0.58 (Silufol-254, CH_2Cl_2 : hexane = 3 : 4). In this system, the Hantsch ester and the corresponding pyridine remain at the start, for C_{60} R_f = 0.8.

Compound **1**: ^{1}H NMR (toluene-d_8), δ: 1.248 (t, 6 H, $2\underline{Me}CH_2$, ^3J = 7.1 Hz); 2.090 (s, 6 H, 2Me); 3.804 (br, 2 H, CH_2); 4.257 (q, 4 H, $2Me\underline{CH_2}$, ^3J = 7.1 Hz). The signal of the NH group (br.s) is overlapped with the quartet from CH_2 (4.457 ppm). Compound **2**: ^{1}H NMR (toluene-d_8), δ: 1.248 (t, 6 H, $2\underline{Me}CH_2$, ^3J = 7.1 Hz); 3.124 (s, 6 H, 2Me); 4.258 (q, 4 H, $2Me\underline{CH_2}$, ^3J = 7.1 Hz); 9.020 (s, 1 H, CH).

The reaction was performed in day light at room temperature in a flask with a magnetic stirrer, a valve for bubbling O_2, and a stopcock for sampling. C_{60} (1.122 mg, 1.56 · 10^{-3} mmol), compound **1** (23.65 mg, 9.34 · 10^{-2} mmol), and toluene (6 mL) were placed in the flask. When the reaction was over (the absence of compound **1** according to TLC), the solvent was distilled off, and the residue was dried and extracted with ethanol. The concentration of **1** and **2** was determined in the extract. The solvent was removed, and the residue was sublimed. Compound **2** (18 mg) was obtained, m.p. 70 °C (*cf.* Ref. 12: 72 °C). Found (%): C, 62.0; H, 6.28; N, 6.00. $C_{13}H_{17}NO_4$. Calculated (%): C, 62.5; H, 6.77; N, 5.57. IR (nujol), ν/cm^{-1}: 790, 880, 1040, 1120, 1215, 1240, 1265, 1295, 1560, 1600, and 1730.

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