Technical Physics Letters, 2025, Vol. 51, No. 2

05

Light Fullerene Poly-nitro-adduct $C_{60}(NO_2)_{18}(OH)_2$

© M.Yu. Arshinov[1], D.I. Subbotin[1], Shan Yanchen[1], V.A. Keskinov[2], N.A. Charykov[1],
M.B. Alikin[1], N.A. Kulenova[2], K.N. Semenov[3], G.O. Yurev[3], V.P. German[1],
M.V. Keskinova[2], D.G. Letenko[4]

[1] St. Petersburg State Technological Institute (Technical University), St. Petersburg, Russia
[2] Veritas Center, D. Serikbayev East Kazakhstan State Technical University, Ust-Kamenogorsk, Kazakhstan
[3] Pavlov First St. Petersburg State Medical University, St. Petersburg, Russia
[4] Saint Petersburg State University of Architecture and Civil Engineering, St. Petersburg, Russia
E-mail: keskinov@mail.ru

Received August 27, 2024
Revised August 27, 2024
Accepted September 29, 2024

By direct heterogeneous non-catalytic nitration of fullerene C_{60} with a mixture of concentrated nitric and sulfuric acids was synthesized poly-nitro-adduct $C_{60}(NO_2)_{18}(OH)_2$. Excess of nitric acid from the reaction mixture was removed by treatment with hydrogen peroxide, and sulfuric acid — by dialysis from aqueous solutions. The identification of the poly-nitro-adduct was carried out using the following methods: elemental C–H–N analysis, energy dispersion spectral microanalysis, infrared spectroscopy, and nuclear magnetic resonance, high-performance liquid chromatography, thermo-gravimetric analysis.

Keywords: poly-nitro-adduct, fullerene C_{60}, synthesis, identification.

DOI: 10.61011/TPL.2025.02.60623.20092

Nitration of hydrocarbons normally results in the formation of two main classes of nitro derivatives: nitro-adducts $R(NO_2)_n$ (R is a saturated, unsaturated, or aromatic radical, which may also contain other functional groups) and nitrate esters $R(O{-}NO_2)_n$ [1,2]. In most cases, the nitrating agent is either nitric acid itself ($OHNO_2$), the $OHNO_2$ conversion products for which the latter is a precursor ($2OHNO_2 \rightarrow NO_2^+ + NO_3^- + HOH$), nitrous acid ($OHNO$), or one of the nitrogen oxides (usually NO_2 ; NO , N_2O_5, and N_2O_3 are used less often). Additional oxidants (O_2, O:, O_3, $H_2O_2, \ldots$) or catalysts (primarily strong mineral acids, such as $OHSO_3H$, or Lewis acids ($AlCl_3$, $ZnCl_2$, BF_3)) are used occasionally in the process. Nitro derivatives are used widely in science and technology as raw materials for the chemical industry, pharmacology, medicine, etc. Examples of such derivatives are nitrobenzene ($C_6H_5NO_2$), which is used for the synthesis of aniline and its derivatives; trinitrotoluene ($C_6H_2CH_3(NO_2)_3$); and trinitroglycerol ($CH_2ONO_2{-}CHONO_2{-}CH_2ONO_2$). The present study is focused on the nitration of unsaturated hydrocarbons (alkenes, aromatic compounds) as the closest analogues of fullerenes (formally categorized as poly-olefins), specifically the simplest of stable ones — C_{60} [3]. We consider the nitration of fullerene with nitric acid, which is the most general nitrating agent that serves as a precursor for the other agents. The process of nitration of double bonds of unsaturated hydrocarbons may proceed in two fundamentally different directions (substitution or addition at the double bond with the formation of six different products).

(1) Substitution of an H atom with a nitro group $-NO_2$ with preservation of the double bond, which is observed, e.g., in the synthesis of nitrobenzene: $C_6H_6 + OHNO_2(H^+) \rightarrow C_6H_5NO_2 + HOH$. This synthesis option is infeasible in the case of nitration of C_{60} due to the lack of a proton at the double bond.

(2) Substitution of H during the formation of mono-nitro-adducts in the interaction of alkenes with N_2O_5 ($2R_1C = CHR_2 + N_2O_5 \rightarrow 2R_1C = CR_2NO_2 + HOH$). It is impossible for the same reason.

(3) Addition of $OHNO_2$ at the double bond with the formation of nitro alcohols — nitrohydroxy adducts: $R_1C = CR_2 + OHNO_2(H^+) \rightarrow R_1COH{-}CR_2NO_2$.

(4) Addition of pure nitric acid (without nitrogen oxide impurities) with the formation of nitrate esters: $R_1C = CR_2 + OHNO_2(H^+) \rightarrow R_1CH{-}CR_2ONO_2$.

(5) Interaction of nitrogen oxides $NO_2\cdot$, N_2O_3, and N_2O_5 with ethylene hydrocarbons, which was studied consistently and thoroughly by Dem'yanov et al. [4]. Specifically, the formation of di-nitro-adducts $R_1C = CR_2 + 2NO_2\cdot \rightarrow R_1CNO_2{-}CR_2NO_2$, mono-nitro-adducts, nitro alcohols, nitrate esters, and their mixtures was demonstrated in these studies.

(6) Addition of NO_2 oxide at the double bond with the formation of a mixture of a nitro-adduct and a nitrohydroxy adduct. An example here is provided by the process of nitration of octene-1 with the formation of a mixture of 1,2-dinitrooctane and 1-nitro-2-hydroxyoctane in a molar ratio of 1:1 [5]: $C_6H_{13}CH = CH_2 + 3NO_2 + HOH \rightarrow C_6H_{13}CHNO_2{-}CH_2NO_2 + C_6H_{13}CHOH{-}CH_2NO_2 + H^+$.

Note that modern study [5] may be viewed as a continuation of research carried out by Dem'yanov et al.

Identification and physical and chemical examination of $C_{60}(NO_2)_{18}(OH)_2$

Research method, instrument	Results of the study
Elemental C–H–N analysis, 5E-CHN2200 analyzer and VEGA-3 TESCAN electron microscope (XRF analyzer)	Composition in atomic ratios (per nucleus of the fullerene C_{60} core): C — 60, N — 18 ± 2, H — 2 ± 1, O — 38 ± 4. Formula: $C_{60}(NO_2)_{18}(OH)_2$
Infrared spectrophotometry, Shimadzu FTIR-8400S ($\tilde{\nu} = 400$–$4000\,\mathrm{cm}^{-1}$, KBr pellets)	$\tilde{\nu}, \mathrm{cm}^{-1}$: $\tilde{\nu}(O{-}H)$ — 3449; $\tilde{\nu}(NO_2)$ — 1647, 1348, 1560; $\delta(NO_2)$ — 733, 638, 617 (scissors); $\tilde{\nu}(C{-}O)$ — 1790, 1647 1152, 1063; $\tilde{\nu}(C{-}N)$ — 1113(*s*), 833; $\tilde{\nu}(C{-}O{-}N)$ — 2982; $\tilde{\nu}$(fullerene core) — 997, 733, 484, 457; $\tilde{\nu}$(fullerene core for C_{60}) — 528, 578, 1183 (not found)
Electron spectrophotometry, UV-VIS-NIR Shimadzu, $\lambda = 200$–$1110\,\mathrm{nm}$; reference — H_2O (distilled)	The only absorption peak in the visible and near ultraviolet region corresponds to $\lambda = 300 \pm 3\,\mathrm{nm}$. The Beer–Bouguer–Lambert law at a wavelength of 300 nm: $C_{C_{60}(NO_2)_{18}(OH)_2}\ [\mathrm{g/dm^3}] = [0.178 \pm 0.003]D_{300}\ (l = 1\,\mathrm{cm})$
Solubility in H_2O, isothermal saturation for 8 h in a thermostatic shaker ($\omega \approx 2\,\mathrm{Hz}$, $\Delta T = \pm 0.1\,\mathrm{K}$)	The only branch of crystallization of dihydrate $C_{60}(NO_2)_{18}(OH)_2 \cdot 2H_2O$. A monotonic increase in solubility with increasing temperature: at 0°C — 11 g/dm^3, at 25°C — 23 g/dm^3, at 50°C — 29 g/dm^3, at 80°C — 33 g/dm^3
High-performance liquid chromatography, HPLC Agilent 1200, column: Agilent Zorbax SB-C18, eluent ($CH_3CN + H_2O$, 1:20), detection — spectrophotometry ($\lambda = 330, 280\,\mathrm{nm}$)	Release time: $t = 2.7\,\mathrm{min}$ — weak peak of impurities (~ 3 sq.%); $t = 3.6\,\mathrm{min}$ — the only strong poly-nitro-adduct release peak (~ 97 sq.%). Primary peak width at half height $d_{1/2} \approx 0.45\,\mathrm{min}$. Chromatographic purity of the product ~ 97–98 mass%
Nuclear magnetic resonance, ^{13}C, AVANCE-II 400WB Bruker, tetramethyl silane, $CDCl_3$, $\nu = 100.4\,\mathrm{MHz}$	δ reflections (in ppm): 142–143 (unmodified fullerene core C–C atoms), ~ 76 (hydroxylated C–OH bonds), ~ 53 (C atoms bound to nitro group $C{-}NO_2$)
Complex thermal analysis, Shanghi Jiahang Instruments Co, atmosphere — air, pressure — 1 atm, temperature range $T = 25$–950°C, rate — 5 K/min	Decomposition of the poly-nitro-adduct crystalline hydrate — external dehydration ($T = 60$–100°C); destruction of hydroxyls — internal dehydration, formation of acetals ($T = 170$–250°C); stage slow destruction of nitro groups ($T = 400$–650°C); explosive rapid destruction of nitro groups ($T = 680$–740°C); oxidation of the fullerene core ($T \geqslant 800$°C). The processes are endothermic
Dynamic light scattering (DLS), Malvern Zetasizer Nano ZS90	Diameter of quasi-spherical associates δ, gross concentration C, ξ-potentials: order 0 (monomers) — $\delta \approx 2\,\mathrm{nm}$, $C \leqslant 0.00195\,\mathrm{g/dm^3}$, $\xi = 0\,\mathrm{mV}$; order I — $\delta \approx 50 \pm 10\,\mathrm{nm}$, $C = 0.00195$–$0.50\,\mathrm{g/dm^3}$, $\xi = -25\,\mathrm{mV}$; order II — $\delta \approx 170 \pm 50\,\mathrm{nm}$, $C = 0.0624$–$2.0\,\mathrm{g/dm^3}$, $\xi = -42 \pm 5\,\mathrm{mV}$; order III (microcolloidal solution) — $\delta \approx 5.0 \pm 0.6\,\mu\mathrm{m}$, $C \geqslant 1.0\,\mathrm{g/dm^3}$, $\xi = -73 \pm 12\,\mathrm{mV}$

Table (continued)

Research method, instrument	Results of the study
Bulk properties, concentration dependence of density of aqueous solutions, average and partial volumes of components, quartz pycnometers, working volume $v \approx 2.5\,\mathrm{cm}^3$, $\Delta T = \pm 0.1\,\mathrm{K}$, reference liquid — H_2O (distilled)	The density of solutions goes through a maximum at $C \approx 2.0\,\mathrm{g/dm}^3$, the average molar volume of a solution goes through a gentle minimum at $C = 0.0624-1.0\,\mathrm{g/dm}^3$, the partial molar volume of the poly-nitro-adduct goes through a gentle maximum, and the partial molar volume of water goes through a gentle minimum at $C \approx 4.0\,\mathrm{g/dm}^3$. The first portions of the poly-nitro-adduct with $C \leqslant 0.0156\,\mathrm{g/dm}^3$ are characterized by huge negative partial volumes, which is indicative of primary structuring (solution densification)
Refractometry of aqueous solutions at 20°C, HRK 9000 A refractometer, $T = 19-22^\circ\mathrm{C}$	The refraction index of solutions goes through a maximum at $C \approx 2.0\,\mathrm{g/dm}^3$, the specific and molar refractions of solutions change significantly at $C \geqslant 2.0\,\mathrm{g/dm}^3$, the molar refraction of the poly-nitro-adduct corresponds to the calculation by additivity: $R_{add} \approx 419\,\mathrm{cm}^3/\mathrm{mol}$
Electrical properties of aqueous solutions at 25°C, LCR meter HAMEGHM8118 (Rohde & Schwarz), quartz cell with Pt electrodes, reference solution — $NaCl-H_2O$	As the concentration increases, the specific conductivity increases monotonically and almost linearly, while the equivalent conductivity drops sharply. The value of thermodynamic dissociation constant $pK_D^{therm} = \lim_{M\to 0} pK_D \approx 6.8$ indicates that the poly-nitro-adduct is a very weak acid (comparable in strength to H_2CO_3)
Acidic properties of aqueous solutions at 25°C, Seven Compact pH meter S220, $\Delta\mathrm{pH} = \pm 0.005$	As the concentration increases, the solution acidifies monotonically: $\mathrm{pH} \approx 6.6 \to \mathrm{pH} \approx 5.5$ The value of thermodynamic dissociation constant $pK_D^{therm} = \lim_{M\to 0} pK_D \approx 6.7$ verifies the weak acid dissociation mechanism of the poly-nitro-adduct

The nitration of fullerenes C_{60} themselves with any kind of nitrating agent has been little studied. It is known only that compounds of the fullerenol class (polyhydroxylated fullerenes $C_{60}(OH)_n$ with $n = 16-20$) form when C_{60} interacts with nitric acid, nitrates, or nitrogen dioxide (NO_2) [6,7] in an acidic medium with subsequent alkaline hydrolysis. This is hardly surprising, since alkaline hydrolysis of polysubstituted nitro-adducts, nitrohydroxy adducts, and nitrate esters predictably yields polyhydroxylated forms: fullerenols or their salts (in strongly alkaline media).

Thus, the aim of the present study is to evaluate the possibility of synthesis of nitro derivatives of C_{60}, classify them, determine the degree of addition, and identify the products by physical and chemical analysis techniques.

Let us discuss the poly-nitro-adduct synthesis in more detail.

(1) Preparation of nitrating mixture HNO_3 (concentrated) + H_2SO_4 (concentrated). Volume of acids in the mixture $V_{HNO_3} = V_{H_2SO_4} \approx 250\,\mathrm{cm}^3$. The characteristics of acids were as follows: $C_{HNO_3} \approx 65$ mass%, reagent-grade, GOST 4461–77, Magna; $C_{H_2SO_4} \approx 94$ mass%, high purity, GOST 14262–78, Chem. Express.

(2) Weighing of light fullerene C_{60}. Mass $m_{C_{60}} \approx 500$ mg, reagent purity $C_{C_{60}} \geqslant 99$ mass% (ZAO ILIP, St. Petersburg).

(3) Mixing of the nitrating mixture and C_{60}. The conditions were as follows: time $t = 7$ days; temperature $T \approx 80 \pm 5^\circ\mathrm{C}$ (water bath); magnetic stirrer ($\omega \approx 2\,\mathrm{Hz}$). An opaque black-blue suspension transformed into a translucent green-brown viscous solution in the process of mixing.

(4) Filtration of the solution through a Schott filter to isolate a transparent light yellow filtrate.

(5) Removal of excess HNO_3 by adding an H_2O_2 (concentrated) solution dropwise at room temperature ($C_{H_2O_2} \approx 37$ mass%, reagent-grade, GOST 177–88, Lenreaktiv). An intense release of brown gas was observed at the start of this process:

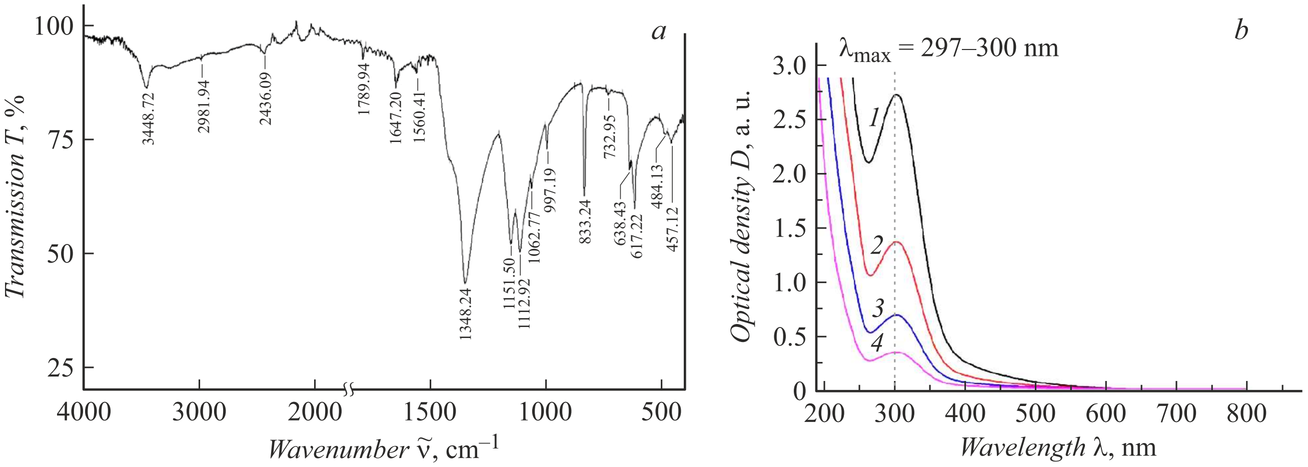

Figure 1. IR spectra (*a*) and electron spectra (*b*) of $C_{60}(NO_2)_{18}(OH)_2$. *C*, g/dm^3: *1* — 0.48, *2* — 0.24, *3* — 0.12, *4* — 0.060.

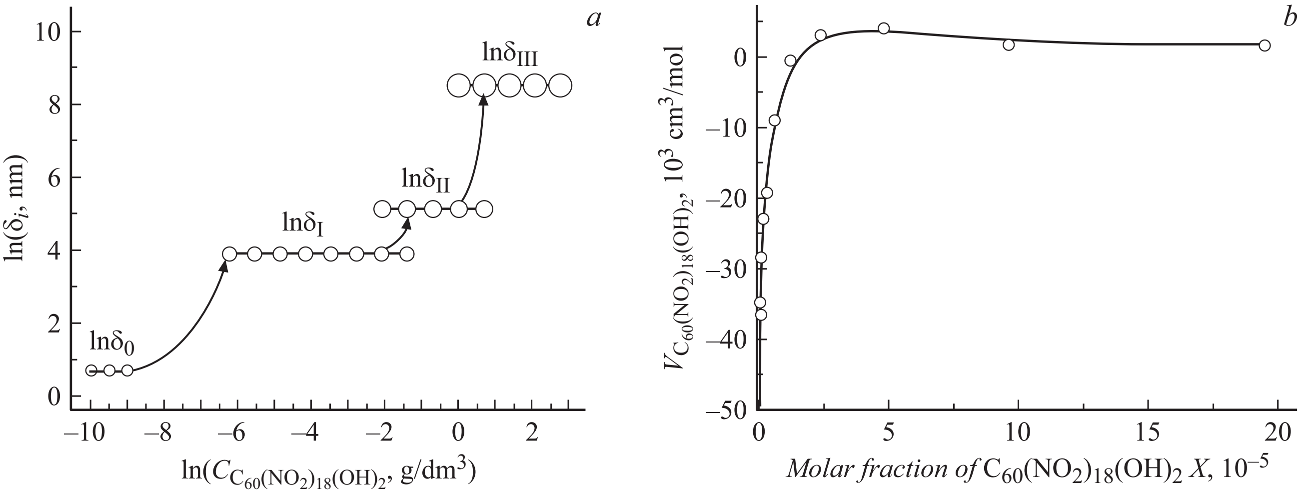

Figure 2. Concentration dependences of associate diameters δ_i (*a*) and partial molar volumes $V_{C_{60}(NO_2)_{18}(OH)_2}$ (*b*).

$2HNO_3 + H_2O_2 \rightarrow 2NO_2 + 2H_2O + O_2$. This was followed by a low-intensity release of colorless gas (O_2). Excess $V_{H_2O_2} \approx 10\,cm^3$ was also added to the reaction mixture, and the solution was left for 24 h to complete the HNO_3 removal reaction.

(6) Neutralization of excess H_2SO_4 in the resulting solution with an aqueous solution of NaOH to pH $\approx 7 \pm 1$ ($C_{NaOH} \approx 30$ mass%, analytic grade, GOST 4328–77, Lenreaktiv).

(7) The resulting solution was evaporated using a rotary vacuum dissolver at temperature $T \approx 80 \pm 5\,^\circ C$ (water bath). Colorless salt crystals (thenardite Na_2SO_4) precipitating in the process were filtered by a Schott filter. The residual volume of the transparent yellow solution was $V_{sol} \approx 100 \pm 10\,cm^3$.

(8) Residual salts were removed from the reaction mixture by dialysis (laboratory dialysis bag MD25 made of regenerated cellulose MW1000 with a length of 1 m; dialysis tube RC 77 mm in diameter).

(9) The obtained solution was evaporated in a vacuum drying oven (temperature $T \approx 50 \pm 5\,^\circ C$, residual pressure $P \approx 18 \pm 3$ mm Hg).

(10) Finely dispersed brown poly-nitro-adduct crystals weighing ~ 475 mg were obtained as a result. With the poly-nitro-adduct formula fixed at $C_{60}(NO_2)_{18}(OH_2)$, this corresponds to a target product yield of $\eta \approx 44\%$ of the theoretically possible value.

Physical and chemical analysis techniques were used to identify and examine certain basic physicochemical properties of the $C_{60}(NO_2)_{18}(OH)_2$ poly-nitro-adduct and its aqueous solutions (see the table and Figs. 1, 2). The identification results presented in the table and figures are in complete agreement with those obtained previously for related C_{60} adducts (see, e.g., [8]).

Thus, fullerene poly-nitro-adduct $C_{60}(NO_2)_{18}(OH)_2$ was synthesized and identified, and some of its physicochemical properties were determined.

Funding

This study was supported by grant No. 23-23-00064 from the Russian Science Foundation (https://rscf.ru/project/23-23-00064).

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] A.I. Vogel, *Textbook of practical organic chemistry*, 3nd ed. (London Group Ltd., London, 1957).

[2] J. Clayden, N. Greeves, S. Warren, *Organic chemistry*, 2nd ed. (Oxford University Press, U.K., 2012).

[3] L.N. Sidorov, M.A. Yurovskaya, A.Ya. Borshchevskii, I.V. Trushkov, I.N. Ioffe, *Fullereny* (Ekzamen, M., 2005) (in Russian).

[4] N.Ya. Dem'yanov, Zh. Russ. Fiz.-Khim. O-va., **33** (4), 275 (1901) (in Russian).

[5] R.E. Ivanov, M.N. Zharkov, S.G. Zlotin, Dokl. Chem., **500**, 209 (2021). DOI: 10.1134/S0012500821100037.

[6] L.Y. Chiang, J.B. Bhonsle, L. Wang, S.F. Shu, T.M. Chang, J.R. Hwu, Tetrahedron, **52**, 4963 (1996). DOI: 10.1016/0040-4020(96)00104-4

[7] L.Y. Chiang, R.B. Upasani, J.W. Swirczewski, J. Am. Chem. Soc., **114**, 10154 (1992). DOI: 10.1021/ja00052a010

[8] V.V. Sharoyko, S.V. Ageev, A.A. Meshcheriakov, N.E. Podolsky, J.P. Vallejo, L. Lugo, I.T. Rakipov, A.V. Petrov, A.V. Ivanova, N.A. Charykov, K.N. Semenov, J. Mol. Liq., **344**, 117658 (2021). DOI: 10.1016/j.molliq.2021.117658

Translated by D.Safin