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SYNTHESIS AND IDENTIFICATION WATER-SOLUBLE TRIS-MALONATE OF LIGHT FULLERENE – $C_{60}[=C(COOH)_2]_3$

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The water soluble tris-malonate adduct of light fullerene – $C_{60}[=C(COOH)_2]_3$ was produced in laboratory quantities. The product was identified by several analytical methods: elementary H–C–O–N analysis, IR-, Electronic, NMR- Spectroscopy, Mass Spectrometry.

Keywords: tris-malonate of light fullerene, synthesis, elementary analysis, IR-, Electronic, NMR- Spectroscopy, Mass Spectrometry.

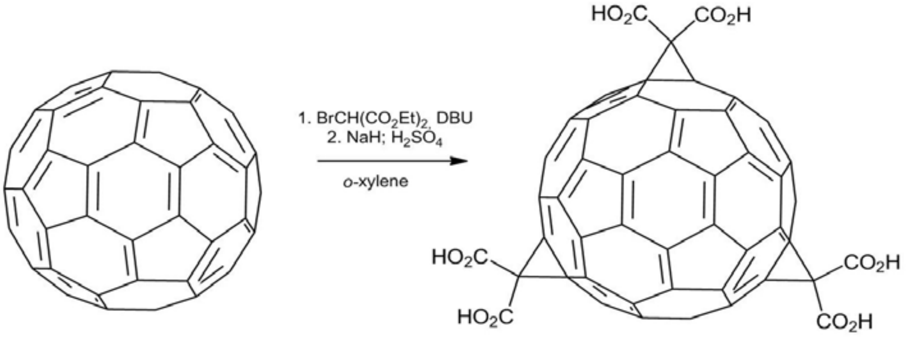
1. The synthesis of tris-malonate C_{60}

Diethyl malonate (100 mg) was dissolved in o-xylene (50 ml) under gaseous nitrogen in the presence of a twentyfold molar excess of NaH for 3 hours at 60 °C. After this procedure, the NaH was almost homogeneously suspended in toluene while the diethyl malonate was unaffected. The transformation of the malonate was accompanied by a vigorous gaseous evolution and the quantitative precipitation of the sodium salt of the tris-malonate C_{60} took place after the addition of methanol (1 ml). After centrifugation and removal of the liquid phase, the precipitate was washed with toluene, 2 M H_2SO_4, then water and finally dried under vacuum at 60 °C for 12 hours. Such scheme was described earlier in the original paper [1]. Scheme of the synthesis is represented lower in the Fig. 1. It is worth noting that carboxylic acid formation probably occurs as a result of acidic hydrolysis during the treatment with 2 M H_2SO_4.

2. Identification of tris-malonate C_{60}

2.1. Element C–H–O–N analysis

EuroEA3028-HT Eurovector Element C–H–O–N analyzator was used. The result of the analysis is represented lower in the Table 1.



or $C_{60}(=C=(COOH)_2)_3$

FIG. 1. Scheme of the synthesis of tris-malonate C_{60}

TABLE 1. Data of element C–H–O–N analysis

Element	Calculated composition C^{cal} (% mass)	Experimental composition C^{exp} (% mass)	$/C^{exp} - C^{cal}/$ (% mass)
C	80.71	80.73	0.002
H	0.59	0.54	0.005
O	18.70	18.73	0.003

2.2. High resolution mass spectrometry

High resolution Electrospray ionization mass spectrometry (positive mode) was performed using a Shimadzu GCMS-QP2010Ultra ($[C_{60}(=C=(COOH)_2)_3 - H]^+$) . The experimental value for M/z (M, z – ion mass in atomic units and ion charge, correspondingly) in the case $z = 1$ was equal to the calculated value of M/z in the positive charged form, represented above: $M/z = 1026 + 1 = 1027$ atomic units.

3. Nuclear magnetic resonance

A Bruker Avance 400 NMR-spectrometer was used. Experimental NMR-peak data (in ppm) were as follows:
δ_H (300 MHz, D_2O): 11.7 (wide singlet, H – from carboxyl groups –COOH);
δ_C (75.5 MHz, D_2O): 166.57, 166.54, 166.27, 150.04, 148.79, 147.91, 147.85, 147.59, 147.05, 146.86, 146.74, 146.68, 146.47, 146.24, 146.15, 146.12, 145.90, 145.68, 145.53, 145.33, 144.85, 144.54, 144.47, 143.54, 143.28, 143.16, 143.07, 140.40, 140.13, 74.32, 69.16, 62.25.

3.1. Infrared Spectroscopy

A Shimadzu IR Spectrometer IRAffinity-1 was used in the wave-numbers range $\tilde{\nu} = 450 - 4500$ cm^{-1}. Solid tablets of tris-malonate C_{60} in dry KBr were used aas samples. Experimental IR main reflexes data in $\tilde{\nu}$ (cm^{-1}) were the following: 3470, 1811, 1723, 1715, 1431, 1405, 1410, 1222, 1231, 1057, 820, 833, 730, 580, 528, 522. One can see that long-wavelength part of spectrum: $\tilde{\nu} = 522{-}1715$ cm^{-1}, corresponds to the oscillations of C–C bonds in fullerene C_{60}, compare with the main absorption data in $\tilde{\nu}$ (cm^{-1}) for C_{60}: [1,2]. At the same, time short- wavelength part of spectrum: $\tilde{\nu} = 1700 - 1725$ cm^{-1}, corresponds to the oscillations of C=O bonds in malonate-groups in $C_{60}[=C(COOH)_2]_3$, $\tilde{\nu} = 3450 - 3550$ cm^{-1} corresponds to the oscillations of rather free O–H groups. A standard absorption at 1811 cm^{-1} we associated with the oscillation of C–C bonds in external cyclopropanes in tris-malonates (see Fig. 1). Similar results were obtained by us earlier in the course of studying of another moderately soluble derivative of light fullerenes C_{60} and C_{70} – fullerenols – $C_{60}(OH)_n$, $C_{70}(OH)_m$ [2–5].

3.2. Electronic Spectroscopy

An Evolution 201 Thermo Fischer spectrophotometer was used for wavelengths ranging from 190 – 1100 nm (water solutions of tris-malonate of C_{60} against pure water). The spectrum is presented lower in Fig. 2.

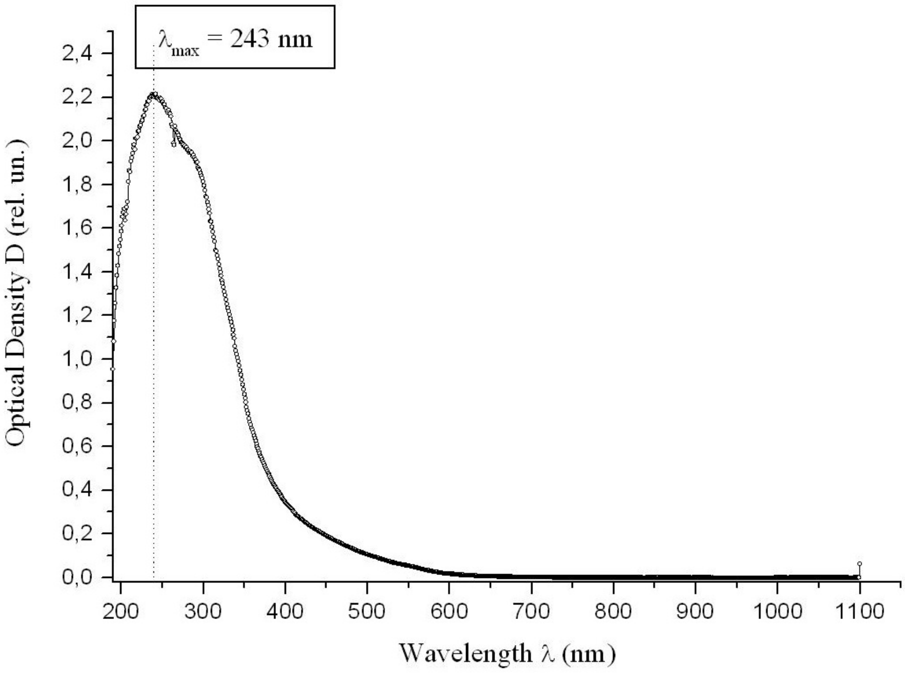


FIG. 2. Electronic spectrum of water solutions of tris-malonate of C_{60} against pure water

One can see that electronic spectrum of tris-malonate of C_{60} in visible and near ultraviolet, near infrared region (250 – 1100 nm) is very simple, it has no light absorption peaks and may be characterized by consequently strengthening of light absorption with the lower wavelengths. In the near infrared region, the spectrum of the tris-malonate C_{60} adduct is practically transparent and has no light absorption. The unique light absorption peak ($\lambda \approx 243$ nm) exists in the spectrum.

The electronic spectrum may be efficiently used for the determination of the concentration via the Beer-Lambert-Bouguer law in near ultraviolet region (for example at $\lambda \approx 330$ nm) (see Fig. 3).

Similar results were obtaines by us earlier during the studying of fullerenols – $C_{60}(OH)_n$, $C_{70}(OH)_m$ [2–5].

3.3. Optical polarizing microscopy

Optical polarizing microscopy was performed with a Leica 4500P instrument. Samples were prepared by crystallization of tris-malonate of C_{60} crystals from water solutions at the isothermal evaporation of water from the solutions with the different concentrations at 25 °C

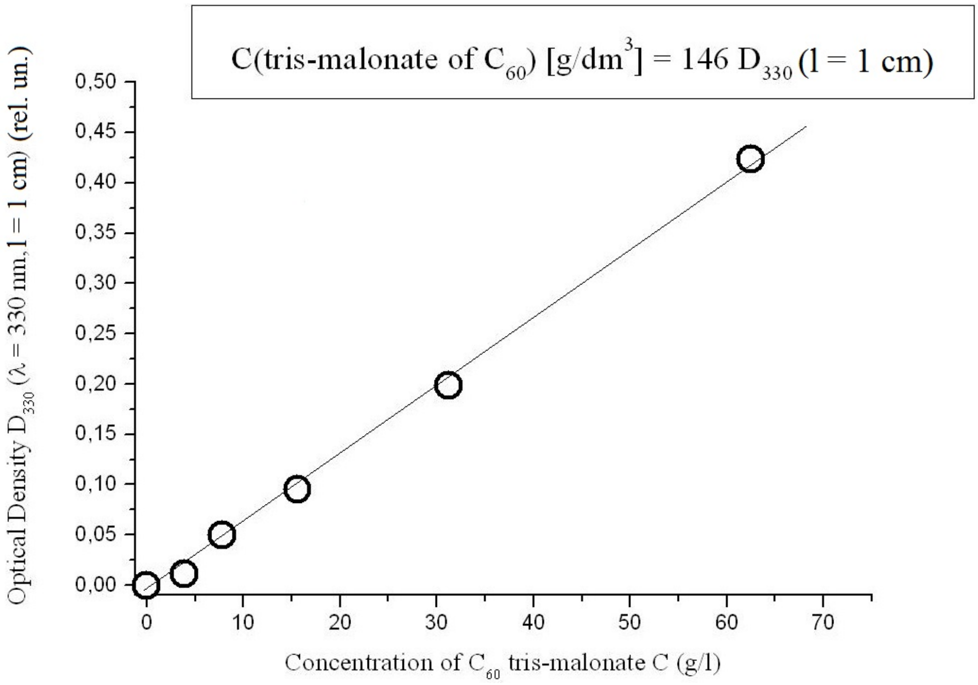


FIG. 3. Buger-Lamber-Ber law at $\lambda = 330$ nm in water solutions of tris-malonate of C_{60}

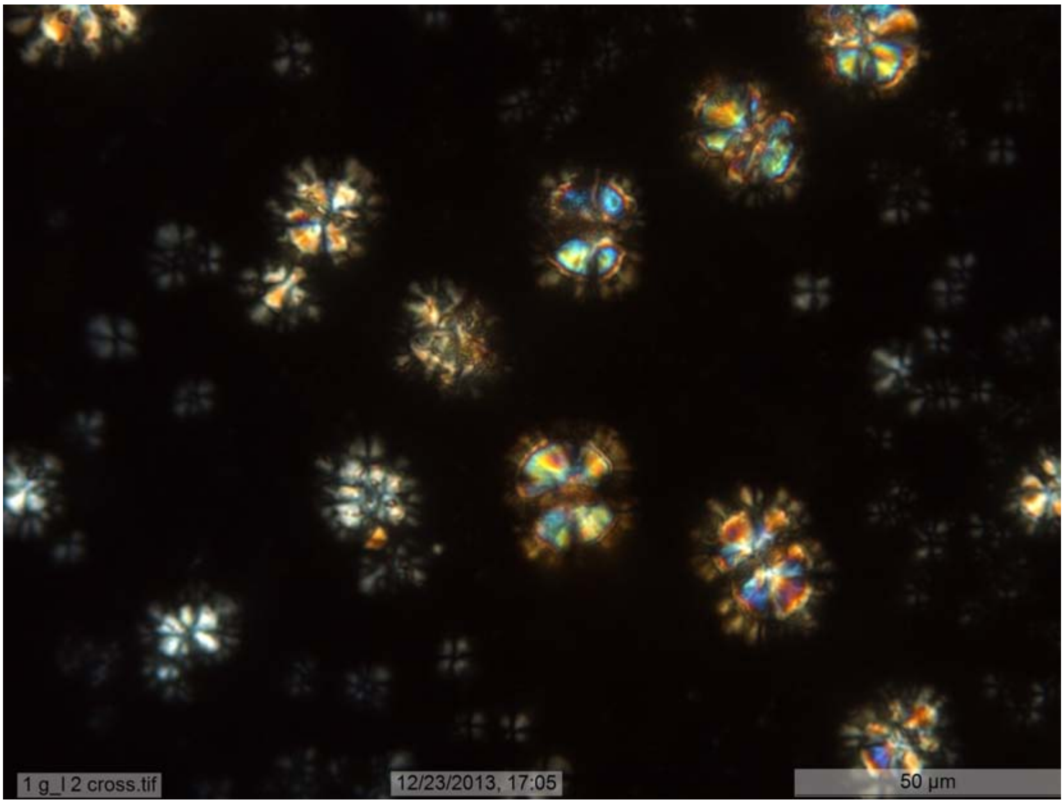


FIG. 4. Optical polarizing microscope photo of the crystals of tris-malonate of C_{60} (scale $\times 500$). Initial (before evaporation) solution had concentration $C = 1$ g of tris-malonate of C_{60} per dm^3

(the drop of the solution was put on the surface of silicate glass). A typical photo is presented in Fig. 4.

Thus, synthesis in gram quantities and identification by the modern methods of physico-chemical analysis of water soluble derivative of light fullerene – $C_{60}[=C(COOH)_2]_3$, was performed.

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