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Spectroscopic study of aqueous solutions of fullerene C_{60} mono-derivatives

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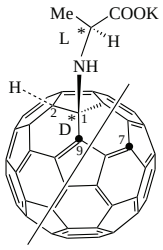
Current spectral study of aqueous solutions of *N*-substituted fullerene C_{60} mono-derivatives of amino acid potassium salts showed that their solutions obey the Bouguer–Lambert–Beer law. On the basis of circular dichroism data, the optical activity was discovered not only for adducts with chiral amino acids but also for those with achiral molecules.



Keywords: C_{60} fullerene, fullerene amino acid derivatives, Bouguer–Lambert–Beer law, ultraviolet–visible spectroscopy, chirality, circular dichroism.

The authors express sincere respect and best wishes to Academician M. P. Egorov on his 70th birthday.

The present research is focused on the study of fullerene C_{60} aqueous colloidal solutions, as well as solutions of salts of *N*-substituted amino acid derivatives of fullerene C_{60}, performed by means of UV–visible spectroscopy (UV). Thus, in the case of water colloidal solutions of fullerene C_{60}, ultraviolet spectra have been found to exhibit an inclined baseline and absorption maxima at 210, 265, and 350 nm.[1,2] The inclined shape of the spectrum can be explained by the presence of nanoparticles and microaggregates of fullerene C_{60} molecules in the studied solutions and thus by the phenomenon of light scattering by particles.[3–5] However, in the case of amino acid derivatives of C_{60} fullerene, a reduction ('smoothing') of the spectral bands is observed (up to complete disappearance of some the bands) with a monotonic decrease in the intensity of the absorption maximum upon transition to the long-wavelength region of the spectrum.[6,7]

In addition to the spectrophotometric method, the circular dichroism (CD) method provided important information about the structural features of the fullerene C_{60} derivatives. Mirror-symmetric CD spectra were presented in work[8] in the wavelength range of 270–770 nm with a maximal band intensity of 6 mdeg for compounds of isobutyrol-D-fullero-3,4-proline-D-alanine-*tert*-butylamine and its stereoisomer in chloroform. Paper[9] describes optically active fulleropyrolidines and fullero-dendrimers for which the Cotton effect is observed in the wavelength range of 400–750 nm with a maximal intensity of about 1–2 mdeg in dichloromethane. Papers[10,11] present the CD spectra of bis-adducts obtained by coupling C_{60} fullerene with chiral malonate derivatives according to the double Bingel reaction. For the mentioned C_{60} fullerene adducts dissolved in dichloromethane or chloroform, mirror-symmetric CD spectra with an intensity of 50–100 or 1–4 mdeg in the wavelength range from 200 to 700 nm were observed, depending on the structure of the obtained compounds.

A rather interesting fact is described concerning enantiomorphic crystallization induction of achiral fullerene derivatives [6,6]-phenyl-C_{61}-butyric acid methyl ester induced by adducts of [6,6]-phenyl-C_{61}-butyric acid, allyl L/D-lactate and *n*-butyl/hydride-terminated polydimethylsiloxane with the formation of surface-segregated monolayers generating films, which demonstrated chiral properties and was useful for chiral organic semiconsductors preparation.[12] Thus, the study of the properties of C_{60} derivatives, including spectrophotometric properties, is of interest not only for the development of fundamental chemistry, but also for practical purposes in organic electronics,[13] cellular imaging, and biomedical applications.[14,15]

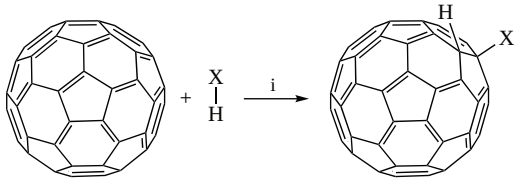
In this work, potassium salts of *N*-substituted amino acid mono-derivatives of fullerene C_{60} **2**–**8** (Table 1) were synthesized according to Scheme 1.[†,16] It was found that for UV-spectra of water solutions of *N*-substituted amino acid mono-derivatives **2**–**8**, the baseline is an inclined curve (see Online Supplementary Materials, Figures S2, S3), and intensive or reduced absorption

[†] Fullerene amino acid mono-derivatives were obtained by the reaction of C_{60} fullerene with the corresponding amino acids.[16] An aqueous colloidal solution of C_{60} fullerene was prepared by extraction into water from an organic (toluene) solvent, using ultrasonic radiation (with a frequency of 42 kHz and a power of 50 W). The concentration of C_{60} fullerene in the resulting aqueous colloidal solution was determined by the gravimetric method.

Table 1 Values of the parameter ε^* for the corresponding aqueous solutions of compounds **1**–**8** (at 210, 265, and 350 nm wavelengths corresponding to the wavelength order, located in the cells from top to bottom).[a]

Code	Name of compound	ε^*/dm^3 mol^{-1} cm^{-1}		
		210 nm	265 nm	350 nm
1	Fullerene C_{60}	73500[b]	33935	28986
2	*N*-(Monohydro-[60]fullerenyl)-L-alanine potassium salt	30619	25012	–[c]
3	*N*-(Monohydro-[60]fullerenyl)-D-alanine potassium salt	17690	13976	–[c]
4	*N*-(Monohydro-[60]fullerenyl)-L-aspartic acid potassium salt	14702 14171	9358	–[c]
5	*N*-(Monohydro-[60]fullerenyl)-D-aspartic acid potassium salt	19231 16658	11019	–[c]
6	*N*-(Monohydro-[60]fullerenyl)-3-aminopropionic acid potassium salt	14360	11579	–[c]
7	*N*-(Monohydro-[60]fullerenyl)-4-aminobutanoic acid potassium salt	34325	25591	–[c]
8	*N*-(Monohydro-[60]fullerenyl)-6-aminohexanoic acid potassium salt	7998	5988	–[c]

[a] Optical density was determined by the sum of absorption and light scattering effects and normatized to the molar concentration calculated based on UV spectra data. The samples were allowed to stand at room temperature for 30 min and mixed thoroughly by shaking before measurement. Absorption spectra were observed in the UV region for aqueous solutions in the range of studied substance concentrations 6.8×10^{-7}–1.0×10^{-4} M. [b] It is not correct to consider the values of the measured parameter ε^* as the values of the extinction coefficient in its conventional meaning, since the value of the extinction coefficient is numerically equal to the value of the absorption intensity recorded in the spectrum. In this case it is the additive value represented by the sum of the effect of the absorption and scattering of light by colloidal particles. [c] The corresponding bands were not detected in the spectra.



1 C_{60} **2**–**8**

2 X = L-Ala (K) residue
3 X = D-Ala (K) residue
4 X = L-Asp (K) residue
5 X = D-Asp (K) residue
6 X = $NH(CH_2)_2CO_2K$
7 X = $NH(CH_2)_3CO_2K$
8 X = $NH(CH_2)_5CO_2K$

Scheme 1 *Reagents and conditions*: i, amino acid potassium salt, *o*-DCB, 18-crown-6, 70 °C, 6 h.

bands are found in the 200–215, 260–275, and 340–355 nm ranges. Figures 1(*a*),(*b*) depict UV-spectra of compound **4** and compound **6**, respectively, demonstrating absorption bands and their intensity.

It has been found that the solutions of both fullerene C_{60} **1** and its amino acid derivatives **2**–**8** obey the Bouguer–Lambert–Beer law (Figure S1), which is consistent with previously published literature data.[17,18] The confirmation of this fact leads to the conclusion that the particle size distribution does not change for at least 30 min after dilution, but this does not exclude a change in the size distribution if incubation after dilution takes a longer time period.

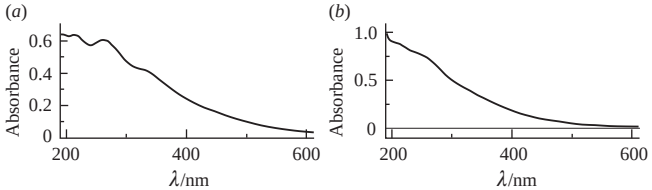


Figure 1 UV-spectra of (*a*) compound **4** at a concentration of 3.6×10^{-5} M and (*b*) compound **6** at a concentration of 9.6×10^{-5} M.

The parameter ε^* is considered here as being numerically equal to the absorption intensity value in the spectrum and conditionally expressing the optical density value as an additive value that characterizes the sum of absorption and light scattering effects (measured for a given wavelength and proportional to the molar concentration). Table 1 shows that all the values of the parameter ε^* decrease with the introduction of a substituent into the fullerene core for each wavelength. This effect appears to be due to the distinctly higher opalescence observed in the aqueous dispersion of fullerene C_{60} than in colloidal solutions of its amino acid derivatives. In addition, it is important to note that the introduction of the substituent into the fullerene core leads to a lower value of ε^* due to interfering effects in the fullerene C_{60} polyethylene system and an increase in the energy of the π–π^* transition. It is also noteworthy that for salts of *N*-substituted amino acids of fullerene C_{60} mono-derivatives containing alanine enantiomers as fragments (compounds **2** and **3**), the ratio of the corresponding values of ε^* is 1.7, which is well correlated with two times different nanoparticle size values observed for solutions of the corresponding compounds.[19]

Considering the proton mobility property of the C_{60}–H bond observed for fullerene derivatives,[20] the quantum-chemical calculations performed in work[21] showed that if two hydrogen atoms were introduced into the fullerene C_{60} structure, the most energetically favorable equilibrium positions of hydrogen atoms in the structure of the fullerene nucleus are positions C(1), C(7) or C(1), C(9) (Figure 2). Taking this into account, we have suggested that the properties of optical activity may occur when adding not only chiral but also achiral amino acid to the fullerene core [see Figure 2(*a*)].

The CD spectra of compounds **2**–**8** were recorded using high resolution equipment to minimize the possible effects of noise caused by nanoparticles or micro-aggregates. The registration of the CD spectra was carried out for aqueous solutions in the concentration range of the studied substances from 2.2×10^{-5} to 1.9×10^{-4} M. Fullerene C_{60} **1** as a symmetrical molecule does not show absorption bands in the CD spectra (Figures S4, S5). The CD spectra of salts of *N*-substituted amino acid mono-derivatives **2**–**8** show the CD values, which lie in the range from 1.5 to 4.5 mdeg for solutions in the concentration range 2.2×10^{-5}–1.9×10^{-4} M in the spectral region from 200 to 250 nm. The position of the detected band relative to the axis corresponding to the scanned wavelengths coincides with that for the individual enantiomers of the corresponding amino amino acid substituents (Figure S4, **6**), which corresponds to the CD values presented in works.[10,11] This fact indicates the appearance of optical properties for the formed adducts in the process of addition of a chiral amino acid to fullerene [see Figure 2(*b*)]. On the basis of the CD

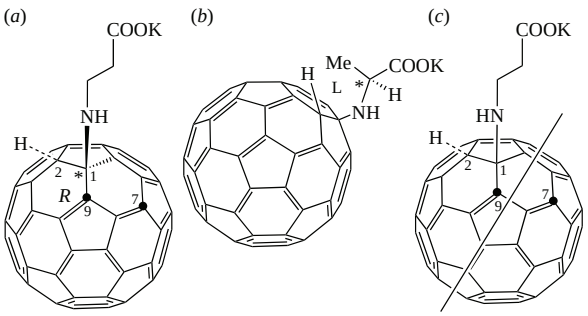


Figure 2 Structure and conformation (*a*) of compound **6** proposing asymmetrical center formation, (*b*) the same for compound **2**, (*c*) for compound **6** proposing a phenomenon of planar symmetry.

spectra data, it has been determined that the addition of achiral amino acids to fullerene C_{60} for the resulting adducts, such as **6**–**8**, may cause the appearance of optical activity. Thus, absorption bands have been found in the CD spectra at 200–300 nm, indicating the presence of optically active adducts as the *R*-isomer [see Figure 2(*a*)]. However, the quality of the CD spectra (signal-to-noise ratio) is low enough, and so they cannot be used for analytical purposes. Such an asymmetry center occurs due to addition of the addend and arises directly at the carbon atom [60] of the fullerene core, which forms a chemical bond with the amino group[22] and the carbon atom [60], bonded to the hydrogen atom.

Thus, using the description of the above mentioned carbon atoms in the fullerene C_{60} structure as the priority positions for adding substitutes for the formation of *N*-substituted amino acid mono-derivatives of fullerene C_{60}, it can be concluded that an adduct with a predominance of a stereoisomer is formed in the reactions, and it has the configuration of an asymmetric center arising in the fullerene structure, defined as *R*-configuration [see Figure 2(*a*)]. This effect can alternatively be explained by the phenomenon of planar chirality [see Figure 2(*c*)]; in this case, the plane of symmetry lies between the substituents in positions C(1) and C(7), C(9) in the adduct [60] fullerene core, and passes through the center of the fullerene sphere.

In accordance with the data obtained in this study, fullerene derivatives **2**–**5** can be considered as diastereomers, for which the ellipticity component of chiral addends exceeds that for the chiral center, the carbon atom of fullerene C_{60} **1**. The results are important for identification (including monitoring of optical activity) of the corresponding compounds or other fullerene C_{60} derivatives, as well as for standardization of their solutions used to solve applied problems in the field of organic electronics and biomedicine.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.10.029.

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