

ORGANIC FUNCTIONALIZATION OF C₆₀ AND C₇₀ FULLERENES BY REACTION WITH ELECTRON-RICH π -SYSTEMS: [8+2]-CYCLOADDITION REACTION - ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL STUDIES

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The reaction of 8-methoxyheptafulvene (**1**) with C₆₀ and C₇₀ leads to tetrahydroazulene-condensed C₆₀ and C₇₀ fullerene derivatives in a 8+2-cycloaddition reaction. The synthesis of C₆₀ with appended fluorogenic subunits is accomplished in a multistep sequence by reacting electron-rich (aryl-)butadienes with C₆₀ fullerene. Spectroscopic data of the new compounds are given. Optoelectrochemical studies were undertaken by using spectroelectrochemical methods.

INTRODUCTION

The present paper summarizes recent results on research in our laboratory dealing with the organic functionalization of fullerenes using electron-rich polyene species. The paper is divided into two sections. The first part describes the syntheses of fullerene derivatives by 8+2 cycloaddition of C₆₀ [1] and C₇₀ and the preparation of fullerene derivatives appended with optoelectronic subunits. In the second section studies to determine the optoelectrochemical properties of fullerenes and the fullerene derivatives by cyclic voltammetry and uv/vis/nir-spectroelectrochemistry are reported.

Fullerene derivatives provide a rich source for optoelectronic applications: The rigidity of the globular molecules together with a multi- π -electron structure leads to fast multistep electron transfer as well as to outstanding optical and photonic properties [2]. Methods to investigate the interplay of electrochemical and spectroscopic properties are provided by optoelectrochemical combination techniques of which uv/vis/nir spectroelectrochemistry is employed in the present study [3].

Cycloaddition reactions have gained supreme acceptance in the functionalization of fullerenes as a successful way for derivatives which by further functionalization lead to covalently attached multifunctional units with perspectives in the field of pharmaceutical, medical and optoelectrochemical materials science chemistry [4].

So far the cycloadditions were limited to the type of 2+1, 2+2, 3+2 and 4+2 reactions [5]. Recently we have shown that electron-rich heptafulvenes are highly efficient 8 π -components in the 8+2 mode of cycloaddition reactions [6]. The underlying synthetic protocol gave access to photochromic dihydroazulenes and electrically conducting polyazulenes (figure 1) [7].

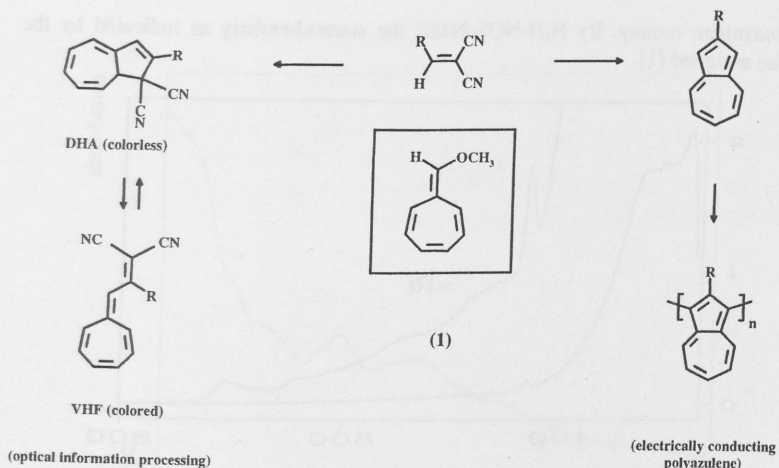


Figure 1: Synthetic 8+2 cycloaddition route of 8-methoxyheptafulvene

The present study reports on the cycloaddition of 8-methoxyheptafulvene (1) with C_{60} (2) and C_{70} (3) in a 8+2 mode generating tetrahydroazulene condensed fullerenes [1]. The strong donor character of 8-methoxyheptafulvene (1) [8] makes it specially suitable for reacting with fullerenes due to their strong electron affinity [9].

[8+2]-CYCLOADDITION REACTIONS OF C_{60} AND C_{70} FULLERENES

The reaction of C_{60} with 8-methoxyheptafulvene (1) leads to a mixture of products from which the main isomer could be isolated by size exclusion chromatography on a polystyrene gel column with chloroform as an eluent. The structure of the C_{60} adduct (4) (figure 2) is proven by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, uv/vis-spectroscopy and the mass spectrum.

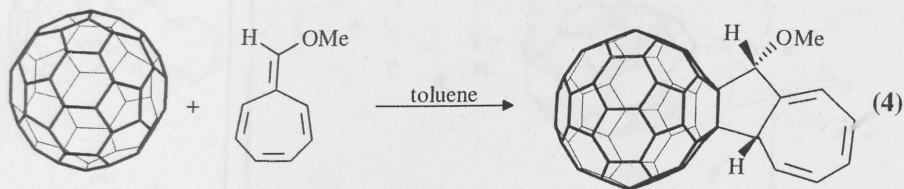


Figure 2: Formation of the 8+2-cycloadduct (4)

The uv/vis-spectrum of (4) (figure 3) has a typical absorption band at 432 nm which is significant of a 6,6-disubstituted fullerene. The $^{13}\text{C-NMR}$ reveals the symmetry reduction from I_h to C_1 accompanied by the cycloaddition. Sixty independent signals of the disubstituted fullerene derivative (4) can be identified for the fullerene core. The $^1\text{H-NMR}$ spectrum reveals

the tetrahydroazulene moiety. By H,H-NOE-NMR the stereochemistry as indicated by the formula can be assigned [1].

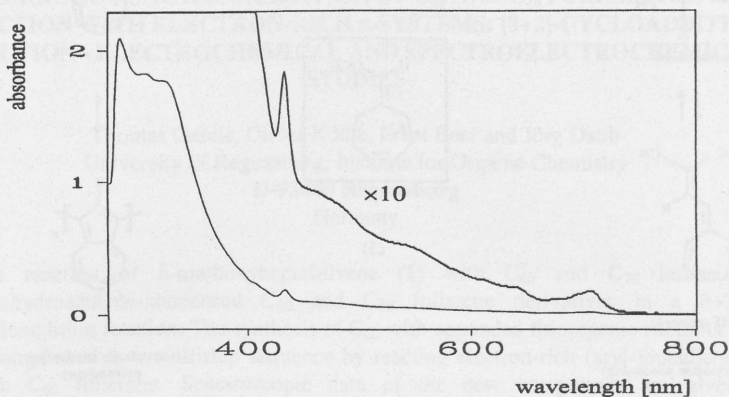


Figure 3: Uv/vis spectrum of (4) in toluene

Cycloaddition reactions at the 6,6-bond moieties can principally occur at four sites of the C_{70} sphere. By all what is known up to now the reaction of (1) with C_{70} at the 6,6-bond close to the pole region under the formation of tetrahydroazulene (5) (figure 4) is preferred due to the adjacent five-membered ring which causes a significant deviation from planarity [10]. The major isomer of the reaction mixture of C_{70} and heptafulvene (1) was separated by size exclusion chromatography on a polystyrene gel column with toluene as an eluent. The structure assignment of (5) follows from $^1\text{H-NMR}$, uv/vis-spectrum and mass-spectrometry. The $^1\text{H-NMR}$ displays the typical absorptions of a tetrahydroazulene substructure (figure 4). The uv/vis-spectrum is displayed in figure 5 showing an absorption at 396 nm which seems to be typical for a reaction at the pole region 6,6-bond [10c].

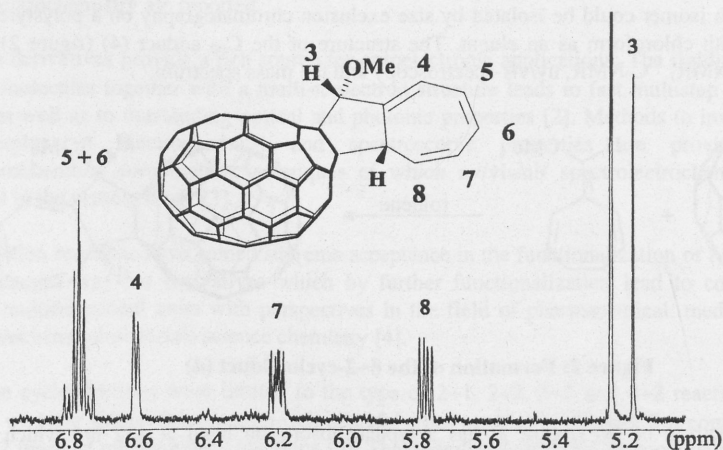


Figure 4: $^1\text{H-NMR}$ in $\text{CD}_2\text{Cl}_2:\text{CS}_2=1:2$ and proposed structure for the c_{70} -tetrahydroazulene (5)

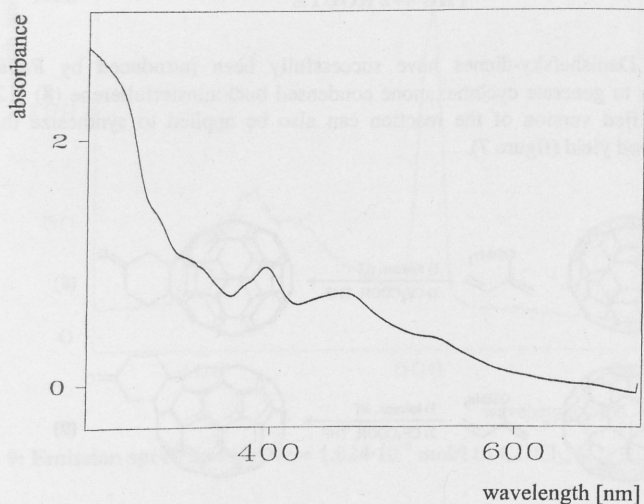


Figure 5: Uv/vis spectrum of (5) in CH_2Cl_2

Tetrahydroazulene subunits provide several options to further functionalize the fullerenes. The reaction of tetrahydroazulene (4) with N-methyltriazaolinedione (6) leads to a mixture of four compounds. The assignment of structure (7) to the main product (figure 6) follows from the mass spectrum and $^1\text{H-NMR}$ which shows an absorption band typical for the polycyclic system [11].

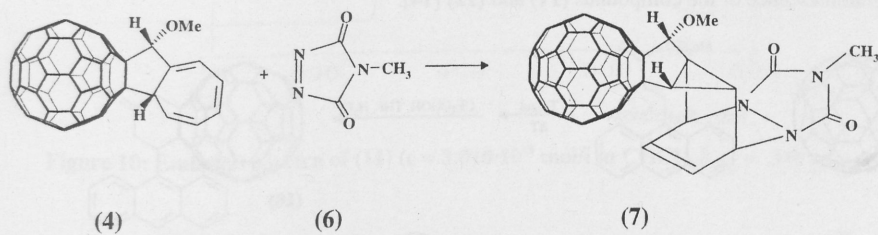


Figure 6: Chemical modification of (4) by reacting with (6)

FULLERENE DERIVATIVES WITH LUMINESCENT FUNCTIONAL GROUPS BY THE 4+2 ROUTE

The electron-rich Danishefsky-dienes have successfully been introduced by *Rubin* and coworkers in order to generate cyclohexanone condensed buckminsterfullerene (**8**) [12]. We found that a modified version of the reaction can also be applied to synthesize the C₇₀-derivative (**9**) in good yield (figure 7).

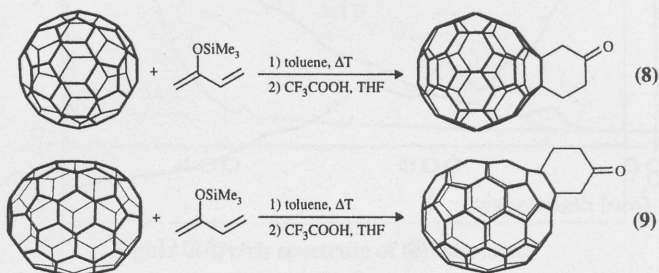


Figure 7: Synthesis of the C₆₀ ketone (8**) and C₇₀ ketone (**9**)**

Furthermore, we applied a butadiene derivative containing an anthracene group to synthesize the anthracene fullerene (**10**). Esterification of the cyclohexanol derivative, obtained by reduction of (**8**), leads to the pyrene derivative (**11**) (figure 8). The structure was proven by ¹H-NMR as well as electron and mass spectroscopy.

As depicted in figures 9 and 10 the pyrene (**11**) and the anthracene (**10**) derivatives show the typical fluorescence spectra of the fluorogenic subunits. The excitation spectra are in agreement with the corresponding uv/vis absorption spectra. The emission intensity in both molecules is increased by at least two orders of magnitude in comparison with the unsubstituted buckminsterfullerene [13]. Investigations are in progress to study the electroluminescence of the compounds (**11**) and (**12**) [14].

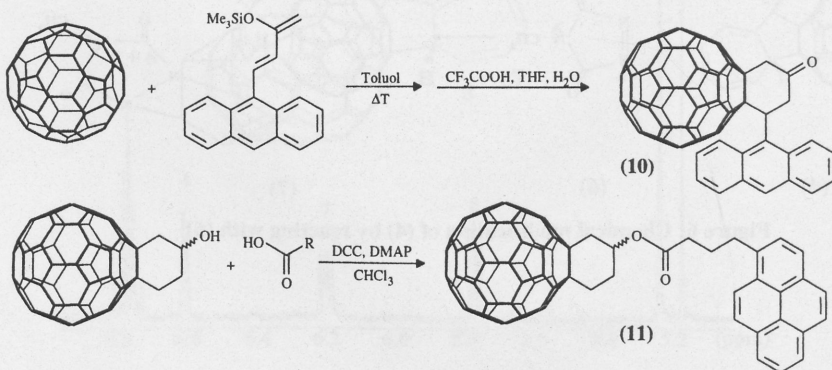


Figure 8: Synthesis of the anthracene(10**) and pyrene derivative (**11**)**

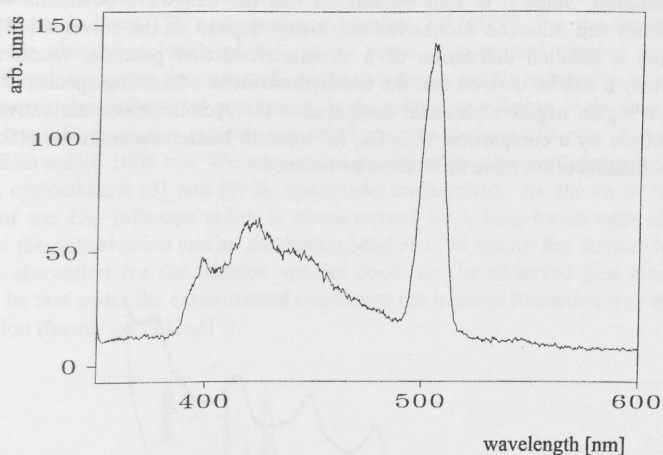


Figure 9: Emission spectra of (10) ($c = 1.024 \cdot 10^{-6}$ mol/l in CHCl_3 , $\lambda_{\text{exc.}} = 252$ nm)

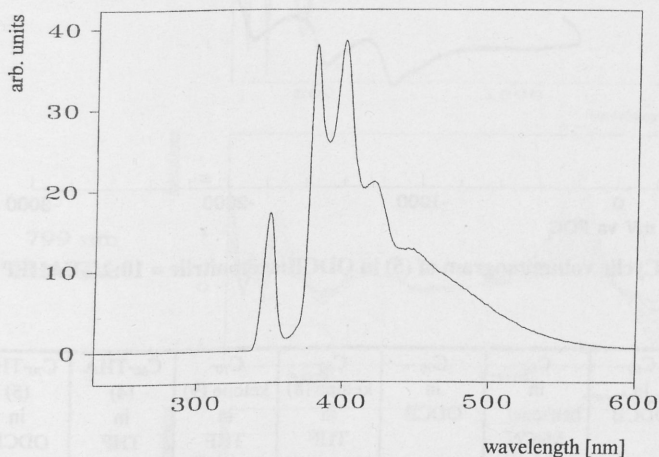


Figure 10: Emission spectra of (11) ($c = 3.010 \cdot 10^{-5}$ mol/l in CHCl_3 , $\lambda_{\text{exc.}} = 346$ nm)

OPTOELECTROCHEMICAL PROPERTIES OF C_{60} AND C_{70} FULLERENES

The electrochemical properties of the C_{60} and C_{70} fullerene cycloadducts (4), (5), (8), and (9) are listed in table 1 together with the reduction potentials of C_{60} (2) and C_{70} (3) for comparison. The cyclic voltammogram of the C_{70} -tetrahydroazulene adduct (5) is shown in figure 1. All the experiments were performed at room temperature using the solvents as indicated and tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. Four reversible waves ($E_{1/2}$) can be obtained on reduction indicating radical anion, dianion, trianion

and tetraanion formation. Since it is well established that the half-wave potentials of the reduction of fullerenes and fullerene derivatives sensitively depend on the solvents [15] one has to refrain from a detailed discussion of a structure/reduction potential relationship. However qualitatively it can be derived that the tetrahydroazulene containing species (4) and (5) are reduced at a higher negative potential compared to the cyclohexanone derivatives (8) and (9). It also follows by a comparison with C₆₀ fullerene in benzene/acetonitrile (10:1) as solvent that the cycloadducts are more difficult to be reduced.

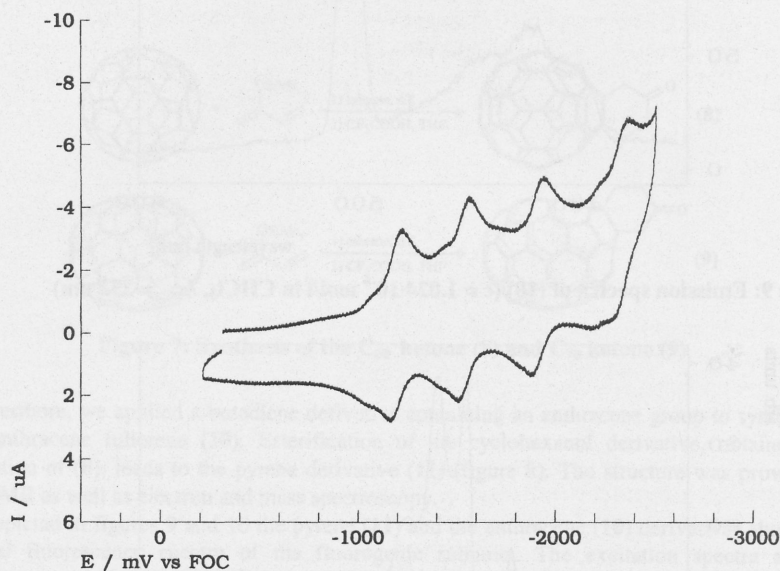


Figure 11: Cyclic voltammogram of (5) in ODCB:acetonitrile = 10:2/TBAHFP

$E_{1/2}$	C ₆₀ in ODCB	C ₆₀ in benzene/ MeCN (10:1)	C ₇₀ in ODCB	C ₆₀ - ketone (8) in THF	C ₇₀ - ketone (9) in THF	C ₆₀ -THA (4) in THF	C ₇₀ -THA (5) in ODCB/ MeCN (10:2)
radical anion	-1120	-990	-1130	-990	-1010	-1090	-1200
dianion	-1500	-1370	-1490	-1540	-1520	-1640	-1540
trianion	-1940	-1900	-1890	-2150	-2020	-2260	-1910
tetraanion	-2400	-2410	-2280	-2610	-2470	-2710	(-2280)

Table 1: Cyclovoltammetric half-wave reduction potentials ($E_{1/2}$) of the parent fullerenes C₆₀ and C₇₀ together with $E_{1/2}$ of the adducts (4), (5), (8), (9) (in mV vs ferrocene, THF = tetrahydrofuran, ODCB = o-dichlorobenzene, TBAHFP = tetra-n-butylammonium hexafluorophosphate, MeCN = acetonitrile)

The reduction processes of the C_{60} adducts (4) and (8) are monitored by uv/vis/nir spectroelectrochemistry (solvent THF, supporting electrolyte TBAHFP). For the tetrahydroazulene adduct (4) the absorption bands of the radical anion, dianion and trianion were obtained, whereas the cyclohexanone derivative (8) could only be reversibly reduced to its radical anion under the spectroelectrochemical conditions. In the following a listing of the long-wavelength absorption bands is given: (4)-radical anion: 984 nm, (4)-dianion: 864 nm, (4)-trianion: 1342 nm, (8)-radical anion: 1006 nm. We were unsuccessful to obtain significant spectral response for the C_{70} cycloadducts (5) and (9) by spectroelectrochemistry. As shown in figure 12 the formation of the C_{70} fullerene anion is characterized by a long-wavelength absorption at 1371 nm for the radical anion and an absorption band at 1174 nm for the dianion form. A long wavelength absorption for the trianion species could not be observed (see also:[15]). The reason may be that under the experimental conditions the trianion formation was accompanied by protonation (formation of $C_{70}H^2$).

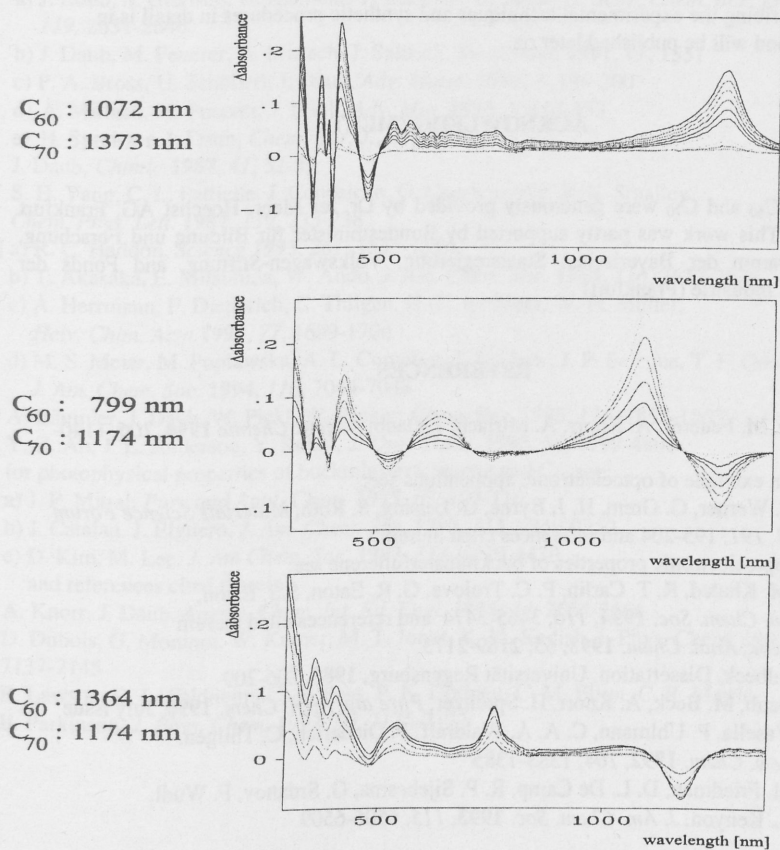


Figure 12: Differential spectroelectrograms of the formation of the radical anion, dianion and trianion of C_{70} in ODCB/TBAHFP. The spectroscopic data for the long-wavelength absorption bands of buckminsterfullerene and C_{70} are given

The buckminsterfullerene derivatives (10) and (11) containing the covalently attached fluorogenic subunits show a cyclic voltammetric and spectroelectrochemical behaviour that is typical for the subunits they are built from. The reversible reductions of (10) and (11) occur almost at the same potentials as the parent C₆₀ fullerene. The spectral changes are also reminiscent to the reduction of the C₆₀ fullerene. The irreversible oxidation peak is due to the fluorogenic dye subunits. While for both species only one reduction step is reversible under thin-layer spectroelectrochemistry conditions, three reversible cyclic voltammetric signals can be detected for the reduction of (11) (half-wave potentials at -1040 mV, -1580 mV, -2190 mV vs ferrocene in THF/TBAHFP). One reversible reduction signal for the radical anion formation of (10) is observed at -1020 mV (vs ferrocene in THF/TBAHFP).

A paper describing the experimental techniques and synthetic procedures in detail is in preparation and will be published later on.

ACKNOWLEDGEMENT

Samples of C₆₀ and C₇₀ were generously provided by Dr. ter Meer, Hoechst AG, Frankfurt (Germany). This work was partly supported by Bundesminister für Bildung und Forschung, Sonderprogramm der Bayerischen Staatsregierung, Volkswagen-Stiftung, and Fonds der Chemischen Industrie (Frankfurt)

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