A facile approach to 2,2'-bipyridine based thiacycrown ethers and their sulfoxides by DA-rDA reaction of 5,5'-bi-1,2,4-triazine thiamacrocycles. The conformation studies

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Abstract

Diels-Alder/retro Diels-Alder (DA-rDA) reactions of 5,5'-bi-1,2,4-triazine thiamacrocycles **4a–c** afforded medium-size 2,2'-bipyridine based thiacycrown ethers **5a–c** in good yield. The latter were oxidized to non-racemic monosulfoxides **7a–c** using Davis oxaziridine and tested as chiral auxiliaries in the asymmetric addition of diethyl zinc to benzaldehyde. The theoretical calculations at DFT /B3LYP/6-311G** level were conducted thus establishing *cis* or *trans* conformational preferences of the target thiamacrocycles.

Keywords: Diels-Alder reaction, thiacycrown ethers, bi-1,2,4-triazine, DFT calculations

Introduction

The macrocycles containing 2,2'-bipyridine (bpy) subunit have a wide range of applications in many areas of chemistry such as catalysis, metal extraction and molecular recognition.¹ Moreover, C₂-symmetric bpy crown-ethers have been developed recently for the enantioselective recognition of amino acids derivatives and chiral organic ammonium salts.² Despite the vast knowledge on sulfur-metal interactions in coordination chemistry,³ the use of S-based ligands derived from bpy appeared to be still rather undeveloped. Such ligands should be able to coordinate to softer metal ions than those containing nitrogen or oxygen as donor atoms, and may constitute a valuable starting materials for the construction of more complex molecular and supramolecular systems.⁴ However, synthetic efforts in this area have been hampered by the lack of the efficient methods of their synthesis.⁵ In our preliminary work⁶ we have shown that 1,2,4-triazine bis-sulfides, tethered to poly(ethylene glycol) chains undergo a remarkably facile, intramolecular cyclization into previously unknown 5,5'-bi-1,2,4-triazine thiacycrown ethers (Scheme 1). The latter undergo an inverse electron demand Diels-Alder/retro Diels-Alder (DA-rDA) reaction with electron rich dienophiles affording bpy, or annulated bpy thiacycrown ethers.⁶

From our preliminary findings and additional applications,⁷ one may assume that the approach is general one for the rings of 13 or more members. Here we would like to present a full account of this work on the synthesis of 16-, 19-, and 22- membered bpy thiacycrown ethers and their conformational studies using the theoretical calculations. The obtained macrocycles were oxidized to non-racemic monosulfoxides by Davis oxaziridine⁸ and tested as chiral auxiliaries in an asymmetric addition of diethylzinc to benzaldehyde.

Results and Discussion

The starting 5,5'-bi-1,2,4-triazine thiacycrown ethers **4a-c** (Scheme 1) were readily prepared via three-step protocol described in our previous paper⁷ which involved, (1) S-alkylation of thiosemicarbazide with the appropriate poly(ethylene glycol)dibromides **1a-c**, (2) condensation of the resulting diquaternary salts **2a-c** with glyoxal and, (3) intramolecular cyclization of such obtained 1,2,4-triazine bis-sulfides **3a-c** with potassium cyanide under high dilution conditions. All steps of the synthesis involve inexpensive, commercially available starting materials and the thiacycrown forming reactions can readily provide 69-77 % yields of **4a-c**.⁷

Scheme 1. Synthesis of cyclophanes **4a-c**.

The preparation of bpy thiacycrown ethers **5a-c** could involve the DA-rDA reaction of **4a-c** with appropriate dienophile (Scheme 2).

Scheme 2. Synthesis of cyclophanes **5a-c** and **6a-b**.

Earlier, it was reported that DA-rDA reactions of 5,5'-bi-1,2,4-triazines with 2,5-norbornadiene in boiling *p*-cymene led to 2,2'-bipyridine derivatives in good yields.⁹ However, this dienophile has never been used in the inverse electron demand DA-rDA reaction of 1,2,4-triazine or bi-1,2,4-triazine based macrocycles. We initially attempted the DA-rDA reaction of **4a** with 2,5-norbornadiene under the reaction conditions mentioned above, (method A), but in addition to the unreacted **4a**, the mixture was obtained containing, as its major component the expected bpy thiacycrown ether **5a** accompanied by some amounts of monoadduct **6a** (Scheme 2). Attempts to increase cycloaddition yields failed, even when long times were used; compound **6a** was still present in the reaction mixture. The similar mixture of products was obtained in reaction of compound **4b** with 2,5-norbornadiene, (Scheme 2). The decrease in reactivity of **6a** and **6b** with 2,5-norbornadiene reflected the decreasing electron-withdrawing effect of pyridine ring in these heterocycles, as compared to starting bi-1,2,4-triazine **4a**. However, when bi-1,2,4-triazine macrocycles **4a-c** were reacted with 2,5-norbornadiene in a sealed Carius tube at elevated temperature under high pressure, (method B), the only products were the corresponding symmetrical derivatives **5a-c** obtained in good yields (Table 1). As the Diels-Alder reaction is known to possess a large negative volume of activation, thus action would serve to raise the ground-state energy of the reactants relative to the transition state, thereby lowering the activation energy.¹⁰ The spectroscopic properties of the bpy thiacycrown ethers **5a-c** are entirely consistent with the functional group present. The preferred conformations of these macrocycles are ascertained by the size of polythioetheral bridge and are determined by analyzing the chemical shifts of 3-pyridyl hydrogens.¹¹ The resonances of such hydrogens in compounds **5a-b** (range from 7.46–7.59 ppm) indicate *cis* arrangement for these biheterocycles. In case of compound **5c** (*n* = 4) however, the chemical shift of 3-H (δ = 8.02 ppm) shows a *trans* conformation for this pentethylene chain ligand. This is consistent with the chemical shifts of pyridine protons (3H, δ = 8.11 ppm) in the parent 6,6'-bis(ethylsulfanyl)-2,2'-bipyridine (Figure 1).¹²

Figure 1. 6,6'-bis(ethylsulfanyl)-2,2'-bipyridine.

Table 1. Reaction conditions, yields and mp of compounds **5a–c**, **6a–b** and **7a–c**

Compound	Method	Time (h)	Yield (%)	Mp (°C)
5a	A ^a	20	31	82–83
5a	B ^b	45	78	82–83
5b	A	24	54	106–107
5b	B	64	70	106–107
5c	B	66	59	118–119
6a	A	20	6	140
6b	A	24	10	138–139
7a	–	24	64	oil
7b	–	24	71	oil
7c	–	24	46	oil

^ain boiling *p*-cymene.^bin sealed Carius tube.

Moreover, these data also prove that twenty two-membered macrocyclic system **4c** exists in *trans* conformation. In contrast, compounds **4a–b**, containing sixteen and nineteen-membered macrocyclic rings exist in *cis* conformation exclusively. Finally, we have evaluated the asymmetric sulfoxidation of compounds **5a–c** using chiral oxaziridine developed by Davis.⁸ The reactions were performed in methylene chloride at room temperature (Scheme 3). Under these conditions the monosulfoxides **7a–c** could be obtained in reasonable or good yield.

Scheme 3. Asymmetric sulfoxidation of cyclophanes **5a–c**.

The preliminary use of these monosulfoxides as chiral auxiliary was tested in asymmetric addition of the diethyl zinc to benzaldehyde, however their catalytic efficiency was poor and the *ee* values of the chiral alcohol thus obtained were much lower than the values observed for other catalysts.¹³

To establish the conformation preferences of 2,2'-bipyridine thiamacrocycles the theoretical calculations for **5a–c** at DFT/B3LYP/6-311++G(d,p) level were undertaken. View of the molecules in conformation obtained after energy minimization and geometrical parameters optimization is shown in Figure 2.

Figure 2. The molecular structures of **5a–c** obtained from DFT/B3LYP/6-311++G(d,p) calculations.

The molecules **5a** and **5b** containing respectively sixteen- and nineteen-membered macrocyclic ring adopt the *cis* (*syn*) conformation with the torsion angle $\phi = \text{N1-C2-C2'-N2'}$ about the central bond of the bipyrindyl system of -23.5° for **5a** and 15.1° for **5b**. In the molecule **5c** with twenty two-membered macrocyclic system the bipyrindyl group is in *trans* (*anti*) conformation with the torsion angle of 163.4° . The calculated conformations of 2,2'-bipyrindine systems in **5a–c** are very similar to those obtained from X-ray analysis of structurally related annulated 2,2'-bipyrindine thiamacrocycles.⁷ In the case of **5a** the *cis* conformation is forced by the strain effect in the twelve-membered thiaethereal chain during the cyclization process. The elongation of the thiaethereal chain in **5b** and **5c** can give the possibility to change the mutual orientation of pyridine rings. The energy effects of the free rotation between the pyridine rings, taking into account the one degree of freedom described by torsion angle ϕ , were calculated for **5b** and **5c** using the AM1 method. The differences in heat of formation, ΔHF , of the conformations were calculated after minimization and all geometrical parameters optimization for each rotation, with a 10° increment from -180 to 180° of ϕ (Figure 3). The calculated conformations with minima of energy are in good agreement with those calculated at *ab initio* DFT level and those observed in the crystalline state of respective annulated 2,2'-bipyrindine thiamacrocycles structurally related to **5b** and **5c**. The energy difference between conformers in maximum (*trans*) and minimum (*cis*) of energy in **5b** is ~ 14.9 kcal/mol. This barrier of energy can inhibit the free rotation at C2-C2' central bond and can prevent the 2,2'-bipyrindyl group changing the *cis* conformation in room temperature. The energy differences between rotamers of **5c**, of about 6.6 kcal/mol, are relatively lower and the tendency in the energy minima distribution to *gauche* and *trans* conformations is good visible. One should notice, that the polarization vectors of N1-C2 and N1'-C2' bonds (as well as C2-C3 and C2'-C3' bonds) in pyridine rings are in the most profitable anti-parallel position in *trans* conformation of 2,2'-bipyrindyl system. The existence of this electronic effect is confirmed by the charge distribution at N1 ($-0.505 e$), C2 ($+0.184 e$), N1' ($-0.508 e$) and C2' ($+0.193 e$) atoms obtained for **5c** from natural bond order (NBO) analysis at DFT/B3LYP/6-311++G9d,p) level. The similar values of charges are also

observed at N1, C2, N1' and C2' atoms of $-0.488 e$, $+0.183 e$, $-0.460 e$ and $+0.207 e$, respectively for **5a**, and $-0.478 e$, $+0.199 e$, $-0.489 e$ and $+0.185 e$, respectively for **5b**, but the *cis* conformation of 2,2'-bipyridyl system in these molecules is the resultant effect of electrostatic dipole-dipole interaction, steric and strain effects in thiaetheral chain, with the predomination of the later. Theoretical calculations showed, that the C_2 symmetry of macrocycles **5a** – **c** is not retained and the conformations of the left and right parts of molecules (*cis-trans-gauche-gauche-gauche-gauche* and *cis-gauche-trans-trans-trans-gauche* in **5a**, *cis-gauche-gauche-trans-gauche-gauche-gauche* and *cis-gauche-trans-trans-trans-gauche-gauche* in **5b** and *cis-gauche-trans-trans-gauche-gauche-trans-gauche-trans* and *cis-gauche-trans-gauche-gauche-trans-gauche-trans-trans* in **5c**) are somewhat different, similarly as in the case of annulated 2,2'-bipyridine thiamacrocycles.

Figure 3. The energy effect upon C2-C2' (ϕ) rotation for **5b** and **5c** using AM1 semiempirical method.

Conclusions

We have demonstrated a facile approach to 2,2'-bipyridine thiacycrown ethers. The preferred conformations of these macrocycles are ascertained by the size of polyetheral bridge and can be determined by ^1H NMR and the theoretical calculations at the DFT level. Further studies on application of the obtained macrocycles as complexing agents are in progress.

Experimental Section

General. Melting points are uncorrected. ^1H and ^{13}C NMR spectra were determined at 200 and 50 MHz, respectively, with a Varian Gemini spectrometer. Chemical shifts (δ) are given in parts per million and coupling constants are given as absolute values expressed in Hertz. Mass spectra

were obtained by using AMD 604 (AMD Intectra GmbH, Germany) and GC/MS QP 5050 Shimadzu (30 m $\times$ 0.25 mm ID-BPX 5 0.25 mm) spectrometers. Elemental analyses were recorded with a Perkin-Elmer 2400-CHN analyzer and the results for indicated elements were within 0.3% of the calculated values. Optical rotation values were measured at room temperature with a JASCO P-2000 polarimeter. The *ee* values were determined by HPLC analysis by using a chiral stationary phase column (chirobiotic T). Thin layer chromatography (TLC) was carried out on aluminium sheets percolated with silica gel 60 F₂₅₄ (Merck). Column chromatography separations were performed by using Merck Kieselgel 60 (0.040-0.060 mm). Solvents were dried and distilled according to standard procedures. Syntheses of 1,8-bis(1,2,4-triazin-3-ylsulfanyl)-3,6-dioxaoctane **3a**, 1,11-bis(1,2,4-triazin-3-ylsulfanyl)-3,6,9-trioxaundecane **3b**, 1,14-bis(1,2,4-triazin-3-ylsulfanyl)-3,6,9,12-tetraoxatetradecane **3c**, 4,7-dioxa-1,10-dithia[10]3,3'-5,5'-bis(1,2,4-triazin-3-ylsulfanyl)cyclophane **4a**, 4,7,10-trioxa-1,13-dithia[13]3,3'-5,5'-bis(1,2,4-triazin-3-ylsulfanyl)cyclophane **4b**, 4,7,10,13-tetraoxa-1,16-dithia[16]3,3'-5,5'-bis(1,2,4-triazin-3-ylsulfanyl)cyclophane **4c** were performed according to our published procedures.^{6,7}

General procedure for the preparation of thiacyclopentanes (**5a-c**) and (**6a-b**)

Method A. A solution of 2,5-norbornadiene (1.8 ml) in *p*-cymene (4 ml) containing compounds **4a-b** (0.59 mmol) was heated for 20-24 h (see Table 1) at 140 °C. The solvent was evaporated in vacuo and the mixture was separated by column chromatography on silica gel, using dichloromethane/acetone (20:1) to give compounds **5a-b**, followed by dichloromethane/acetone (10:1) to afford monoadducts **6a-b**.

Method B. A solution of 2,5-norbornadiene (1.8 ml) in *p*-cymene (4 ml) was added to a Carius tube containing **4a-c** (0.59 mmol). The tube was tightly closed and the mixture was heated for 45-66 h as indicated in Table 1 at 140 °C. The solvent was evaporated in vacuo and the product was purified by column chromatography on silica gel, using dichloromethane/acetone (20:1) as eluent to give pure compounds **5a-c**.

4,7-dioxa-1,10-dithia[10](6,6')-2,2'-bis(pyridine)cyclophane (5a). Method A. 61 mg, 31%; Method B. 153 mg, 78%; white crystals; mp 82-83 °C (lit.⁶ mp 82-83 °C).

4,7,10-trioxa-1,13-dithia[13](6,6')-2,2'-bis(pyridine)cyclophane (5b). Method A: 132 mg, 54%; Method B: 156 mg, 70%; 106-107 °C; ¹H NMR (200 MHz, CDCl₃) δ 3.34-3.37 (m, 4H, SCH₂), 3.49-3.61 (m, 8H, OCH₂), 3.78 (t, *J* = 6.9 Hz, 4H, OCH₂), 7.24 (d, *J* = 7.2 Hz, 2H, pyridine hydrogen atoms), 7.57-7.62 (m, 4H, pyridine hydrogen atoms); ¹³C NMR (50 MHz, CDCl₃) δ 29.3 (SCH₂), 69.7 (OCH₂), 70.8 (OCH₂), 71.1 (OCH₂), 117.8, 122.8, 136.4, 156.2, 158.0 pyridine carbon atoms. Anal. Calcd for C₁₈H₂₂N₂O₃S₂: C, 57.14; H, 5.82; N, 7.41. Found: C, 56.99; H, 5.80; N, 7.26.

4,7,10,13-tetraoxa-1,16-dithia[16](6,6')-2,2'-bis(pyridine)cyclophane (5c). Method B. 132 mg, 75%; mp 63-64 °C; ¹H NMR (200 MHz, CDCl₃) δ 3.07 (s, 2H, CH₂), 3.32-3.37 (m, 4H, CH₂), 3.49-3.56 (m, 8H, OCH₂), 3.76 (t, *J* = 6.4 Hz, 4H, OCH₂), 7.23 (d, *J* = 8.4 Hz, 2H, pyridine hydrogen atoms), 7.58 (d, *J* = 7.8 Hz, 2H, pyridine hydrogen atoms) 8.02 (d, *J* = 7.6 Hz, 2H, pyridine hydrogen atoms); ¹³C NMR (50 MHz, CDCl₃) δ 29.2 (SCH₂), 70.1 (OCH₂), 70.2

(OCH₂), 70.5 (OCH₂), 71.2 (OCH₂), 117.0, 122.9, 136.6, 155.3, 157.4 pyridine carbon atoms. HRMS (EI) calcd for C₂₀H₂₆N₂O₄S₂: 422.13340; found: 422.13504.

10,13-Dioxa-7,16-dithia-4,5,21,22-tetraaza-tricyclo[15.3.1.1^{2,6}]docosa-1(21),2(22),3,17,19-hexaene (6a). Method A. 12 mg, 6%; mp 140 °C; ¹H NMR (200 MHz, CDCl₃) δ 3.47-3.62 (m, 4H, 2xCH₂), 3.68 (s, 4H, 2xCH₂), 3.75-3.93 (m, 4H, 2xCH₂), 7.23 (dd, 1H, *J* = 2.2, 6.6 Hz, pyridine hydrogen atoms), 7.64-7.71 (m, 2H, pyridine hydrogen atoms) 9.36 (s, 1H, triazine hydrogen atom); ¹³C NMR (50 MHz, CDCl₃) δ 28.6 (SCH₂), 29.2 (SCH₂), 69.6 (OCH₂), 69.9 (OCH₂), 70.5 (OCH₂), 70.6 (OCH₂), 119.3, 125.2, 136.6, 142.5, 150.8, 154.0, 160.8 pyridine carbon atoms, 174.6 triazine carbon atoms. HRMS (EI) calcd for C₁₄H₁₆N₄O₂S₂: 336.07147; found: 336.07138.

10,13,16-Trioxa-7,19-dithia-4,5,24,25-tetraaza-tricyclo[18.3.1.1^{2,6}]pentacosa-1(24),2(25),3,20,22-hexaene (6b). Method A. 22 mg, 10%; mp 138-139 °C; ¹H NMR (200 MHz, CDCl₃) δ 3.33-3.49 (m, 4H, CH₂), 3.50-3.61 (m, 8H, OCH₂), 3.72-3.84 (m, 4H, OCH₂), 7.38 (dd, 1H, *J* = 0.9, 7.9 Hz, pyridine hydrogen atom), 7.68 (t, 1H, *J* = 7.6 Hz, pyridine hydrogen atom), 7.79 (dd, 1H, *J* = 1.0, 8.1 Hz, pyridine hydrogen atom), 9.56 (s, 1H, triazine hydrogen atom), ¹³C NMR (50 MHz, CDCl₃) δ 28.6 (SCH₂), 30.6 (SCH₂), 69.4 (OCH₂), 70.4 (OCH₂), 70.6 (OCH₂), 70.7 (OCH₂), 70.8 (OCH₂), 71.0 (OCH₂), 118.9, 125.3, 128.8, 136.8, 142.9, 151.2, 153.8 pyridine carbon atoms, 159.8 triazine carbon atoms. HRMS (EI) calcd for C₁₆H₂₀N₄O₃S₂: 380.09768; found: 380.09817.

General procedure for the preparation of sulfoxides (7a–c) (Davis method)

To a solution of the sulfide **5a–c** (1 mmol) in anhydrous methylene chloride (30 ml), (+)-(8,8'-dichlorocamphorylsulfonyl)oxaziridine (0.75 mmol) was added and the reaction mixture was stirred at room temperature for 24 h. Afterwards, the solvent was evaporated and the residue was purified by flash chromatography using CH₂Cl₂-acetone (10:1.5) as eluent to yield pure monosulfoxides **6a–c**.

4,7-Dioxa-1,10-dithia[10](6,6')-2,2'-bis(pyridine) sulfoxide (7a). 224 mg, 64%; oil; *ee* 22%, [α]_D²⁰ = -32 (*c* 1.0, CH₂Cl₂). ¹H NMR (200 MHz, CDCl₃) δ 3.08-3.38 (m, 2H, OCH₂), 3.50-3.67 (m, 5H, OCH₂), 3.74-4.13 (m, 4H, OCH₂), 4.16-4.27 (m, 1H), 7.22 (d, *J* = 7.7 Hz, 1H, pyridine hydrogen atom), 7.49 (d, *J* = 7.4 Hz, 1H, pyridine hydrogen atom), 7.58 (t, *J* = 7.6 Hz, 1H, pyridine hydrogen atom) 7.77-7.84 (m, 1H, pyridine hydrogen atom), 7.98-8.07 (m, 2H, pyridine hydrogen atoms); ¹³C NMR (50 MHz, CDCl₃) δ 27.7 (SCH₂), 57.1 (SOCH₂), 64.8 (OCH₂), 70.1-71.2 (3C overlapped, OCH₂), 117.6, 119.0, 122.3, 122.4, 136.6, 138.5, 154.9, 156.3, 158.5, 166.0 pyridine carbon atoms. HRMS (EI) calcd for C₁₆H₁₈N₂O₃S₂: 350.07588; found: 350.07552.

4,7,10-Trioxa-1,13-dithia[13](6,6')-2,2'-bis(pyridine) sulfoxide (7b). 278 mg, 71%; oil; *ee* 61%, [α]_D²⁰ = -172 (*c* 1.0, CH₂Cl₂). ¹H NMR (200 MHz, CDCl₃) δ 2.86-3.62 (m, 13H, OCH₂), 3.71-3.78 (m, 1H, OCH₂), 3.96-4.22 (m, 2H, OCH₂), 7.24 (d, *J* = 7.8 Hz, 1H, pyridine hydrogen atom), 7.61 (t, *J* = 7.7 Hz, 1H, pyridine hydrogen atom), 7.87 (d, *J* = 7.6 Hz, 1H, pyridine hydrogen atom), 7.96-8.05 (m, 2H, pyridine hydrogen atom), 8.24-8.33 (m, 1H, pyridine hydrogen atoms); ¹³C NMR (50 MHz, CDCl₃) δ 28.1 (SCH₂), 51.8 (SOCH₂), 60.5 (OCH₂), 69.3

(OCH₂), 69.7 (OCH₂), 70.2 (OCH₂), 70.3 (OCH₂), 70.7 (OCH₂), 117.5, 119.5, 122.1, 123.4, 136.8, 137.9, 154.9, 156.1, 157.1, 163.8 pyridine carbon atoms. HRMS (EI) calcd for C₁₈H₂₂N₂O₄S₂: 394.10210; found: 394.10202.

4,7,10,13-Tetraoxa-1,16-dithia[16](6,6')-2,2'-bis(pyridine) sulfoxide (7c). 201 mg, 46%; oil; *ee* 33%, [α]_D²⁰ = -137 (*c* 1.0, CH₂Cl₂). ¹H NMR (200 MHz, CDCl₃) δ 2.92-3.90 (m, 18H, OCH₂), 4.03-4.16 (m, 2H, OCH₂), 7.26 (d, *J* = 8.0 Hz, 1H, pyridine hydrogen atom), 7.23 (t, *J* = 7.9 Hz, 1H, pyridine hydrogen atom), 7.96-8.09 (m, 3H, pyridine hydrogen atom), 8.42-8.53 (m, 1H, pyridine hydrogen atoms); ¹³C NMR (50 MHz, CDCl₃) δ 27.8 (SCH₂), 49.4 (SOCH₂), 59.3 (OCH₂), 68.9-69.8 (6C overlapped, OCH₂), 115.6, 118.7, 120.0, 122.1, 135.5, 136.7, 153.0, 154.2, 156.3, 162.9 pyridine carbon atoms. HRMS (EI) calcd for C₂₀H₂₆N₂O₅S₂: 438.12831; found: 438.12754.

Theoretical calculations

The energy, geometrical parameters (bond lengths, angles and torsion angles) and charge distribution on the atoms for structures **5a**, **5b** and **5c** were calculated with GAUSSIAN 03¹⁴ at the DFT/B3LYP level with 6-311++G(d,p) basis set. The structures were fully optimized without any symmetry constraints. The AM1 semi-empirical SCF-MO method¹⁵ implemented in the program package WINMOPAC¹⁶ were undertaken to investigate the conformational preferences of 2,2'-bipyridine system of the investigated molecules.

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