ORIGINAL PAPER



Synthesis, crystal structure, theoretical study and application of 1-(4-methylphenyl)-3-(2- (trifluoromethyl)phenyl)triaz-1-ene 1-oxide in the extraction of Ni ions

Synthesis of a new triazene 1-oxide derivative, X-ray crystal structure and its theoretical studies

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Abstract

The crystal structure of 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide (L) is monoclinic and has a space group of $P2_{1}/c$ with a=8.066(2) Å, b=16.740(5) Å, c=11.730(4) Å, $\beta=117.76(3)^{\circ}$ and Z=4. In this study, direct procedures were used to solve the crystalline structure of this complex and refine it by full-matrix least-squares to ultimate values of R1=0.0610 and wR2=0.1661 with 1474 reflections (I>2 σ (I)). The molecule is included in inter-hydrogen bonding with C₅-H₅ acting as donors and O atoms of N-oxide groups as acceptors (O₁······H₅) with a distance of 2.638 Å. These results were also confirmed by theoretical studies. The spectrophotometric titrations of the synthesized L with metal ions showed a substantially greater stability constant for its nickel ion complex with a mole ratio equal to 1. Consequently, the ligand was used for the selective extraction and spectrophotometric determining the Ni²⁺ ion in natural water. Under optimized conditions, the calibrating curve was linear over a nickel concentration range of 9.2×10^{-7} - 8.4×10^{-3} M. The detecting limit of this method was 6.0×10^{-7} M Ni²⁺. No considerable interference was found from at least 100 times concentrations of a number of possibly interfering ions.

Keywords Triazenes \cdot X-ray structure \cdot Hydrogen bond \cdot Solution studies \cdot Extraction \cdot Ni^{2+}

Introduction

Over the last 130 years, numerous compounds such as 1,2,3-triazene moieties have been studied for their interesting structural, biological, pharmacological, and reactivity features. These compounds are utilized in combinatorial chemistry, medicinal, organometallic ligands, and in natural synthesis [1]. Meldola (1887) performed the first comprehensive study on a triazene derivative's coordination chemistry (1,3-diphenyltriazene) [2].

The main characteristic of the triazene compounds is having a diazoamino group (-N = NN) normally with a trans

Behrooz Rezaei rezaei128@yahoo.com; rezaei_b@lu.ac.ir configuration in the ground mode [3]. Hydroxytriazenes as the single crystal are transformed into N-oxide form and represent the structure's tautomeric form. Kuroda [4] synthesized 3-(4-carbamoylphenyl)-1- methyltriazene 1-oxide and reported anti-tumor activity of this group of compounds in hydroxyl and N-oxide forms. The N-oxide instead of N-hydroxyl form is adopted by the molecule consistent with the X-ray and spectroscopic evidence.

This study is the continuation of our previous works on the synthesis, complexation, and theoretical studies of a new triazene derivative—i.e., 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide (Scheme 1) [5–7]. Similar to the specific complexing ability of triazene derivatives toward transition metal ions, it was found that the absorbance of the title compound (**L**) leads to a considerable decrease upon addition of Ni²⁺ ion in a selective manner. Thus, the analytical application of ligand **L** is studied

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Scheme 1 Chemical structure of the title compound

regarding the selective extraction and spectrophotometric determining of Ni^{2+} ion in aqueous solutions.

Experimental

Reagent

Analytical-grade reagents including n-Hexane, chloroform, acetonitrile, ethanol, ether, carbon tetrachloride, and carbon tetrachloride (from Merck or Aldrich) were used without any further purification. The materials for the synthesis (4-nitro toluene and 2-aminobenzotrifluride) were bought from Fluka and used as received. All bases and acids, which had the maximum purity, were purchased from Merck and utilized as received. Throughout the tests, deionized doubledistilled water was utilized. Nitrate salts of other cations (all from Merck) and analytical grade nickel(II) nitrate had the maximum available purity and utilized without further purification, expect vacuum drying. The normal stock solution of Ni(II) was prepared by dissolving a proper quantity of nickel(II) nitrate in 2 mL concentrated nitric acid and diluting it to 100 mL with water. The stock solution was diluted appropriately to prepare working solutions.

Apparatus

A Shimadzu spectrophotometer with (Japan) model 1650PC double-beam was utilized to run the electronic absorption spectra. The pH modifications were performed using the Jenway pH meter (model 3020) equipped with an integrated glass-calomel electrode.

Computational details

Structures of the title compound in two conformations and in dimer form were optimized using B3LYP [8, 9] method and also exchange and association functional with 6-311 g(d,p) base set. The vibrational frequencies were done at the identical level of theory to confirm all structures are in global minimum. All calculations were completed using the Gaussian 09 package [10]. The electronic density of state (DOS) for the optimized structures of monomer and dimer was done using GaussSum03. Gap energy (Eg) was calculated based on DOS results:

$$E_g = E_{\text{LUMO}} - E_{\text{HOMO}}$$

where E_{HOMO} is the energy of highest occupied molecular orbital (HOMO), and E_{LUMO} is the energy of lowest unoccupied molecular orbital (LUMO). The NBO analysis was done to estimate the natural charge distribution around the dimer of molecule.

Results and discussion

Synthesis of 1-(4-methylphenyl)-3-(2-(trifluoromet hyl) phenyl) triaz-1-ene 1-oxide

The ligand L was synthesis with essentially the same method reported elsewhere for the synthesis of its isomer, with some modifications [7]. Zinc dust (35 g) and ammonium chloride (16.0 g) were used to reduce an aqueous-alcoholic (2:1) solution with 0.2 M (26.47 g) of 4-nitrotoluene at 60–65 °C. Zinc dust was completely added in around 1 h. Next, the obtained N-hydroxy-4-methylaniline was combined with the diazotized product of 2-aminobenzotrifluoride 0.1 M (12.39 ml) at 0-5 °C. It led to a yellowish-brown precipitate filtered under suction that was rinsed with ice-cold water. Ethanol was used twice to recrystallize the crude product, and yellow needles were attained (the yield of almost 60%). The compound's m.p. was 115 °C.

To prepare appropriate single crystals, a branched tube technique was used. The title compound (0.2 g) was located in one arm of a branched tube and both arms were filled by adding n-Hexane carefully. Then, the tube was sealed and the arm comprising ligand was submerged in a bath at 50 °C, while the other arm was maintained at ambient temperature. The crystals were deposited in the cooler arm after 5 days during which the arm was filtered-off, rinsed with ether, and dried in the air [5, 6].

X-ray crystallographic structure of 1-(4-methylphen yl)-3-(2-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide

Crystallographic measurements were performed at 293(2) K utilizing a Nonius kappa-CCD diffractometer. Using direct approaches, the structure of 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide was solved and refined via full-matrix least-squares methods on F^2 utilizing SHELXTL. [11] The values of geometric parameters of the title compound are in standard experimental errors and ranges. The title compound's geometric parameters are

within the common ranges. It is crystallized in the monoclinic system, space group $P2_1/c$ with a = 8.066(2) Å, b=16.740(5) Å, c=11.730(4) Å, β =117.76(3)° and Z=4. With 1474 reflections, the crystal structure was solved to ultimate values wR2=0.1661 and R1=0.0610 (I>2 σ (I).

The N–H hydrogen atom was placed in a Fourier map with a different density to refine its locations at a standard deviation of 0.02 Å and an N-H distance of 0.86 Å. All other hydrogen atoms were placed in the assigned locations. Also, all H atoms were refined considering an isotropic displacement parameter of 1.5 (methyl) or 1.2-times (all others) isotropic displacement parameter of the nearby nitrogen or carbon atom. Table 1 represents the equivalent structural refinements and crystal. Also, Table 2 provides all atomic coordinates and corresponding isotropic displacement parameters.

The crystal contains discrete molecules (Fig. 1a). The torsion angles of C(1)-N(1)-N(2)-N(3) and N(1)-N(2)-N(3)-C(8) are—178.2(2)° and 179.3(2)°, and the triaz-1-ene group is planar. According to Fig. 1b, the molecules are included in inter-hydrogen bonding with C_5 -H₅ acting as donors and

 Table 1
 Crystal data and structure refinement details for 1-p-tolyl-3-(3-(trifluoromethyl)phenyl)triaz-1-ene-1-oxide

Chemical formula: C ₁₄ H ₁₂ F ₃ N ₃ O		
Formula weight = 295.27		
T = 293(2) K		
Crystal system: monoclinic	space group: P21/c	
a = 8.066(2) Å	$\alpha = 90.00$	
b = 16.740(5) Å	$\beta = 117.76(3)$	
c = 11.730(4) Å	$\gamma = 90.00$	
$V = 1401.6(7) \text{ Å}^3$	Z=4	
$D_x = 1.453 \text{ g/cm}^3$		
Radiation: Mo K α ($\lambda = 0.71069 \text{ Å}$)		
μ (Mo K _a) = 0.118 mm ⁻¹	F(000) = 608	
Crystal size = $0.60 \times 0.45 \times 0.40$ mm		
No. of reflections collected $= 3911$		
No. of independent reflections $=$ 2000		
θ range for data collection: 1.0 to 23.3°		
Data/restraints/parameters = 2000/60/220		
Goodness-of-fit on $F^2 = 1.040$		
<i>R</i> indices $[I > 2\sigma(I)]$: <i>R1</i> = 0.0610, <i>wR2</i> = 0.1661		
<i>R</i> indices (all data): $R1 = 0.0810$, wR2 = 0.1848		
$(\Delta/\delta)_{\rm max} = 0.001$		
$(\Delta \rho)_{\rm max} = 0.353 \ {\rm e}{\rm \AA}^{-3}$	$(\Delta \rho)_{\rm min} = -0.228 \ {\rm e}{\rm \AA}^{-3}$	
Measurement: Nonius kappa-CCD		
diffractometer		
Program system: SHELXL-97		
Structure determination: SIR97		
CCDC deposition number: 721301		

Table 2 Atomic coordinates and equivalent isotropic displacement parameters [in $Å^2$] for 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

Atom	X	Y	Z	U(eq)
O(1)	0.0216(3)	0.27238(13)	0.1040(3)	0.0913(8)
N(1)	0.0785(3)	0.41558(14)	0.1509(2)	0.0669(7)
N(2)	0.1942(3)	0.37985(14)	0.1145(2)	0.0627(7)
N(3)	0.1562(3)	0.30580(14)	0.0925(2)	0.0655(7)
C(1)	0.0953(4)	0.49725(16)	0.1755(2))	0.0585(7)
C(2)	0.2396(4)	0.54016(16)	0.1717(3)	0.0675(8)
C(3)	0.2548(5)	0.62114(18)	0.1949(3)	0.0789(9)
C(4)	0.1274(5)	0.66083(19)	0.2218(3)	0.0815(10)
C(5)	-0.0143(5)	0.61873(19)	0.2275(3)	0.0788(9)
C(6)	-0.0323(4)	0.53748(17)	0.2050(3)	0.0657(8)
C(7)	-0.1875(5)	0.49481(18)	0.2112(3)	0.0904(10)
F(1)	-0.3046(4)	0.4604(2)	0.1010(3)	0.1379(14)
F(2)	-0.2951(4)	0.54017(17)	0.2413(4)	0.1405(14)
F(3)	-0.1333(5)	0.4345(2)	0.2928(4)	0.1609(17)
C(8)	0.2694(4)	0.26017(16)	0.0508(3)	0.0638(8)
C(9)	0.4184(4)	0.29470(18)	0.0428(3)	0.0752(9)
C(10)	0.5221(5)	0.2492(2)	0.0010(3)	0.0832(10)
C(11)	0.4805(5)	0.1696(2)	-0.0326(3)	0.0810(10)
C(12)	0.3306(5)	0.1370(2)	-0.0237(3)	0.0864(10)
C(13)	0.2238(5)	0.18116(18)	0.0173(3))	0.0768(9)
C(14)	0.5990(6)	0.1207(3)	-0.0738(4)	0.1174(15)

Estimated standard deviations are given in parentheses

N-oxide groups' O atoms as acceptors $(O_1 \dots H_5)$ with a distance of 2.638 Å. Packing the resultant crystal (Fig. 2) demonstrates the creation of a one-dimensional network. This network is attributed to the existence of intermolecular weak hydrogen bonding and C_9 - H_9 - \dots F_1 interactions with the distance of 2.626 Å between the neighboring molecules, which are responsible for the one-dimensional framework of the crystal. Table 3 provides the equivalent distances for the hydrogen bonds. Moreover, face-to-face π - π stacking interactions exist within aromatic rings of the nearby chains in this compound.

Theoretical studies

Figure 3 presents the optimized structures of the title compound in two enol and enoxide forms.

The results of geometry optimization and energy analysis show that structure A is more stable than B. This result is in accordance with experimental observations. To study the hydrogen bonding formation between two monomers, the structure of its dimer was optimized, which its geometry is illustrated in Fig. 4.

The optimized geometry of dimer shows that the hydrogen bonding formed between the hydrogen of the phenyl





Fig. 1 a ORTEP representation and b showing hydrogen bonding in the compound 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide

group in one monomer and O and F in the other monomer. The IR spectrum of this dimer is shown in Fig. 5.

The lack of imaginary frequency in the calculated IR spectrum confirms the stability of the structure of this dimer. Using the optimized structures of monomer and dimer, the DOS spectra for them was calculated. The result of DOS calculation is illustrated in Fig. 6.

Employing the DOS spectra the HOMO and LUMO energies were calculated and the results of $E_g = 3.73$ and $E_g = 3.29$ were obtained for monomer and dimer structures, respectively. A minor reduction of E_g was observed in dimerization of the structure. For dimer structure, the NBO

analysis was done to estimate the charge distribution around its structure. In Fig. 7, the result of NBO analysis is shown.

As depicted in NBO analysis, the hydrogen atoms which contribute in hydrogen bonding formation have positive values (+0.235 and +0.215) and the oxygen and fluorine atoms contributed in hydrogen bonding formation have negative values (-0.557 and -0.362). From the NBO analysis, it can be estimated that the hydrogen bonding between the hydrogen and oxygen atoms has relatively more strength than the hydrogen bonding created between the hydrogen and fluorine atom. The HOMO and LUMO profile of the dimer structure were calculated, which is illustrated in Fig. 8. **Fig. 2** Packing and O…N and F…H interactions shown between the parallel molecules in the 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl)triaz-1ene 1-oxide



Table 3 Hydrogen bond distances (in Å) of 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl) triaz-1-ene 1-oxide

	d(D-H)	d(HA)	d(DA)
C ₅ -H ₅ O ₁	d=0.931	d=2.638	d=3.261
C ₉ -H ₉ F ₁	d=0.930	d=2.626	d=3.425

The results of Fig. 8 show that the HOMO orbital mainly located on the specie which have hydrogen of hydrogen bonding and LUMO orbital mostly located on the specie having the oxygen and fluorine atoms.

Spectral features

Complexing the molecule 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl)triaz-1-ene 1-oxide by increasing the concentration of the various metal ions was evaluated spectrophotometrically at room temperature in acetonitrile solution. For the sake of simplicity, we indicated only the absorption spectra of the title compound known as Ni²⁺. As can be seen from Fig. 9, the robust absorption of the ligand at about 350 nm declined by increasing the concentration of the Ni²⁺. Figure 10 presents the resulting absorbance as a function of [metal ion]/[triazene] mole ratio for different metal ions. According to Fig. 10, for most of the other investigated metal ions, i.e., Pb²⁺, Ag⁺, Mn²⁺, Cd²⁺⁺, Hg²⁺, Cu²⁺, Co²⁺, and Zn²⁺, small or insignificant variations in the



Fig. 3 The structures of title compound in enol (A) and enoxide (B) forms



Fig. 4 The optimized structure of the dimer of title compound







Fig. 6 The results of DOS calculation for the monomer and dimer structures



Fig. 7 The NBO analysis of dimer structure



HOMO

Fig. 8 The HOMO and LUMO profiles of the dimer structure



LUMO



Fig. 10 Absorbance of a 5×10^{-5} M of L ligand solution at about 350 nm, as a function of metal ion/triazene mole ratio for different metal ions

Fig. 9 Absorbance spectra of a 5×10^{-5} M of L ligand solution in acetonitrile, at different Ni²⁺ concentrations. The arrow shows the direction of absorbance changes by increasing the metal ion concentration

absorbance maximum are found by altering the [metal ion]/ [triazene] mole ratio. Also, in all studied cases, the creation of a 1:1 complex in the solution is represented by such an absorbance-mole ratio plots performance (Fig. 10). The curve-fitting program KINFIT [7, 12] was used to evaluate the formation constant from the absorbance versus [metal ion]/[triazene] mole ratio data. The results showed that logK_f of 5.60 ± 0.01 for Ni²⁺, 3.67 ± 0.01 for Co²⁺, 3.41 ± 0.02 for Pb²⁺, 3.29 ± 0.02 for Cd⁺², and < 3 for other metal ions. Hence, considering the selectivity orders gained from the solution examinations, in the next step, **L** was used as a very suitable and selective complexing reagent to recognize Ni^{2+} over the other metal ions in an analytical application and separation processes. However, various factors exist that need to be enhanced prior to use.

Analytical application

Another goal of this study was to assess the possibility of using L (Scheme 1), as a chelating agent for the extraction and preconcentration of Ni(II) in natural waters, under optimum conditions. The effects of various experimental factors such as pH, nature of the organic solvent, salt effect, period of extraction, ligand concentration, and the volume ratio of organic phase on the extraction yield were investigated, and



Fig. 11 Effect of pH on the extraction percent of Ni²⁺ using L. 10 ml of 1.0×10^{-5} M Ni²⁺ in aqueous solution was extracted by 2 ml of 5.0×10^{-5} M L as an extractant in chloroform

Ni²⁺ was determined from 10 ml of the aqueous solution as described in [13]. The metal ion concentration in the organic phase was defined by spectrophotometry.

The findings indicated that extracting the nickel ions was complete in the pH range of 6.5–8.5 (Fig. 11). Therefore, pH=7.5 was selected as the optimal pH for further works. Greater pH values (>10) were not utilized due to the likelihood of the Ni(II) hydroxide formation in solution.

The extraction time was studied in the time range of 30 to 210 s. The quantitative extraction of Ni(II) was obtained in 120 s. Prolonged shaking did not have any considerable impact on the target analyte extraction.

The suitability of several solvents such as carbon tetrachloride, chloroform, benzene, and hexane was assessed for the extraction of Ni^{2+} ions from the aqueous phase. It was indicated that chloroform could be used to extract the complex of the metal ion. In other diluents, extraction was incomplete. The other analytical data for the extraction were investigated as reported in [10]. A list of the experimental conditions in the liquid–liquid extraction is given in Table 4.

As shown in Fig. 12, λ_{max} of the complex in the organic phase is 421 nm, while the L did not show a significant absorbance at this wavelength. Hence, 421 nm was chosen for measuring the absorbance. The proposed extraction

Parameter	Analytical feature
Extraction time	120 s (at room temperature)
рН	7.5
Concentration ratio of L to Ni ²⁺	5:1
The salt concentration	0.5 M
Ratio of organic to aqueous phase	1:5 ratio
Limit of detection (mol l^{-1})	6.0×10^{-7}
Linear range (mol l^{-1})	$9.2 \times 10^{-7} - 8.4 \times 10^{-3}$
Regression equation, $[Ni^{2+}]$ (mol.L ⁻¹)	$y = 78750[Ni^{2+}] + 0.014$



Fig. 12 Absorption spectra for ligand L (curve 1), and its Ni²⁺ complex (curve 2) in chloroform. Condition: 10 ml 0f 4.0×10^{-5} M Ni²⁺ in aqueous solution extracted by 2 ml of 4.0×10^{-5} M L in chloroform

procedure is described in the following: A 10-ml aliquot of an aqueous solution containing 8.0×10^{-6} M of Ni(II) at pH=7.5 was transported to a separatory funnel. Adding 2 ml chloroform containing 4.0×10^{-5} M of L to funnel, it was shaken for 2 min until reaching the desired mixture. The two phases were permitted to relax and discrete completely. Then, the yellow-colored organic phase was separated, and its absorbance was measured at 421 nm versus a reagent blank solution.

To assess the selective separation and determine Ni²⁺ ions from binary mixtures with various metal ions, an aliquot of solution (10 ml) was taken comprising 5.0×10^{-5} M of Ni(II) ions and a varying amount of some other cations. As shown in Table 5, Ni²⁺ ions in the binary mixtures were extracted almost completely and do not represent significant interfering impacts at a 1:100 ratio.

The suggested technique was used for separating and determining Ni^{2+} ions in some natural water samples. The findings of the analysis provided in Table 6 indicate a good consistency within the values measured utilizing the suggested technique and those reported with atomic absorption spectrometry (AAS) laboratory at Lorestan University, Khorramabad, Iran. Overall, it can be concluded that the new triazene-1-oxide derivative **L** is selective to Ni^{2+} and can be utilized in the determination of this ion in real specimens.

Conclusion

X-ray spectroscopy was used to synthesize and characterize the 1-(4-methylphenyl)-3-(2-(trifluoromethyl)phenyl)triaz-1ene 1-oxide (L). The compound L crystallizes in the space group $P2_1/c$ of a monoclinic system with 4 molecules in

Table 5 Effect of various metal ions on the preconcentration and determination of Ni(II) ions with the recommended method^a

Interfering ion	Ratio interfering ions/ Ni ²⁺	Recovery of Ni ²⁺ ions (%)
Ag ⁺	200	98.2
Ca ²⁺	200	98.3
Ba ²⁺	200	98.6
Cd^{2+}	100	97.2
Cu ²⁺	150	96.5
Co ²⁺	100	97.2
Zn ²⁺	200	98.5
Pb ²⁺	100	97.6
Fe ³⁺	200	96.7
Cr ³⁺	200	97.6
Hg ²⁺	150	97.9
Mg ²⁺	200	96.9
Pd ²⁺	200	98.1
Mn ²⁺	200	98.0
Na+	300	98.9
K+	300	98.4

^a5.0 ×10⁻⁵ M of Ni(II) ions and different amounts of other cations in 10 mL of sample solution was used. (In the final solution: $CHCl_3$ volume = 2 mL, shaking time: 2 min, [L] = 2.0×10^{-4} M, period of extraction = 120 s, pH = 7.5)

Samples	$\mathrm{Ni}^{2+} (\mathrm{mol} \ \mathrm{L}^{-1})^{\mathrm{a}}$		
	proposed method	AAS	
River water of kakareza	$2.63(\pm 0.24) \times 10^{-6}$	2.47×10^{-6}	
Spring water of Golestan	$2.16(\pm 0.18) \times 10^{-6}$	2.09×10^{-6}	
Spring water of Tirebazar village	$1.35(\pm 0.19) \times 10^{-6}$	1.45×10^{-6}	

 $^{\mathrm{a}}\text{Values}$ in the parentheses are % RSD based on the three replicate analyses

the unit cell of dimensions a = 8.066(2) Å, b = 16.740(5) Å, c = 11.730(4) Å, $\alpha = 90.00^{\circ}$, $\beta = 117.76^{\circ}$, and $\gamma = 90.00^{\circ}$. The complexation studies of triazene-1-oxide derivative **L** with a variety of metal ions including Ni²⁺, Ag⁺, Pb²⁺, Mn²⁺, Hg²⁺, Cd²⁺, Zn²⁺, Cu²⁺, and Co²⁺ were carried out by a spectrophotometry method in acetonitrile solution at room temperature. Therefore, based on the selectivity orders attained from the solution studies, the ligand was successfully used as an extractant for the selective extraction of Ni²⁺ ion over the other metal ions in separation processes.

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Compliance with ethical standards

Conflict of interest The authors state that they have no conflicts of interest.

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