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Structural, electrochemical and optical properties of di-2-pyridyl ketone 2-furoic acid hydrazone (dpkfah)

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Abstract

Crystals of di-2-pyridyl ketone 2-furoic acid hydrazone (dpkfah), obtained from a dmso (dimethylsulfoxide) solution of dpkfah, are in the monoclinic space group, $P2_1/n$. Structural analysis reveals planar hydrazone moiety, non-coplanar pyridine rings and infinite chains of anti-parallel dpkfah dimers interlocked via a web of hydrogen bonds. Electrochemical measurements on dpkfah in non-aqueous solvents show solvent dependence, single and multi-electronic transfers and electrochemical transformation(s) following the first oxidative or reductive electronic transfer. Optical measurements on dpkfah in non-aqueous solvents show strong solvent dependence. In non-polar solvent such as CH₂Cl₂ a single electronic absorption band with extinction coefficient of 18,600 \pm 2000 M⁻¹ cm⁻¹ appeared at 325 nm and in polar solvents a low-energy absorption band at ~396 nm and a high-energy absorption band at ~320–335 nm appeared that are concentration, temperature and salt dependent. In the presence and absence of NaBF₄ and NaBH₄, extinction coefficients of $21,000 \pm 2000$ and $22,500 \text{ M}^{-1} \text{ cm}^{-1}$, and 17,200 \pm 2,000 and 23,000 M⁻¹ cm⁻¹ were calculated for the low and high energy electronic states of dpkfah in dmf and dmso, respectively at 295 K. Thermo-optical measurements on dpkfah in dmso and dmf confirmed the reversible interconversion between the high and low energy electronic states of dpkfah and allowed calculations of their thermodynamic activation parameters and gave changes in enthalpy (ΔH^{\varnothing}) of +47.5 ± 1.2 and -16.3 ± 0.4 kJ mol⁻¹, entropy (ΔS^{\varnothing}) of $+147.7 \pm 3.8$ and -64.4 ± 1.64 J mol⁻¹ K⁻¹ and free energy (ΔG^{\emptyset}) of $+3.49 \pm 0.2$ and $+2.85 \pm 0.2$ kJ mol⁻¹ and hence equilibrium constant (K) of $+0.25 \pm 0.05$ and $+0.32 \pm 0.05$ in dmso and dmf, respectively. The reversible BH₄⁻/BF₄⁻ interconversion of the electronic states of dpkfah points to weak non-covalent interactions between these species and dpkfah and possible use of dpkfah as a spectrophotometric sensor for a variety of physical and chemical stimuli. Chemical stimuli in concentrations $< 1.00 \times 10^{-6}$ M can be detected and determined using dpkfah in non-aqueous media.

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Keywords: Sensors; Hydrazones; di-2-pyridyl ketone; X-ray

1. Introduction

The development of molecular sensors is of interest for their use to monitor their surroundings [1-8].

Bistability, i.e. the ability of the system (substrate plus surrounding molecules) to exist in two states (electronic or conformational), is essential for molecular recognition as the interconversion between states allows to explore their structural relaxation and interactions with their environment [9]. We have been interested in the chemistry of di-2-pyridyl ketone and its oxime and hydrazone derivatives and described

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2. Experimental

2.1. Reagents

Solvents were reagent grade and thoroughly deoxygenated prior to use. All other reagents were obtained from commercial sources and used without further purification. The compound dpkfah was prepared by refluxing a mixture of di-2-pyridyl ketone and 2-furoic acid hydrazide, ethanol and a few drops of HCl in a procedure similar to that reported for the synthesis of dpkbz and other related compounds [10,15].

2.2. X-ray crystallography

Single crystals of dpkfah were obtained from a DMSO solution of dpkfah when allowed to stand at room temperature for several days. A single crystal was selected and mounted on a glass fiber with epoxy cement. A Bruker AXS with a Mo K_{α} radiation and a graphite monochromator was used for data collection and the SHELXTL software package version 5.1 was used for structure solution [25,26]. Cell parameters and other crystallographic information are given in Table 1 along with additional details concerning data collection, and Table 2 gives a list of atomic coordinates. All non-hydrogen atoms were refined with anisotropic thermal parameters.



the synthesis, optical, electrochemical and structures

of a series of di-2-pyridyl ketone derivatives [10-22].



dpkbz

dpkfah

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Table 2

Table 1 Crystal data and structure refinement for dpkfah

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement
parameters (Å ² × 10 ³) for dpkfah. $U(eq)$ is defined as one third of
the trace of the orthogonalized Uij tensor

Empirical formula	$C_{16}H_{12}N_4O_2$	the trace of the orthogonalized Uij tensor						
Formula weight	292.30			.				
Temperature	298(2) K		x	у	z	U(eq)		
Wavelength	0.71073 Å							
Crystal system,	Monoclinic, P21/n	O(2)	2758(2)	2831(2)	9512(1)	57(1)		
space group		N(1)	-327(2)	4856(2)	12280(2)	52(1)		
Unit cell dimensions	$a = 10.706(2)$ Å, $\alpha = 90^{\circ}$	N(3)	1022(2)	3323(2)	10556(2)	46(1)		
	$b = 9.9008(17) \text{ Å}, \beta = 108.76(2)^{\circ}$	N(4)	833(2)	2355(2)	9826(2)	48(1)		
	$c = 13.8795(15) \text{ Å } \gamma = 90^{\circ}$	C(11)	-35(3)	5869(3)	12957(2)	57(1)		
Volume	1393.1(4) Å ³	C(1)	58(2)	3643(2)	10887(2)	41(1)		
Z, calculated density	4, 1.394 Mg/m ³	C(15)	420(3)	4719(2)	11679(2)	39(1)		
Absorption coefficient	0.096 mm^{-1}	C(2)	1729(3)	2178(3)	9334(2)	43(1)		
<i>F</i> (000)	608	C(14)	1490(3)	5559(3)	11775(2)	51(1)		
Crystal size	$0.6 \times 0.9 \times 0.7 \text{ mm}$	C(12)	975(3)	6764(3)	13077(2)	55(1)		
Theta range for	2.11-17.50°	C(13)	1752(2)	6591(3)	12472(2)	59(1)		
data collection		N(2)	-1469(2)	1879(2)	10056(2)	51(1)		
Limiting indices	$-1 \le h \le 9, -1 \le k \le 8, -11 \le l \le 11$	C(25)	-1323(3)	3106(3)	10508(2)	42(1)		
Reflections	1282/879 [R(int) = 0.0316]	O(1)	251(2)	431(2)	8394(1)	57(1)		
collected/unique		C(32)	2029(2)	684(3)	7927(2)	55(1)		
Completeness to	100.0%	C(31)	1395(2)	1146(3)	8556(2)	44(1)		
theta = 17.50		C(22)	-3788(3)	2043(3)	9694(2)	66(1)		
Absorption correction	None	C(21)	-2684(4)	1380(3)	9664(2)	62(1)		
Refinement method	Full-matrix least-squares on F^2	C(23)	-3643(3)	3300(3)	10134(2)	61(1)		
Data/restraints/	879/0/200	C(24)	-2403(3)	3844(2)	10535(2)	49(1)		
parameters		C(34)	212(3)	-483(3)	7653(2)	64(1)		
Goodness-of-fit on F^2	1.010	C(33)	1264(3)	-366(3)	7352(2)	65(1)		
Final R indices $[I > 2 \text{sigma}(I)]$	R1 = 0.0275, wR2 = 0.0987							
<i>R</i> indices (all data)	R1 = 0.0289, wR2 = 0.1017		C/NID an a stre	matan) 10	Deceline com	nantiana		

2.3. Optical sensing studies

Extinction coefficient

Largest diff. peak

and hole

A stock solution of dpkfah in polar non-aqueous solvent and stock solutions of stimulus (ZnCl₂, CdCl₂, HgCl₂, NaBH₄ or NaBF₄) in polar non-aqueous solvent were prepared separately. Optical changes (electronic absorption spectral changes) were measured on a solution prepared by mixing appropriate volumes of dpkfah and stimulus solutions to prepare the desired solution (see figure captions for details). With the exception of the thermodynamic studies all measurements were made at room temperature.

0.050(6)

0.101 and $-0.084 \text{ e} \text{ Å}^{-3}$

2.4. Physical measurements

Electronic absorption spectra were recorded on a HP-8452A spectrophotometer or a Perkin-Elmer UV/VIS/NIR spectrometer λ -19. Baseline corrections on blank solvents were recorded prior to measurements. A Lauda-Brinkmann RM6 circular bath was used for temperature control. Electrochemical measurements were performed with the use of a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat and Model 276 interface in conjunction with a 286 PC. Data were acquired with the EG&G PARC Headstart program and manipulated using the Microsoft Excel Program. Measurements were performed in solutions that were 0.1 M in [N(n-Bu)₄](PF₆). The $E_{p,a}$, $E_{p,c}$ and $E_p = (E_{p,a} + E_{p,c})/2$ values were referenced to the potassium chloride saturated calomel electrode, SCE, at room temperature and are uncorrected for junction potentials. The number of electrons on the redox waves was determined using the oxidative peak current of the reversible one-electron couple of $FeCp_2/FeCp_2^+$ couple as an internal standard. $E_p((\text{FeCp}_2/\text{FeCp}_2^+) = +0.47 \pm 0.02, +0.45 \pm 0.02$ $+0.45 \pm 0.02 \ V ~~200.6 \ mV \ s^{-1} ~~versus$ and SCE in CH₂Cl₂, CH₃CN and DMF, respectively.

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Electrochemical cells were of conventional design based on scintillation vials or H-cells. A glassycarbon disc was used as the working electrode and Ptwire as a counter electrode.

3. Results and discussion

3.1. Structural studies

Fig. 1. The molecular structure of dpkfah. The thermal ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

The molecular structure of dpkfah is shown in Fig. 1 and selected bond distances and angles are given in Table 3. The furan acetic hydrazone moiety and the pyridine ring of N1 are planar and the pyridine rings are not co-planar. The non-coplanarity of the pyridine rings are normal and similar to those observed in dpkbz and other related compounds.

Table 3 3 Selected bond distances (Å), angles (°) and hydrogen bonds for dpkfah

		-		
N(1)-C(15)	1.334(3)	C(15)-N(1)-C(11)	117.5(2)	
N(1)-C(11)	1.341(3)	N(1)-C(11)-C(12)	124.6(2)	
C(11)-C(12)	1.366(3)	N(1)-C(15)-C(14)	121.4(2)	
C(15)-C(1)	1.490(3)	N(1)-C(15)-C(1)	117.9(3)	
N(2)-C(21)	1.333(3)	C(21)-N(2)-C(25)	118.3(2)	
N(2)-C(25)	1.352(3)	N(2)-C(25)-C(24)	121.1(2)	
C(24)-C(25)	1.379(3)	N(2)-C(25)-C(1)	115.8(2)	
C(25)-C(1)	1.499(3)	C(24) - C(25) - C(1)	122.9(3)	
C(1)-N(3)	1.296(3)	N(3)-C(1)-C(15)	112.9(2)	
N(3)-N(4)	1.362(2)	N(3)-C(1)-C(25)	126.6(2)	
N(4)-C(2)	1.356(3)	C(15)-C(1)-C(25)	120.3(2)	
C(2)-O(2)	1.232(3)	C(1)-N(3)-N(4)	119.4(2)	
C(2)-C(31)	1.446(3)	C(2)-N(4)-N(3)	120.3(2)	
C(31)-C(32)	1.347(3)	O(2) - C(2) - N(4)	124.4(2)	
C(31)-O(1)	1.369(2)	O(2)-C(2)-C(31)	120.7(2)	
C(33)-C(34)	1.327(3)	N(4)-C(2)-C(31)	115.0(3)	
C(34)–O(1)	1.360(3)	C(32)-C(31)-C(2)	132.0(3)	
		C(32)-C(31)-O(1)	109.2(2)	
		O(1)-C(31)-C(2)	118.8(3)	
		C(33)-C(34)-O(1)	110.9(2)	
		C(34)-O(1)-C(31)	106.0(2)	
Donor-H···Acceptor	d(D-H)	$d(H \cdot \cdot \cdot A)$	$d(D \cdot \cdot \cdot A)$	<(D-H···A)
$N(4)-H(4)\cdots O(1)$	0.86	2.30	2.677(3)	106.6
$N(4)-H(4)\cdots N(2)$	0.86	1.96	2.627(3)	133.7
$C(12) - H(12) \cdot \cdot \cdot O(2)^{1}$	0.93	2.59	3.352(3)	139.0
$C(24)-h(24)\cdots n(1)$	0.93	2.41	2.889(3)	111.9
$C(24)-H(24)\cdots O(2)^2$	0.93	2.51	3.312(3)	145.2
$C(32)-H(32)\cdots N(1)^3$	0.93	2.53	3.277(4)	137.8

Symmetry transformations used to generate equivalent atoms: 1. -x + 1/2, y + 1/2, -z + 5/2; 2., -x, -y + 1, -z + 2 and 3. x + 1/2, -y + 1/2, z - 1/2x.

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Fig. 2. A view of the packing of dpkfah.

The bond distances and angles are of the same order as those reported for dpkbz, di-2-pyridylketone-2-aminobenzoylhydrazone (Hdpa), di-2-pyridyl ketone 2-pyridylhydrazone (dpkph) and other related species [13–18,27]. For example in dpkbz, the hydrazone C=N, N–N and N–C bond distances of 1.30(2), 1.36(2), 1.36(3) and bond angle of C–N–N and N–N–C 118.5(2) and 120.6(2) of were observed [13].

The molecules pack reveals infinite chains of antiparallel dpkfah (see Fig. 2) interlocked via a network of hydrogen bonds. Table 3 gives a list of hydrogen bonds and Fig. 3 shows views of intermolecular hydrogen bonds. The bond distances and angles of these bonds are of the same order as those reported for a variety of compounds containing such bonds. [13– 18,27–30]. For example, $d_{(H \cdots A)}$ and < (D–H···A) of 2.46 Å and 136° were observed for the C-H···O hydrogen-bond in Na⁺·C₅H₃N₂O₃⁻·3H₂O²⁷ and hydrogen bond parameters of 2.61 Å and 129° were reported for the (N-H...N) in dpkph [28].

3.2. Electrochemical properties

The electrochemical properties of dpkfah in nonaqueous solvents were investigated using voltammetric techniques. Cyclic voltammograms of dpkfah in DMF, CH₃CN and CH₂Cl₂ are shown in Fig. 4. On a reductively initiated scan in dmf (Fig. 4(a)) an irreversible one electron reduction appeared at $E_{\rm p,c} = -1.74$ V, irreversible two electrons oxidation appeared at $E_{\rm p,a} = +1.86$ V and a reductively generated product wave appeared at $E_{\rm p,a} = +0.62$ V. On an

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Fig. 3. Views of the intermolecular hydrogen bonds in dpkfah. Symmetry transformations used to generate equivalent atoms: 1. -x + 1/2, y + 1/2, -z + 5/2; 2. -x, -y + 1, -z + 2 and 3. x + 1/2, -y + 1/2, z - 1/2x.

oxidatively initiated scan (Fig. 4(b)) the electrochemically generated product wave at $E_{p,a} = +0.62 \text{ V}$ disappeared and new oxidatively generated product waves appeared at $E_{p,c} = -0.72$ and -1.37 V. On a -1.0 to -3.0 reductive scan (Fig. 5(a)) a three electrons reduction wave appeared at $E_{p,c} = -$ 2.53 V and on an oxidatively generated scan from +1.0 to +3.0 V (Fig. 5(b)) two irreversible reduction waves two electrons each appeared at $E_{p,a} = +1.80$ and +2.05 V. In CH₃CN, electrochemical behavior similar to that observed in dmf was noted except on oxidative scan from +1.0 to +3.0 V sequential electronic transfers followed the first multi-electronic oxidation. In CH₂Cl₂ under similar scanning conditions as in dmf and CH₃CN a single one electron irreversible reduction appeared at $E_{p,c} = -2.19 \text{ V}$ and a single irreversible one electron oxidation



Fig. 4. Cyclic voltammograms of dpkfah in DMF (a and b), CH_3CN (c and d) and CH_2Cl_2 (e and f) solutions 0.1 M in [N(n-Bu)₄](PF₆) at a glassy carbon working electrode at a scan rate of 400 mVs⁻¹ versus SCE.

appeared at $E_{p,a} = +2.14$ V. These voltammetric results reveal sensitivity of the redox potentials of dpkfah to solvent variations and point to solventsolute interactions. No signs of reversible redox behavior were observed when the scan rates were varied from 100 to 10000 mV s⁻¹. The irreversibility of the reduction waves suggests electrochemical reactions following the electronic transfer(s). The appearance of electrochemically generated product waves following the first electronic transfer suggest that the electrochemically generated radical anion is unstable and undergoes decomposition as shown in Scheme I. The appearance of multi-electronic reduction (three electrons) following the first electronic reduction in DMF and CH3CN may hint to electron(s)/proton(s) coupled transfer(s) leading to the reduction of the imine radical to ammine (see Scheme I). The proposed scheme is similar to that we reported for the reduction of di-2-pyridyl ketone oxime to di-2pyridylmethyl amine in non-aqueous media [22].





Fig. 5. The same as above on -1.0 to -3.0 V reductive scans and +1.0 to 3.0 V oxidative scans at 200 mV s⁻¹ versus SCE.

3.3. Optical behavior

The electronic absorption spectra of dpkfah in nonaqueous solvents are shown in Fig. 6. In non-polar solvent, CH₂Cl₂, a single absorption band with extinction coefficient of 18,600 M⁻¹ cm⁻¹ appeared at 325 nm and polar solvents (see Fig. 6) two absorption bands appeared at 396 and 335-320 nm. These spectra hint to strong solvent-solute interactions as apparent from the dependence of the absorption bands on solvent variations. In DMF, the low- and high-energy absorption bands at 396, and 325 are concentration and temperature dependent. As the concentration of dpkfah decreases the ratio of A₃₉₆/A₃₂₅ increases and a plot of A₃₂₅ versus concentration is non-linear point to direct solventsolute interactions and deviation from Beer's Law. In mixed binary polar/non-polar co-solvent systems, the intensity of the low energy absorption band of dpkfah increases as the volume % of polar solvent increases. In DMSO, as the temperature increases the ratio of A₃₉₆/A₃₂₅ increases and the reverse was observed when the temperature was decreased. These results point to reversible interconversion between the highand low-energy electronic states of dpkfah and





Scheme 1.





Fig. 6. The electronic absorption spectra of dpkfah in (1) DMF, 2.0×10^{-5} M; (2) DMSO 2.20×10^{-5} M; (3) CH₃CN 2.00×10^{-5} M and (4) CH₂Cl₂ 2.00×10^{-5} M.

allowed calculations of its thermodynamic activation parameters in a procedure similar to that we reported for fac-Re(CO)₃(dpknph)Cl and dpkbh [11,13]. A plot of $\ln(A_{396}/A_{396}$ versus $1/T \times 10^3 \text{ K}^{-1}$ (Fig. 7) gave straight lines with a slope of -570 ± 70 and $+197 \pm 23$ with intercepts of $+17.70 \pm 2.0$ and -7.75 \pm 0.5 that gave changes in enthalpy (ΔH^{\varnothing}) of $+47.5 \pm 1.2$ and -16.3 ± 0.4 kJ mol⁻¹, entropy (ΔS^{\varnothing}) of $+147.7 \pm 3.8$ and $-64.4 \pm 1.64 \text{ J mol}^{-1} \text{ K}^{-1}$ and free energy (ΔG^{\varnothing}) (ΔS^{\varnothing}) of $+3.49 \pm 0.2$ and $+2.85 \pm 0.2$ kJ mol⁻¹ and hence equilibrium constant (K) of $+0.25 \pm 0.05$ and $+0.32 \pm 0.05$ in DMSO and DMF, respectively. The reversible interconversion between the highand low-energy electronic states of dpkfah, their low activation parameters and high value for the extinction coefficient of the high-energy electronic states allows for the use of these systems (dpkfah and surrounding molecules) as molecular sensors for variety of stimuli. These results are similar to those reported for the optical behavior of fac-Re(CO)₃(dpknph)Cl, dpkbh and other related species [11,13-16].

When NaBH4 in dmf were allowed to interact with a DMF solution of dpkfah (see

Fig. 8) the low-energy electronic state becomes favorable and when stoichiometric amounts of NaBF₄ were allowed to interact with the resulting solution, the reverse was observed. In dmf in the presence of excess NaBH₄ the equilibrium shifts all the way to the low-energy conformation and that extinction an coefficient gave of $21,000 \pm 2000 \text{ M}^{-1} \text{ cm}^{-1}$ for the low-energy electronic state of dpkfah and hence extinction coefficient of $17,200 \pm 2000 \text{ M}^{-1} \text{ cm}^{-1}$ for the high energy absorption band at 295 K. In the case of DMSO, extinction coefficients of $22,500 \pm 2000$ and $23,000 \pm 2000 \text{ M}^{-1} \text{ cm}^{-1}$ were calculated at 295 K for the low- and high-energy absorption bands from temperature studies. These results demonstrate the reversible interconversion between the high and low electronic states of dpkfah and point to weak non-covalent intermolecular interactions which may be due to donor/acceptor hydrogen bonding between dpkfah and stimulus as demonstrated in this study using the electron rich/deficient NaBH₄/NaBF₄, solvent and temperature variations. This is consistent with the web of



Fig. 7. A plot of $\ln(A_{396}/A_{325})$ versus $1/T \times 10^3$ K₋₁ of DMSO and DMF solutions of dpkfah 1.0×10^{-5} M.





Fig. 8. Electronic absorption spectra of dpkfah 2.00×10^{-5} M in DMF (1) in the presence of 5.00×10^{-5} M (2), 1.00×10^{-4} M (3), 2.00×10^{-4} M (4) and 5.00×10^{-4} M (5) NaBH₄.



Fig. 9. A plot of the absorbance of dpkfah 2.00×10^5 M in DMF at 396 nm (1, 2 and 3) and 325 nm (4,5 and 6) versus concentration of ZnCl₂ (series 1 and 4), CdCl₂ (series 2 and 5) and HgCl₂ (series 3 and 6).

hydrogen bonds observed in the solid state and low values of the activation parameters for the interconversion between the high and low energy conformations of dpkfah. The disturbance of the equilibrium distribution of the high and low electronic states of dpkfah upon the addition of stimulus improves the optosensing properties of dpkfah as relaxation to the equilibrium position allows for the exploration of the structural relaxation and the use of these systems (dpkfah and surrounding molecules) as molecular sensors for a variety of species. When DMF solutions of Group 12 metal ions were added to DMF solutions of dpkfah the intensity of the low-energy absorption band increases and the intensity of the highenergy absorption band decreases. This is in contrast to the optosensing behavior of fac-Re(CO)₃(dpknph)Cl where the intensity of the low energy absorption band decreases and the intensity of the high energy absorption band increases upon the addition of Group 12 metal ions in dmf [11]. A plot of the absorbance of dpkfah versus concentration of Group 12 metal ions in DMF is shown in Fig. 9. These results reveal that chemical stimuli in concentration $< 1 \times 10^{-6}$ M can be detected and determined using dpkfah in non-aqueous media. In previous studies on the optical determination of trace amounts of iron and scandium using dpkfah in aqueous media competing species such as NH₄Cl, NH₄OH, NaOH and others, all of which interact with dpkfah and influence its optical properties, were used to adjust the pH [23,24].

Owing its convenient synthesis and rich physicochemical properties, together with our continued interest in molecular sensors, the coordination chemistry and optosensing behavior of dpkfah towards a variety of stimuli, including biomolecules, remain under investigation in our laboratories.

4. Conclusion

Structural and optical studies of dpkfah have revealed the presence of hydrogen bonds in the solid state, reversible interconversion between its high- and low-energy electronic states and use of dpkfah as an optical sensor for a variety of chemical stimuli.

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