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STRUCTURAL TRANSFORMATION OF PUSH–PULL 5-SUBSTITUTED-4-OXOTHIAZOLIDINES DURING HEATING

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The thermal stability of push-pull 5-substituted-4-oxothiazolidines was studied by DSC, IC and X-ray diffraction techniques. It was shown that the compounds are stable in the temperature range from room temperature to melting point. The melting is combined with breaking crystal structure and forming glass material as a new phase that forms crystals by cooling it very slowly. The rate constant, activation energy as well as activation parameters of process were determined.

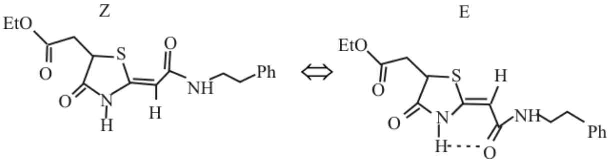
Keywords: *activation energy, phase transformation, push–pull-oxothiazolidines*

Introduction

Many new and different reactions, concerning isomerization, dimerization and polymerization, activated thermally and photochemically, which modify the state of the molecules in the crystalline media are being studied in many institutions [1–5]. So, one can say that solid-state reactions have now entered into the mainstream of organic chemistry. The physicochemical properties and chemical reactivity of numerous functionalized compounds type of push–pull alkenes have been studied in numerous recent reviews [6–9]. These compounds represent an excellent model for investigation of the effects of weak non-covalent interactions on relationships between structure and reactivity in solution and in the solid-state [10–12].

The series of stereo-defined oxothiazolidines, synthesized according to procedures we reported [13, 14], attracted our attention due to their potential biological activity and applicable as precursors for the synthesis of push–pull polyenes. We have shown that the equilibrated mixtures of structurally related 4-oxothiazolidines consist of the intra-molecularly H-bonded (*E*)-isomer and inter-molecularly H-bonded (*Z*)-isomer in varying proportions depending on the solvent polarity and temperature [15].

Here, we report the first kinetic and thermodynamic studies of thermal Z/E isomerization of substituted 4-oxothiazolidine derivative in solid state, according to reaction Scheme 1.



Scheme 1

Experimental

The thermal stability and structural transformations were investigated by non-isothermal analysis (DSC) using a DuPont Thermal Analyzer (model 1090). In this case, samples weighing several milligrams were heated in the DSC cell from room temperature to 170°C, at heating rate in the range of 5 to 20°C $\min^{-1}$, in a stream of nitrogen at normal pressure. The masses of the samples were in the range 3–7 mg. The peaks of temperature (T_p) were determined from DSC curve using the program Interactive DSC V1.1.

IR spectra in the 4000–400 cm^{-1} range were measured on a Perkin Elmer 983GxFTIR spectrophotometer, using KBr discs technique. Spectra at higher temperature were recorded in an adapted variable-temperature cell model VLT.2 (RIIC London).

The X-ray powder diffraction (XRD) patterns were recorded on a Philips PW-1710 automated diffractometer using a Cu tube operated at 40 kV and 30 mA. The instrument was equipped with a diffracted beam curved graphite monochromator and Xe-filled proportional counter. For routine characterization, diffraction data were collected in the range 2Θ Bragg angles, 4–100° counting for 0.1 s. A fixed 1° divergence and 0.1 mm receiving slits were used. Silicon powder was used as an external standard for calibration of diffractometer. All XRD measurements were recorded with solid samples at ambient temperature.

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Results and discussion

Investigation of thermal behavior in the temperature interval of 20–200°C, Fig. 1a, shows that solid (Z)-5-ethoxycarbonylmethyl-4-oxothiazolidine-2-ylidene)-N-(2-phenyl-ethyl)-ethanamide was stable up to approximately 136°C [16]. On heating after this temperature, Z-isomer first melts (T_p=145.1°C) and then vitrifies (forms glass) on cooling (Fig. 1a). During 2nd heating, the formed glassy material starts slightly to crystallize around 80°C (the exothermal peak weak defined at ~110°C, Fig. 1b). This phenomenon is sometimes called 'cold crystallization'. The formed solid phase has a different melting point. (T_p=130.9°C, Fig. 1b). The breaking of crystal structure of Z-isomer during melting results in the formation of another isomer, E-isomer, that has a different enthalpy of transformation and melting point.

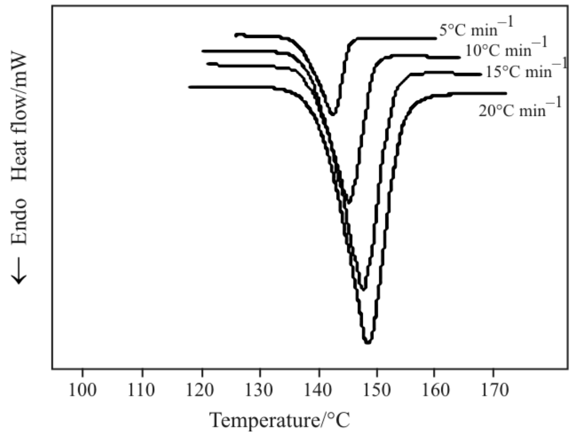

Fig. 2 DSC curves of (Z)-5-ethoxycarbonylmethyl-4-oxo-thiazolidine-2-ylidene)-N-(2-phenylethyl)-ethanamide at different rates of heating

The change of the peak temperature, T_p, with the change of heating rate (Fig. 2) indicates that a well defined endothermic peak on DSC curves corresponds to some thermal activated steps participating in this phase transformation besides the melting of the compound. That can be the process of isomerization as was shown by X-ray diffraction and IR spectra.

The structures of both isomers were inspected by studying X-ray diffractograms, Fig. 3. Diffractogram with finely formed peaks indicate good crystallinity of the Z-isomer form, diffractogram a, Table 1. On the other hand, X-ray diffractograms of melted isomer after cooling indicate a very disordered structure with a wide weakly defined maximum translated to regions of lower 2Θ values that is characteristic for non-ordered structures, diffractograms b and c. A sharp peak for 2θ=6.35° corresponds to a small quantity of E-isomer present in a matrix of amorphous material. This amorphous structure remains stable for a long time period according to the intensity of peak E-isomer rising very slightly with time, as shown in diffractogram c of the same sample after 4 months staying in a desiccator.

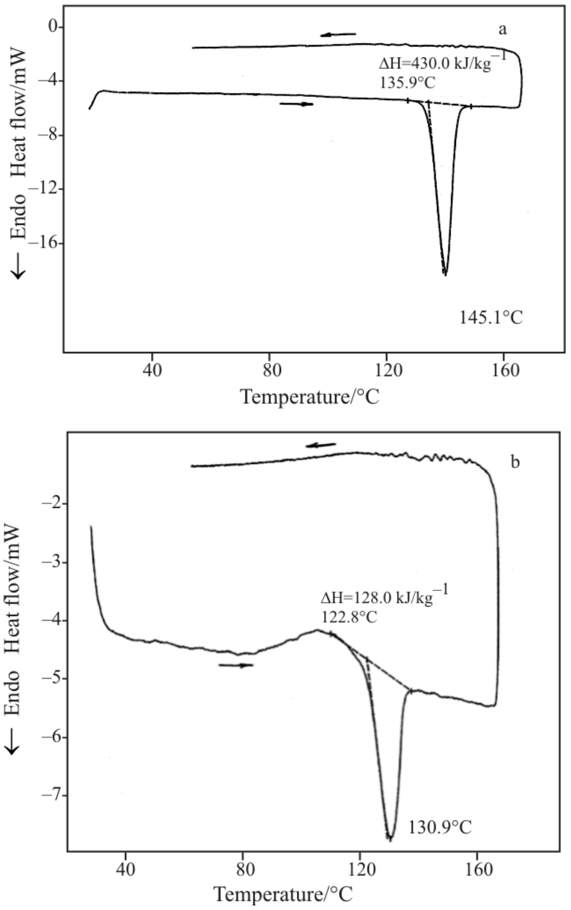

Fig. 1 DSC curves of (Z)-5-ethoxycarbonylmethyl-4-oxo-thiazolidine-2-ylidene)-N-(2-phenylethyl)-ethanamide: a – first cycle of heating and cooling, b – second cycle of heating and cooling, in a stream of nitrogen at normal pressure at heating rate 10°C min^{-1}

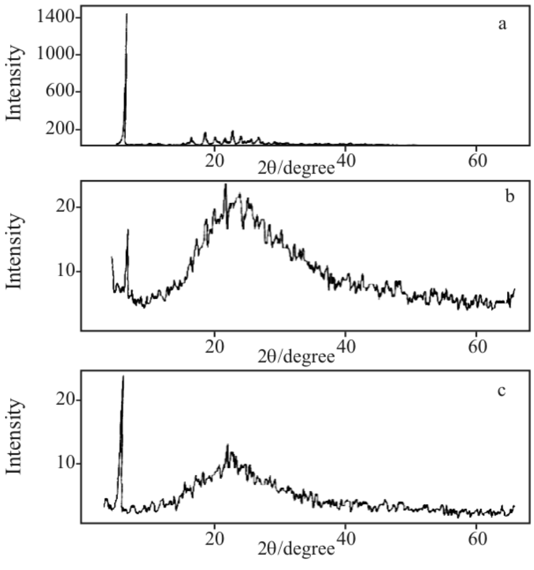

Fig. 3 X-ray diffractograms of (Z)-isomer a – before melting, b – the same sample after melting and cooling, c – the same sample after 4 months

Table 1 Powder diffraction data for (Z)-5-ethoxycarbonylmethyl-4-oxothizolidin-2-ylidene)-N-(2-phenylethyl)-ethanamide

Peak No.	d/ Å	2θ /°	Half of width/°	$I/I_{\max}$/ %
1	16.8825	5.230	0.080	100.00
2	5.6289	15.730	0.120	6.88
3	4.9621	17.860	0.230	10.22
4	4.5727	19.393	0.240	6.74
5	4.2327	20.970	0.240	5.27
6	4.0125	22.135	0.160	11.66
7	3.7737	23.555	0.100	6.32
8	3.3870	26.290	0.320	6.18

Table 2 IR frequencies of (Z)- and (E)-5-ethoxycarbonylmethyl-4-oxothizolidin-2-ylidene)-N-(2-phenylethyl)-ethanamides

Type of frequency	Z-isomer	E-isomer
NH	3320	3355
NH	3296	
C=O ester	1733	1733
Lactam	1719	1726
C=O...HN (inter)	1695	
C=O....HN (intra)		1639
C=C-C enamine		1563
NH	1532	1515

IR spectrum of the starting Z-isomer at room temperature, Fig. 4a significantly differs from the corresponding spectra at 150 and 170°C, Figs 4b and c, indicating an existence of another isomer on higher temperatures. The greatest differences in this IR spectra are noted in regions of NH group vibrations (at about 3300 cm^{-1}) and vibrations of the C=O ester and lactam group (at about 1700 cm^{-1}), while the band at 1733 cm^{-1} attributed to C=O ester group vibrations is present in the spectra of both isomers, Table 2.

Thus the central band of strong intensity at 3320 cm^{-1} belonging to the amide functional group in the Z-isomer spectrum is at 3355 cm^{-1} in the E-isomer spectrum. The band at 3296 cm^{-1} corresponding to the expanding vibration of the NH lactam group present in the Z-isomer spectrum is not present in the E-isomer spectrum while the bending vibration of the NH lactam group giving the band at 1532 cm^{-1} in the Z-isomer spectrum occurs at 1515 cm^{-1} in the E-isomer spectrum. Furthermore, the band at 1719 cm^{-1} from the C=O lactam group is translated to 1726 cm^{-1} in the E-isomer spectrum. The band at 1695 attributed to the C=O amide group participating in the formation of intermolecular bonds with neighboring molecules disappears in the E-isomer spectrum. However, the spectrum of this isomer has a new band at 1639 cm^{-1} characteristic for the E-isomer that is stabilized by an intra-molecular hydrogen bond formed between C=O and NH lactam groups. A new band at 1526 cm^{-1} also appears in this spectrum corresponding to the en- amine group presence.

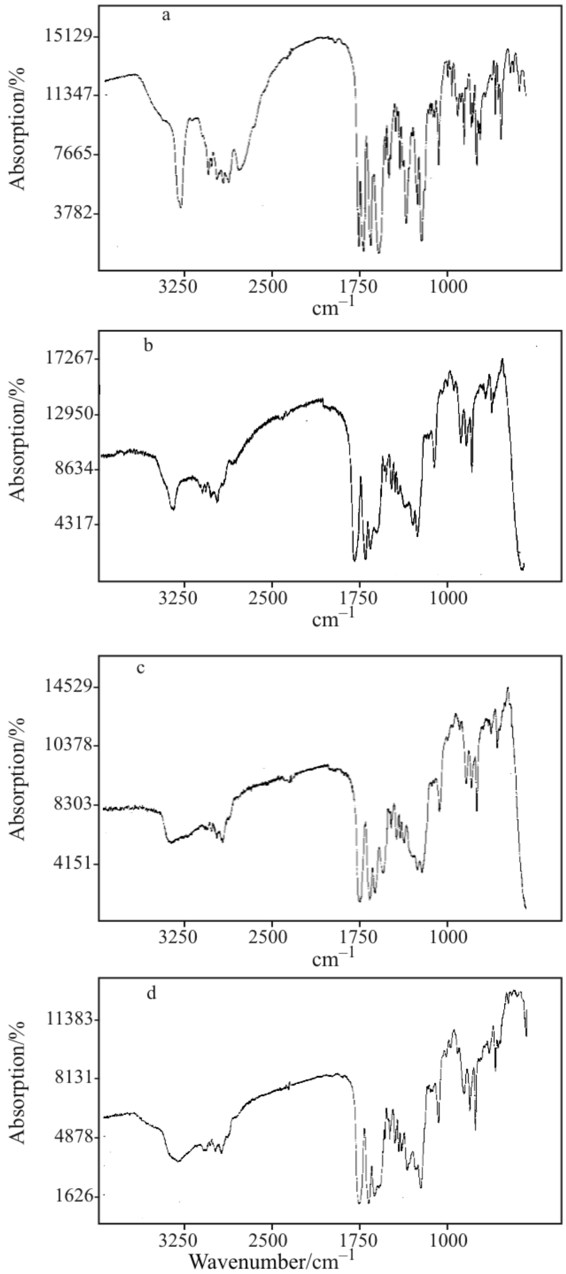

Fig. 4 IR spectra of (Z)-5-ethoxycarbonylmethyl-4-oxo-thiazolidine-2-ylidene)-N-(2-phenylethyl)-ethanamide at a – room temperature, b – 150, c – 170°C, d – room temperature after 24 h, in range 4000–250 cm^{-1}

Kinetic analysis of the configurational isomerization

The mathematical description of data for a single step solid-state reaction is usually defined in terms of a kinetic triplet involving activation energy E_a, Arrhenius parameter A and algebraic expression of the kinetic model in function of the fractional conversion α, f(α).

In non-isothermal conditions, the rate of solid-state reaction can be expressed as a product of temperature dependent rate constant $k(T)$ and conversion dependent kinetic function $f(\alpha)$ [17]

$$\beta\frac{d\alpha}{dT}=k(T)f(\alpha) \tag{1}$$

where β is the heating rate; the rate constant follows Arrhenius equation $k(T)=A\exp(-E_a/RT)$, where A is the pre-exponential factor, R the gas constant and T the absolute temperature.

In the most generalized equation for kinetic analysis of solid-state conversions proposed by Erofeev [18] using various approaches for the transition to constant rates of heating β and the characteristic temperatures T_p corresponding to the temperature of peak of DSC curves at given rates of heating β, we can obtain the expression for the calculation of the activation energy of process [19–21] in the form:

$$\ln\left(\frac{\beta}{T_p^s}\right)=\frac{E_a}{RT_p}+C_i \tag{2}$$

where s=1 for Ozawa's [19] and s=2 for Kissinger's [20] method.

The model-free approach to kinetic analysis is based on the isoconversion approach according to which the reaction rate at a constant extent of conversion is only a function of temperature. In non-isothermal kinetics, several isoconversion methods were developed by conducting of a series of experiments at different heating rates [22].

The integral isoconversional method suggested independently by Flynn and Wall [23] and Ozawa [24] uses Doyle' approximation [25] for temperature integral yields

$$\ln(\beta_i)=\text{constant}-\frac{E_\alpha}{RT} \tag{3}$$

Thus, for α=constant, the plot $\ln\beta_i$ *vs.* $1/T$ obtained from curves for different heating rates, should be a straight line whose slope gives activation energy, Table 3.

The Kissinger–Akahira–Sunose method [20, 26] is based on the Coats–Redfern approximation [27]

$$\ln\frac{\beta_i}{T^2}=\text{constant}-\frac{E_\alpha}{RT} \tag{4}$$

Thus, for α=const, the plot $\ln(\beta_i/T^2)$ *vs.* $1/T$ should be a straight line whose slope gives the activation energy, Table 3.

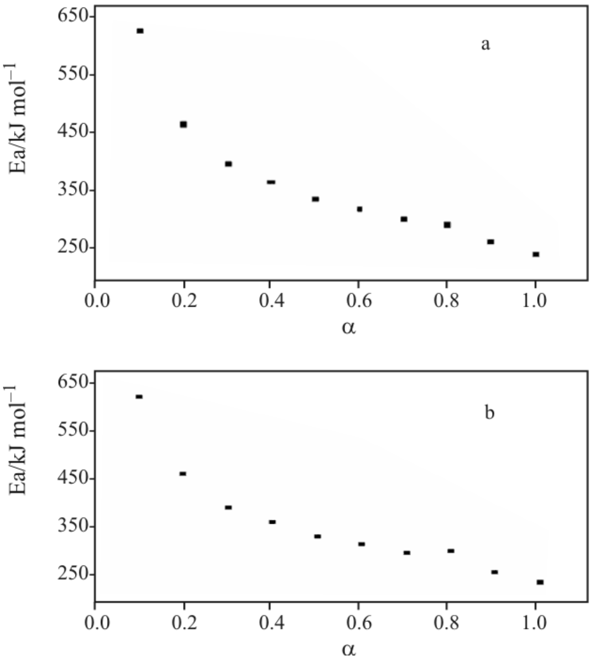

Fig. 5 The dependences of activation energy on degree of conversion according methods: a – Flynn–Wall–Ozawa and b – Kissinger–Akahira–Sunose

The volume fraction (degree of conversion, α) has been obtained from the DSC curves as $\alpha=S_T/S$, where S is the total area of the peak between the temperature T_i, where the reaction just begins and the temperature T_f, where the reaction is completed, and S_T is the area between the initial temperature and a generic temperature, T, ranging between T_i and T_f.

The activation energy of solid-state transformations, involving of a series of different elementary acts given transformation, from the point of view of some researchers has not a physical sense but only empirical character and only establishes in practice the dependence of the rate of conversion on temperature. The activation energy represents the threshold value of energy above which the fluctuation of energy in the activation complex is sufficient for the elementary reaction to occur. This energy can be spent, not for overcoming the activation barrier but, mainly for its downturn due to co-operative displacement of atoms. In these experi-

Table 3 The activation energies of structural transformation determined by different methods

Method	E_a/ kJ mol^{-1}	α-range	ln*A*
Kissinger	350.4		1.95
Ozawa	355.2		3.10
Kissinger–Akahira–Sunose	318.4	0.4–0.8	–
Flynn–Wall–Ozawa*	322.6	0.4–0.8	–

*The average value in given interval of α values ments, the total value of energy spent both to the down-turning the potential activation barrier and to its overcoming was determined. The isomerization in solid-state is a complex process accompanied by breaking existing bonds, forming new bonds and displacement of atoms under continuous varied conditions of chemical surroundings in a zone of conversion. Obviously, such a process occurs not only with the single value of activation energy and not by formation of a single configuration of activated complex. In practice with the multitude of probable ways of process only those mechanism and activated complexes of the isomerization process will be realized that are most probable at a given temperature. High values of activation energy (about 350 kJ mol^{-1}) of isomerization, first of all, testify that many steps and many atoms participate in the elementary act of structure reorganization. More atoms should simultaneously move in different directions at the elementary act of the crystallization, the activation energy of process crystallization increases what prevents re-crystallization of E-isomer which appearances as amorphous.

The kinetic parameters, appearing in Arrhenius-like kinetic law of reaction $k=Z\exp(-E_a/RT)$, can be then evaluated and used to provide a valid description of the thermal behavior of the observed process, Table 4.

Table 4 Kinetic and thermodynamic parameters of structural transformation

Isomer	T_p/°C	ΔH/J g^{-1}	k/s^{-1}	$t_{1/2}$/s
Z-form	145.1	434.0	4.48	0.15
E-form	130.9	134.0	9.75	0.07

The rate constant can be expressed as:

$$k=\frac{k_B T}{h}K^{\ddagger} \quad (5)$$

where $K^{\ddagger}$ is the equilibrium constant.

The change in molar Gibbs energy of activation is:

$$\Delta G^{\ddagger}=-RT\ln K^{\ddagger} \quad (6)$$

Having in mind that the enthalpy of activation for monomolecular reaction in solid-state is $\Delta H_a^{\ddagger}=E_a-RT$, we calculated the activation parameters relating to the process of thermal isomerization of given push–pull 5-substituted-4-oxothiazolidines as follows from Table 5.

Table 5 Activation parameters relating to the rate constant k of structural transformation

$K^{\ddagger}$/	$\Delta G^{\ddagger}$/ kJ mol^{-1}	$\Delta H^{\ddagger}$/ kJ mol^{-1}	$\Delta S^{\ddagger}$/ J K^{-1} mol^{-1}
1.40·10^{12}	-94.6	348.5	681.5

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References

1 G. Kaupp, J. Schmeyers, M. Kato, K. Tanaka and F. Toda, J. Phys. Org. Chem., 15 (2002) 148.
2 G. M. Schmidt, J. Pure Appl. Chem., 27 (1971) 647.
3 N. B. Singh, R. J. Singh and N. P. Singh, Tetrahedron, 50 (1994) 6441.
4 W. J. Kusto, M. Bertault and J. Even, J. Phys. Chem. B, 103 (1999) 10549.
5 M. Oda and N. Sato, J. Phys. Chem. B, 102 (1999) 3283.
6 J. Sandström, Top Stereochem., 14 (1983) 83.
7 S. Rajappa, Tetrahedron, 55 (1999) 7065.
8 L. Chaira, A. Gómez-Sánchez and J. Bellanato, J. Chem. Soc. Perkin Trans., 2 (1998) 1797.
9 E. Kleinpeter, A. Koch, M. Heydenreich, K. S. Chatterjee and D. W. Rudorf, J. Mol. Struct., 356 (1995) 25.
10 E. Forlani, C. Mezzina and M. Forconi, Eur. J. Org. Chem., (2001) 2779.
11 P. Gilli, V. Bertolasi, V. Ferreti and G. Gill, J. Am. Chem. Soc., 122 (2000) 10405.
12 C. J. Zhuo, Magn. Respon. Chem., 35 (1997) 311.
13 R. Marković, Z. Džambaski and M. Baranac, Tetrahedron, 57 (2001) 5833.
14 R. Marković and M. Baranac, Heterocycles, 48 (1998) 893.
15 R. Marković and M Baranac, J. Serb. Chem. Soc., 63 (1998) 165.
16 B. Wunderlich, J. Therm. Anal. Cal., 89 (2007) 321.
17 M. E. Brown, D. Dollimore and A. K. Galwey, Reactions in the Solid State. Comprehensive Chemical Kinetics, Vol. 22, Elsevier, Amsterdam 1980.
18 B. V. Erofeev, Doklady Akademii Nauk, USSR, (1946) 512.
19 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
20 H. E. Kissinger, Anal. Chem., 29 (1957) 1702.
21 A. A. Soliman, J. Therm. Anal. Cal., 89 (2007) 389.
22 A. K. Burnham and N. Dinh, J. Therm. Anal. Cal., 89 (2007) 493.
23 J. H. Flynn and L. A. Wall, J. Res. Nat. Bur. Standards A, 70 (1966) 487.
24 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
25 C. D. Doyle, Appl. Polym. Sci., 6 (1962) 639.
26 T. Akahara and T. Sunose, Res. Rep. Chiba Inst. Technol., 16 (1971) 22.
27 A. W. Coats and P. J. Redfern, Nature, 201 (1964) 68.

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