Thermal strain tensors for benzotrifuroxane and pentaerythritol tetranitrate molecular crystals

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Abstract. In this paper, we present the thermal strain tensors for two energetic materials: pentaerythritol tetranitrate (PETN) and benzotrifuroxane (BTF). These tensors are calculated from the data of the x-ray polycrystal diffraction in the range of temperatures from 150 to 370 K for PETN and from 150 to 450 K for BTF. Points of structural changes in energetic materials are recorded in increments of 10 K. The x-ray diffractometry data were calculated using the Rietveld method with the molecular structure quantum simulation cycle being integrated into the computation algorithm. Principle crystallographic axes and characteristic surfaces of the thermal strain tensor were determined. Thermal strain tensors and their temperature dependence are given numerically, algebraically, and graphically. The obtained results can be used to derive equations of state of condensed BTF and PETN, and also to calibrate ab-initio models.

1. Introduction

According to the condensed matter physics, many fundamental properties of a solid material are known to depend on its structure: atom type, atomic packing (ordered or disordered), and interatomic binding. Many individual energetic materials turn out to be strongly anisotropic crystalline substances having metastable structural condition. At the same time, materials such as pentaerythritol tetranitrate (PETN), benzotrifuroxane (BTF) and cyclotrimethylene-trinitramine (RDX) being energetic materials are characterized by the least anisotropy and practically are not inclined to obvious polymorphism.

In the general case, a material property can be described as its capability of responding to any given external effect through changing its parameters, e.g. crystal packing parameters. In general terms, a property can be described by the relation \( t = r/q \), where \( r \) is an induced reaction of a body to external effect \( q \) and \( t \) is a quantitative characteristic or a factor of proportionality (heat capacity, thermal strain, pyroelectric constants, chemical activity, etc) between related parameters of the effect and the object [1]. The considered characteristics of materials can be mathematically presented in the tensorial form.

Aware of the existence of three polymorphs of PETN, they are denoted as I, II and III. Under normal conditions, there is only PETN-I and II, and the latter is stabilized only under certain crystallization conditions.
Table 1. Thermal deformation coefficients of PETN-I single crystals ($\times 10^5 \text{ K}^{-1}$) at 293 K.

| Measurement method                      | Temperature range (K) | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ | $\beta$ | Source |
|-----------------------------------------|-----------------------|------------|------------|-----------|-------|--------|
| Dilatometry on single crystals          | 298–423               | 6.88       | 9.39       | 23.15     | [1]   |
| Dilatometry on single crystals          | 113–373               | 7.1        | 9.2        | 23.4      | [2]   |
| Diffraction on single crystals          | 10–300                | 7.1        | 8.5        | 24.8      | [3]   |

It should be noted that the study of thermal deformation of tain molecular crystals was carried out earlier by the authors of [1–3]. By x-ray diffraction in the work of [3] single crystals of PETN-I were obtained anisotropic coefficients of thermal expansion, and the thermal deformation of single crystals of PETN are presented in tensor form. In the works of [1, 2] determination of thermal deformation coefficients of PETN crystals was carried out in two directions by dilatometry, which is known to require the cultivation of monocrystals of good quality and sufficient size, as well as the exact orientation of the crystals with respect to the measuring probe. The results of measurements obtained earlier for clarity are listed in table 1.

There is no information on thermal deformation (expansion and compression) of BTF crystals in the literature. However, from the point of view of fundamental science, this material is also interesting, first of all, because of the pronounced resonance processes in the relations between the N and O atoms.

In the present work, our focus is on the thermal strain tensor obtained from the results of powder x-ray diffraction, which eliminates the need for growing single crystals of good quality. When describing the material, we will follow the next sequence: first, we consider the theoretical foundations of thermal deformation of substances in the tensor form (section 2), then describe the experimental formulation with the results of measurements (section 3), then analyze the obtained x-ray diffraction data and present the result in the tensor form (section 4), then conclude (section 5).

2. Thermal strain tensor

In the general case, thermal expansion of solid bodies being anisotropic in nature is described by the symmetrical tensor $e_{ik}$ that appears to be the thermal strain tensor [1, 4]:

$$e_{ik} = \alpha_{ik} \Delta T.$$ (1)

Proportionality factors $\alpha_{ik}$ are said to be thermal expansion coefficients (dimensionality K$^{-1}$).

When a body if uniformly heated, $\Delta T$ is a nilvalent tensor and $e_{ik}$ is a tensor in 2 dimensions. So, $\alpha_{ik}$ shall be the tensor in the same dimensions. In the general case, it is as follows:

$$\begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix}.$$ 

Diagonal components, just as in the strain tensor, demonstrate changes in dimensions and off-diagonal components—changes in the body shape under heating.

From the symmetry of the tensor $\alpha_{ik}$, it follows that the tensor can be reduced to main axes:

$$\begin{pmatrix} \alpha_{1} & 0 & 0 \\ 0 & \alpha_{2} & 0 \\ 0 & 0 & \alpha_{3} \end{pmatrix}.$$
Components $\alpha_k$ ($k = 1, 2, 3$) are known as the main coefficients of the thermal expansion tensor. They express relative changes in the crystal size $\Delta l/l$ along the main tensor axes with the temperature increase by 1 K and are calculated from equation:

$$\alpha_k = \frac{\Delta l}{l} \Delta T. \tag{2}$$

Due to this expansion, the unit cube is changing into the rectangular parallelepiped with edges $(1 + \alpha_1), (1 + \alpha_2), (1 + \alpha_3)$. With certain approximation, the unit volume expansion $\beta$ (the volume expansion coefficient) of the cube can be written as

$$\beta \approx (1 + \alpha_1)(1 + \alpha_2)(1 + \alpha_3) - 1 \approx \alpha_1 + \alpha_2 + \alpha_3, \tag{3}$$

i.e. the volume expansion coefficient of a crystal is equal to the sum of the main linear coefficients of the crystals thermal expansion tensor.

In crystals having 3 mutual-perpendicular crystallographic axes (an orthorhombic system and more symmetric systems), the main axes of the tensor coincide with these crystallographic axes. In order to have complete description of thermal expansion of these crystals, it is sufficient to estimate values of their thermal expansion coefficients along these three axes: $\alpha_1$, $\alpha_2$, and $\alpha_3$. BTF and PETN crystals in normal conditions belong just to this group of crystals.

In monoclinic crystals, the $\alpha_2$-direction coincides with the $Y$-axis of the crystal while two other directions are determined experimentally. In a triclinic crystal, e.g. in triaminotrinitrobenzene (TATB), all three directions are determined by experiment.

Coefficients of the thermal strain tensor are calculated according to the formal description presented in [4]. The temperature dependence of the primitive unit cell (PUC) parameters is approximated by the first-order and second-order polynomials though less often—by the third-order polynomials:

$$P = k_0 + k_1T + k_2T^2 + k_3T^3,$$

where $P$ is a parameter of the PUC: $a$, $b$, $c$, $\alpha$, $\beta$ and $\gamma$; $k_i$ denotes coefficients.

The coefficient of the crystals thermal expansion in an arbitrary direction $N$ can be expressed of the following form:

$$a_N = l_1^2\alpha_i = l_1^2\alpha_1 + l_2^2\alpha_2 + l_3^2\alpha_3, \tag{4}$$

where $l_1$, $l_2$, and $l_3$ are directional cosines of the selected direction $N$ relative to the main axes of the tensor. If we represent the expression (4) in expanded form in the direction $hkl$, then:

$$\alpha_{hkl} = \alpha_{11}x_{hkl}^2 + \alpha_{22}y_{hkl}^2 + \alpha_{33}z_{hkl}^2 + 2\alpha_{12}x_{hkl}y_{hkl} + 2\alpha_{23}y_{hkl}z_{hkl} + 2\alpha_{13}x_{hkl}z_{hkl}, \tag{5}$$

where $\alpha_{hkl}$ are coefficients of thermal expansion in the intended direction $hkl$, $\alpha_{ij}$ are coefficients of the thermal strain tensor, and $x_{hkl}$, $y_{hkl}$, $z_{hkl}$ is the matrix of directional cosines ($l_1$, $l_2$, and $l_3$) of the direction $hkl$.

Values of $x_{hkl}$, $y_{hkl}$, $z_{hkl}$ are calculated from the following relations:

$$x_{hkl} = \frac{h|a^*| + k|b^*| + l|c^*| \cos \beta^*}{|H_{hkl}|},$$

$$y_{hkl} = \frac{k|b^*| \sin^2 \gamma^* + l|c^*| (\cos \alpha^* - \cos \gamma^* \cos \beta^*)}{\sin \gamma^* |H_{hkl}|},$$

$$z_{hkl} = \frac{l|c^*| \sin \alpha \sin \beta^*}{|H_{hkl}|}.$$

Values of the thermal expansion coefficient $a_{hkl}$ in the direction $hkl$ are determined from the formula:

$$a_{hkl} = \frac{dd_{hkl}}{d_{hkl}dT} = -\frac{d^2_{hkl}}{2} \left( \frac{\partial f}{\partial a} \frac{da}{dT} + \frac{\partial f}{\partial b} \frac{db}{dT} + \frac{\partial f}{\partial c} \frac{dc}{dT} + \frac{\partial f}{\partial \alpha} \frac{d\alpha}{dT} + \frac{\partial f}{\partial \beta} \frac{d\beta}{dT} + \frac{\partial f}{\partial \gamma} \frac{d\gamma}{dT} \right),$$

$$d_{hkl}^2 = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} + \frac{2hk \cos \gamma^*}{a^*b^*} + \frac{2kl \cos \alpha^*}{b^*c^*} + \frac{2hl \cos \beta^*}{a^*c^*}. $$
Figure 1. Characteristic indicator surfaces of crystals thermal expansion tensor [1, 4] when (a) \( \alpha_1 = \alpha_2 > \alpha_3 > 0 \) and (b) \( \alpha_1, \alpha_2 > 0; \alpha_3 < 0 \), where \( \alpha_1, \alpha_2 \) and \( \alpha_3 \) are the main coefficients of thermal strain tensor.

In order to determine the thermal strain coefficients matrix \( \alpha_{ij} \), we write down the system of six equations (5) for directions [100], [010], [001], [110], [101], and [011]. Once this is done, we draw figures of thermal expansion coefficients (figure 1).

In the general case, the director surface \( \alpha_N \) has the form of the three-axis ovaloid with axes \( \alpha_1, \alpha_2, \) and \( \alpha_3 \). If two coefficients are equal, this ovaloid turns into the two-axes one, see figure 1(a), and if three coefficients are equal, it takes the spherical shape. If one or two coefficients are negative, then the indicator surfaces of the tensor will consist of individual cavities that characterize regions of the positive or negative thermal expansion of the crystal. Figure 1(b) shows the director surface of the tensor for the thermal expansion of the calcite crystal with a negative coefficient along the \( X_3 \)-axis (\( \alpha_3 \)-axis).

Regions with negative values of \( \alpha_N \) are shown in black. It is obvious that directions lying at the boundary between these regions have a zero thermal expansion coefficient. The directional cosines of these directions can be determined from the expression (4) setting it equal to zero.

For the biaxial crystal with \( \alpha_1 = \alpha_2 \), this expression takes on the following form:

\[
\alpha_N = (l_1^2 + l_2^2) \alpha_1 + l_3^2 \alpha_3 = 0.
\]  

(6)

Bearing in mind that the sum of the squared directional cosines is one \( (l_1^2 + l_2^2 + l_3^2 = 1) \) [1, 4], and substituting this expression in equation (6) we have \( l_3^2 = \alpha_1 / (\alpha_1 - \alpha_3) \).

As an example, for the calcite crystal with \( \alpha_1 = \alpha_2 = -5.6 \times 10^{-6} \text{ K}^{-1} \) and \( \alpha_3 = 25 \times 10^{-6} \text{ K}^{-1} \), calculation gives \( l_3^2 = 0.183 \) that corresponds to the angle of 64.7°. In other words, in the calcite crystal all its directions making the angle of 64.7° with the \( X_3 \)-axis have a zero thermal expansion coefficient.

The work [3] presents the thermal expansion tensor for PETN-I and also describes thermal behavior of other energetic materials. But, directions of main axes turn out to be ambiguously determined and this complicates construction of the thermal strain tensor surfaces.

3. Experiment

Previously, papers [5, 6] analyzed the x-ray diffraction data recorded for BTF and PETN under heating, identified scanning ranges, as well as quantity and rate of heating. Equipment was also calibrated and crystallographic models were constructed in these works.

Changes taking place in the HE crystal structure (more precise definition of the crystalline and microstructural parameters of a PUC, i.e. microdistortions, microstresses, and crystallite sizes) were experimentally measured in the standard configuration using a diffractometric station and a parabolic mirror that helps to obtain a parallel monochromatic x-ray beam.
Table 2. Experimental conditions for various modifications of explosives: I and II are the types of polymorphic modifications; meta means the metastable state.

| Material name       | Temperature (K) | Pressure (GPa) | Scanned angular range 2θ | Holding time, recording time (min) |
|---------------------|-----------------|----------------|---------------------------|----------------------------------|
| BTF                 | less than 473   | $10^{-7}$–$10^{-4}$ | $7°–45°$                  | 3–20                             |
| PETN-I              | less than 414   | $10^{-7}$–10   | $12°–65°$                  | 3–20                             |
| PETN-II (meta)      | 400–413         | $10^{-4}$      | $12°–55°$                  | less than 0.2                    |
| PETN-II             | less than 400   | $10^{-4}$      | $12°–55°$                  | 3–20                             |

Figure 2. Changes in the diffraction pattern of x-rays reflected from PETN-I crystals under heating within 150–370 K. Green color corresponds to the least intense reflexes; blue and yellow—reflexes of medium intensity; red—the most intense.

Individual ranges of reflexes were recorded and adjusted with the purpose to have higher-precision values of scatter angles, higher-precision parameters of the profile and wave electron-density-distribution functions, as well as points of the internuclear and electronic interaction. Further, in order to have a more accurate solution, in particular cases, we made one more x-ray diffraction image in the diverging and parallel beam optics, i.e. in the duplicating mode. This helps to take into account how results depend on the total thermal strain, the increase in resolution in the case of phases superposition in the sample, as well as to reduce effect due to systematic extinctions in order existence of other than basic phases would not interfere with the profile description, indexing, and updating of atomic coordinates.

Preparation for investigations was the following. Smooth layers of the test powdered explosive materials (BTF and PETN) were placed into measuring cells with an embedded thermocouple.
Figure 3. Changes in the diffraction pattern of x-rays reflected from BTF crystals under heating within 150–450 K. Green color corresponds to the least intense reflexes; blue and yellow—reflexes of medium intensity; red—the most intense.

Then, these measuring cells were placed directly onto the platform with a heating element inside the TTK 450 low-high-temperature chamber that was preliminarily mounted at the center of the goniometer focusing circle. Further, this assembly was calibrated, i.e. the initial x-ray diffraction image of the sample was recorded under normal conditions and then positions of main recorded reflexes were compared with the reference and (or) the database. The sample was exposed to the monochromatic x-ray of the 8-keV quanta energy and the x-ray diffraction imaging was performed with the help of the semiconductor detector. The sample was exposed to a sliding x-ray beam with the purpose to reduce dependence on the texture (orientation).

Calibration was performed under normal conditions against NIST 1976a reference standard and the powdered LaB$_6$. Next, we determined the initial state of the test BTF and PETN samples, updated their crystalline structure relative to the monocrystal model: PUC parameters, coherent-scattering region size (crystallite), microdistortion, extinction.

The thermoradiographic experiment was then carried out. This study used the following kinetic parameters of the diffraction system operation:

- heating and cooling rate—10 K/min;
- exposure—7 min.

Theoretical methods of classical electrodynamics [7] and also thermographic analysis methods (table 2) were used to estimate experimental conditions of thermoradiography and to plan the experiments. The x-ray imaging was performed and the pattern of changes in the data on the x-ray powdered PETN-I diffraction (figure 2) and the x-ray powdered BTF diffraction (figure 3) was constructed in the above experimental setup. Figures also give the comparative analysis.
Figure 4. Relative anisotropic changes in the structure of PETN-I crystals under heating within 150–370 K: (a) $\varepsilon = a/a_{293}$, $b/b_{293}$ and $c/c_{293}$; (b) $\varepsilon = V/V_{293}$ and $\rho/\rho_{293}$. The subscript 293 corresponds to parameters at a temperature of 293 K.

Figure 5. Relative anisotropic changes in the structure of BTF crystals under heating within 150–450 K: (a) $\varepsilon = a/a_{293}$, $b/b_{293}$ and $c/c_{293}$; (b) $\varepsilon = V/V_{293}$ and $\rho/\rho_{293}$. The subscript 293 corresponds to parameters at a temperature of 293 K.

how changes in the PUC parameters ($a$, $b$, and $c$) relate to the shift of reflexes indexed under normal conditions. The analysis indicates the relative contribution of changing the position of the reflexes in the change of the cell parameters, for example, $a > b = c$ means that a change in the position of the reflex during thermal exposure has a great impact on parameter $a$, and equally affects the parameters $b$ and $c$.

Graphic representation of thermo x-ray results in the GNU Octave code served as a tool for high-quality visual analysis of x-ray diffraction images obtained at different temperatures [8]. In this situation, there is an analogy with the record of diffraction lines on the photographic plate when the level of darkening (in our case—color) corresponds to the line strength; color scaling was performed both on the length scale, and on a logarithmic scale.
Table 3. Coefficients of the equations.

| Material name | Parameter | \( k_0 \) | \( k_1 \times 10^4 \) | \( k_2 \times 10^6 \) | \( k'_1 \times 10^5 \) | \( 2k'_2 \times 10^7 \) |
|---------------|-----------|-----------|----------------|----------------|-----------------|-----------------|
| \( a = b \)   |           | 9.33056   | -2.94645       | 1.72604        |                 |                 |
| \( c \)       |           | 6.64965   | -1.53038       | 1.32788        |                 |                 |
| PETN-I        | \( V \)  | 579.3074  | -541.4081      | 341.1403       |                 |                 |
| \( \alpha_1 = \alpha_2 \) |           |           | -3.134         | 3.672          |                 |                 |
| \( \alpha_3 \) |           |           | -2.277         | 3.952          |                 |                 |
| \( \beta \)   |           |           | -9.115         | 11.487         |                 |                 |
| \( a \)       |           | 6.87229   | 2.27032        | 0.09405        |                 |                 |
| \( b \)       |           | 19.33581  | 0.30515        | 2.81001        |                 |                 |
| \( c \)       |           | 6.51857   | 0.18855        | 0.16906        |                 |                 |
| BTF           | \( V \)  | 866.4307  | 299.8122       | 168.1724       |                 |                 |
| \( \alpha_1 \) |           |           | 3.270          | 0.271          |                 |                 |
| \( \alpha_2 \) |           |           | 0.156          | 2.870          |                 |                 |
| \( \alpha_3 \) |           |           | 0.288          | 0.517          |                 |                 |
| \( \beta \)   |           |           | 3.370          | 3.781          |                 |                 |

4. Processing of the experiment and results

The x-ray diffraction images were preprocessed by the Le Bail method [9] taking no account of the molecular and atomic structure of materials. The next stage was a more precise definition of the material structure with the help of the Rietveld method [7] and the whole powder pattern modeling (WPPM) [10]. After revealing the primary signs of changes in the molecular structure, we carried out the quantum-chemical analysis in order to optimize the molecular geometry at certain temperatures. Then, the quantum processing cycle was incorporated into the Rietveld method and WPPM, the script was created in the GNU Octave code [8], and all x-ray images were comprehensively analyzed using the conjugated method [11, 12].

Initial conditions for calculation of the x-ray diffraction patterns were taken as follows:

- the crystallographic model is the result of the primary x-ray spectrum (x-ray diffraction—XRD) analysis [13–15];
- the radiation source is the x-ray tube with a copper anode (K\(_{\alpha1} = 1.5406\) Å);
- the semiconductor detector;
- the profile pseudo-Voigt function;
- the simulated range 2\( \theta \) is 5º–60º;
- the initial parameter of FWHM is 0.01.

Processing gave us the PUC parameters and also the microstructure parameters (crystallite size \( d \), microdistortion \( s \), \( ds \)) of the test explosive materials at a certain temperature of the experiment. Furthermore, the curves for relative variation of the PUC parameters (\( a, b \) and \( c \)), as well as of volume and density under heating (figures 4 and 5) were obtained from this processing. The regression analysis and statistical computations gave us the thermal strain tensor equations for the test explosive materials. The General form of the equation: \( P = k_0 + k_1T + k_2T^2 \), where \( k_0, k_1 \) and \( k_2 \) are coefficients; \( P \) is parameter of the PUC: \( a, b \) and \( c \). Differentiating this expression we will obtain the equation for the coefficients of thermal deformation \( \alpha_1, \alpha_2, \alpha_3 \) and \( \beta \): \( P' = k'_1 + 2k'_2T \), where \( k'_1 \) and \( k'_2 \) are equation coefficients. The calculated coefficients of the equations are given in table 3.
Figure 6. Graphic presentation of the thermal strain tensor for molecular crystals at 293 K: (a) BTF and (b) PETN-I, where $\alpha_1$, $\alpha_2$ and $\alpha_3$ are the main axes of the thermal strain tensor.

At temperature $T = 293$ K we obtain $\alpha_1 = \alpha_2 = 7.624 \times 10^{-5}$ K$^{-1}$, $\alpha_3 = 9.302 \times 10^{-5}$ K$^{-1}$, $\beta = 24.542 \times 10^{-5}$ K$^{-1}$ for PETN-I and $\alpha_1 = 4.063 \times 10^{-5}$ K$^{-1}$, $\alpha_2 = 8.565 \times 10^{-5}$ K$^{-1}$, $\alpha_3 = 1.802 \times 10^{-5}$ K$^{-1}$, $\beta = 14.448 \times 10^{-5}$ K$^{-1}$ for BTF.

Surfaces of the thermal strain tensor of the test explosive materials are given in figure 6. A rather large strain coefficient for BTF crystals in $b$-direction, see figure 6(a), indicates weak intermolecular bonds in the family of crystal planes [010]. In PETN-I crystals, weak intermolecular bonds dominate in the direction of the family of crystal planes [111]. The conventional anisotropy coefficient for BTF is 2.7 and for PETN-I is 1.33. The relation between the thermal strain tensor and the crystal structure turns out to be not quite obvious due to insufficiency of data on intermolecular bonds in a crystal.
As the test explosive materials belong to the tetragonal and orthorhombic systems, possibly it is fair to say that principle crystallographic axes in the PETN-I and BTF crystals coincide with the vectors \((a, b\text{ and } c)\) indicating increase of PUC parameters. This fact becomes quite obvious from the work [5] after comparing the data on the linear and volume strain of crystals.

5. Conclusion
The paper presents the thermal strain tensor for two molecular crystals of explosive materials, i.e. BTF and PETN-I. The thermal strain anisotropy was estimated and the character of changes in the molecular and crystalline structure of BTF and PETN-I under heating was analyzed. The developed models of the crystal structure of individual explosive materials at different temperatures were presented in the form of cif-files. Surfaces of the thermal strain tensor for the test explosive materials are analyzed.

Our investigation has led to the following conclusions:

- In order to have high-quality powder XRD data whatever the effect, an experiment needs to be planned to include a preliminary theoretical estimate of the system parameters. This work theoretically estimated detection regions (identification regions) and picked up optimal modes of diffraction data recording for the test explosive materials. This work gave the experimental pattern how the powdered PETN-I XRD data and the powdered BTF XRD data are changing under heating from 150 to 370 (450) K. This pattern characterizes changes in the structure of explosive materials in the indicated temperature range.

- Crystals of PETN show little anisotropy of thermal deformation in contrast to the BTF, the coefficients of anisotropy are respectively equal to 1.33 and 2.7. As a result of thermal exposure on the electrical below 150 K there is a complete freeze of its structure, in this limit the density of 1.804 g/cm\(^3\). The greatest thermal deformation of the BTF crystals is observed in the directions perpendicular to the planes of the family [010] and [1x1], which affect to a greater extent the parameter \(b\) of the PUC. With the regard for force interaction “atom–atom”, the full-profile analysis was used for mathematical processing of experimental data on the x-ray powdered HE samples diffraction under heating within 150 to 370 (450) K in increments of 10 K. A total about of 130 x-ray diffraction images were processed in the duplicating mode.

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