

# Synthesis, structural, spectral and optical characterization of Barium Bis- Paranitrophenolate paranitrophenol Tetrahydrate (BBPT) NLO single crystal

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**Abstract** - A semi-organic non linear optical single crystal of barium bis-paranitrophenolate paranitrophenol tetrahydrate was successfully grown by slow evaporation technique. Structural analysis was carried out by single crystal X-ray diffraction which confirmed that the crystal belongs to orthorhombic crystal system with space group Fdd2. The crystal structure revealed that the eight coordinate barium atom lie on a crystallographic two axis in an environment of two pairs of symmetry related nitro chelating ligand anions, a pair of nitro-O coordinating neutral p-nitrophenolate ligand and four water molecule give a single super molecular structure to the title compound. Functional groups were identified by FTIR and Micro-Raman spectra. The optical study revealed that the crystal has high transmittance in the visible region which is useful for optoelectronics applications. The second harmonic generation (SHG) efficiency of the crystal was examined by performing Kurtz-Perry powder technique and it was found to be 16.2 times that of KDP.

**Key Words:** Single -XRD, Super molecule, Micro-Raman, FTIR and NLO material.

## 1. INTRODUCTION

Nonlinear optical (NLO) materials play a vital role in fast developing field such as photonics and optoelectronics [1-3]. The organic crystals have large nonlinearity but they have poor mechanical and thermal stability compared to organic counter parts. Inorganic crystals have excellent mechanical and thermal properties but they possess relatively modest optical nonlinearity due to the lack of extended  $\pi$ -electron delocalization [4-7]. Hence, investigations were done to develop various semi-organic crystals which are more suitable for device fabrication [8-12].

Nitrophenol family crystals are of much interest to the researchers due to their intensive applications in the field of optoelectronics. Hence paranitrophenol is found to be

one of the best proton acceptors for the metallic hydroxide complexes. In paranitrophenoxide metal complex crystals the organic ligand (nitrophenoxy ion) is ionically bonded to the metal ion along with the intermolecular hydrogen bonding imparts higher stability to the crystal [13-16]. There are only a few reports available on the growth and characterization of BBPT single crystal. The thermal and mechanical properties of title compound were reported by Varjula et al, [17] and also the same crystal was grown using S-R method by Uthrakumar et al, [18] but they are not resolved crystal structure. In the present work, we solved the crystal structure and report the systematic studies on the growth, optical, spectral studies and the optical nonlinearity of the compound was investigated by Kurtz powder technique.

## 2. EXPERIMENTAL DETAILS

The barium bis-paranitrophenolate paranitrophenol tetrahydrate compound was synthesized using the purified p-nitrophenol and barium hydroxide in the stoichiometric ratio of 4:1. The ratio was estimated according to the following chemical reaction:



The synthesized salt was further purified by repeated recrystallization process and it was used for the preparation of saturated solution and taken in a beaker with perforated lid in order to control the evaporation rate. The saturated solution of BBPT was kept in side a constant temperature bath maintained at a temperature of 30°C with an accuracy of  $\pm 0.01^\circ\text{C}$ . Single crystal of dimensions with  $15 \times 11 \times 6 \text{ mm}^3$  was harvested in a period of 4 weeks by slow evaporation of solvents and the as grown single crystal of the title compound was shown in Figure. 1.

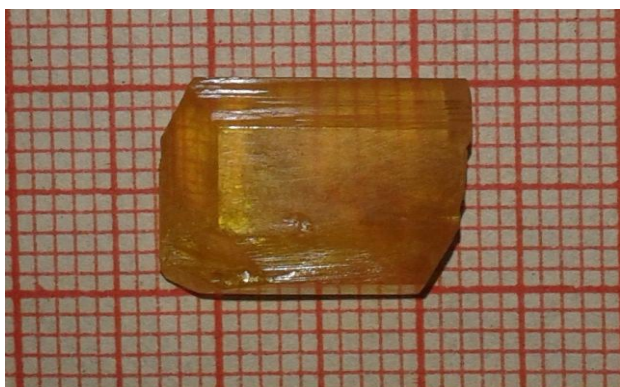


Fig-1: Photograph of as grown single crystal of BBPT.

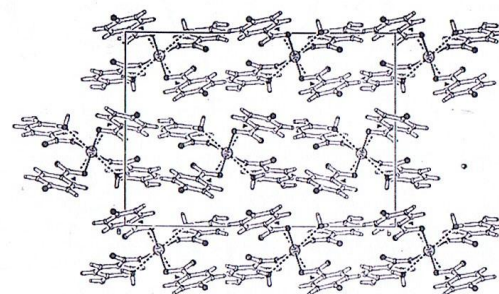


Fig-3: Packing of BBPT molecules in unit cell

### 3. RESULTS AND DISCUSSION

#### 3.1. Single crystal X-ray diffraction study

Single crystal data of the title compound were collected using ENRAF NOUIS CAD 4 X-ray diffractometer. The XRD data revealed that the BBPT crystal belongs to orthorhombic system with non centrosymmetric space group  $Fdd2$  and the lattice parameters were found to be  $a = 19.901(5) \text{ \AA}$ ,  $b = 28.022(6) \text{ \AA}$ ,  $c = 10.746(4) \text{ \AA}$ . The observed results agreed very well with the reported value within the limits of standard deviation. The three dimensional diffraction intensity data was collected and the crystal structure was redetermined by the direct methods using SIR 92 program. The present residual factor of refinement was 0.0207 as compared to 0.028 that of Jack M Harrowfield. Also the data confirms that R factor is better than the available one in literature [19], Crystal data and structure refinement parameters are presented in Table 1, the selected bond length and bond angles in the asymmetric unit are given in Table 2 and 3. The hydrogen coordinates and isotropic displacement parameters are given in Table 4, and the hydrogen bonding and angles are given in Table 5. Figure 2 shows the ORTEP representation of the molecule with 50 % probability ellipsoids for non hydrogen atom and Figure 3 represents the unit cell packing of the molecule projected along the c-axis.

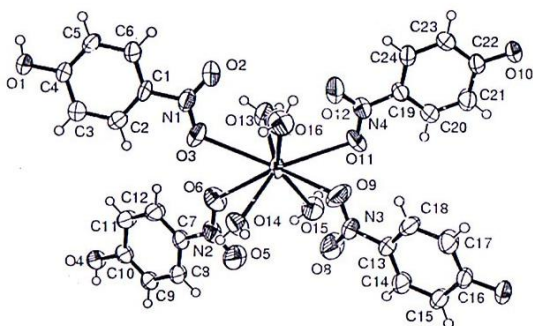


Fig-2: ORTEP representation of BBPT single crystal

Table-1: Crystal data and structure refinement parameters for BBPT crystal

Identification code	BBPT crystal
Empirical formula	$C_{24} H_{26} Ba N_4 O_{16}$
Formula weight	763.83 g
Temperature	293 (2) K
Wavelength	0.71069 $\text{\AA}$
Crystal system,	Orthorhombic,
space group	$Fdd2$
Unit cell dimensions	$a = 19.901(5) \text{ \AA}$ , $\alpha = 90^\circ$ $b = 28.022(6) \text{ \AA}$ , $\beta = 90^\circ$ $c = 10.746(4) \text{ \AA}$ , $\gamma = 90^\circ$
Volume	5992 (3) $\text{\AA}^3$
Z, Calculated density	8, 1.692 $\text{Mg/m}^3$
Absorption coefficient	2.628 $\text{mm}^{-1}$
F (000)	3056
Crystal size	0.3 $\times$ 0.3 $\times$ 0.2 mm
Theta range for data collection	2.27 to 24.97 deg.
Limiting indices	$0 < h < 23$ , $-33 < k < 33$ , $0 < l < 12$
Reflection collected /unique	2748/1392 [R (int) = 0.0322]
Completeness to theta = 24.97	100.0%
Absorption correction	Psi-scan
Max. and min. transmission	0.9994 and 0.6870
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	1392/143/222
Goodness-of-fit on $F^2$	1.049
Final R Indices [ $I > 2 \sigma(I)$ ]	$R1 = 0.0207$ , $wR2 = 0.0521$
R indices (all data)	$R1 = 0.0248$ , $wR2 = 0.0539$
Absolute structure parameter	0.000
Extinction coefficient	0.00038 (6)
Largest diff. peak and hole	0.360 and -0.33 $e \cdot \text{\AA}^{-3}$

From the Figure 2, it is confirmed that the crystal was composed of four distinct chromophores that were organized in herringbone motifs along the inorganic chain of Ba-O. The 8 coordinate barium atom lie on a crystallographic 2 axis in an environment of two pairs of symmetry related nitro chelating ligand anions and a pair of nitro-O coordinating neutral paranitrophenolate ligand and the four water molecule. The whole [Ba (4-np) 2, (4-npH) 2.4H<sub>2</sub>O] array may be envisaged as a single neutral (super) molecule. The donor acceptor distances of the hydrogen bonding O(6)-H(6) O(3)#3, O(7)-H(7B)-O(6)#3, O(7)-H(7A)-O(3)#4, O(8)-H(8A)-O(3)#5, O(8)-H(8B)-O(6)#6 are 2.505(5), 2.857157Å, 2.836 (5) Å, 2.7414(6) Å and 3.172(6)Å respectively indicating that the hydrogen bonding were strong and the hydrogen bonds between confronting phenoxides of the neutral paranitrophenolate (4npH) components of the parent and the paranitrophenol (4-np) components of neighboring molecules link the whole into a three dimensional array.

Table -2: Selected bond length [Å] for BBPT crystal.

Bonds	Bond Length
C (4) – O (3)	1.325 (6)
C (9) – C (10)	1.366 (8)
C (10) – O (6)	1.355 (6)
N (1) – O (2)	1.218 (6)
N (1) – O (1)	1.218 (6)
N (2) – O (5)	1.214 (6)
N (2) – O (4)	1.236 (6)
O (1) – Ba	2.959 (5)
O (2) – Ba	3.288 (5)
O (4) – Ba	2.939(4)
O (6) – H (6')	0.82000
O (7) – Ba	2.708 (4)
O (7) – H (7B)	0.9299(12)
O (7) – H (7A)	0.9299(12)
O (8) – Ba	2.724 (4)
O (8) – H (8A)	0.9300 (12)
O (8) – H (8B)	0.9300 (12)
Ba – O (7) #1	2.708 (4)
Ba – O (8) #1	2.724 (5)
Ba – O (4) #1	2.939 (4)
Ba – O (1) #1	2.959 (5)
Ba – O (2) #1	3.288 (5)

Symmetry transformations used to generate equivalent atom: #1 -X+3/2, -Y+1/2, Z

Table -3: Selected bond length [Å] for BBPT crystal.

Bonds	Bond angles ( deg)
O (6) – C (10)-C (9)	122.7(4)
O (6) – C (10)-C (11)	117.0(5)
C (7) – C (12)-H (12)	120.3
O (2) – N (1)-O (1)	120.0(5)
O (2) – N (1)-C (1)	120.0(5)
O (1) – N (1)-C (1)	119.9(5)
O (5) – N (2)-O (4)	122.1(5)
O (5) – N (2)-C (7)	119.8 (4)
O (4) – N (2)-C (7)	118.1(5)
N (1) – O (1) - Ba	108.5(4)
N (1) – O (2) - Ba	91.7(3)
N (2) – O (4) - Ba	128.3(4)
C (10) – O (6) – H (6')	109.5
Ba-O (7) – H (7B)	128(4)
Ba-O (7) – H (7A)	124(3)
H (7B)-O (7) – H (7A)	107(5)
Ba-O (8) – H (8A)	110 (5)
Ba-O (8) – H (8B)	130 (6)
H (8A)-O (8)-H (8B)	120 (8)
O (7) – Ba - O (7) #1	139.26(19)
O (7) – Ba - O (8)	103.62(17)
O (7) #1 – Ba - O (8)	86.59(16)
O (7) – Ba - O (8) #1	86.59(16)
O (7) #1 – Ba - O (8) #1	103.62(17)
O (8) – Ba - O (8) #1	150.7(19)
O (7) – Ba - O (4) #1	74.78(14)
O (7) #1 – Ba - O (4) #1	70.56(13)
O (8) – Ba - O (4) #1	134.72(19)
O (8)#1 -Ba-O(4) #1	74.25 (15)
O (7) – Ba - O (4)	70.56 (13)
O (7) #1 – Ba - O (4)	74.78 (14)
O (8) – Ba - O (4)	74.25(15)
O (8) #1– Ba - O (4)	134.72(15)
O (4) #1– Ba - O (4)	62.42(19)
O (7) – Ba - O (1)	76.69 (15)
O (7) #1 – Ba - O (1)	143.43(14)
O (8) – Ba - O (1)	90.62 (15)
O (8) #1– Ba - O (1)	64.74(15)
O (4) #1– Ba - O (1)	130.76(15)
O (4) – Ba - O (1)	138.99(12)
O (7) – Ba - O (4) #1	143.43 (14)
O (7) #1 – Ba - O (1) #1	76.69 (15)
O (8) – Ba - O (1) #1	64.74 (15)
O (8) #1 – Ba - O (1) #1	90.62 (15)
O (4) #1 – Ba - O (1) #1	138.99 (12)
O (4) – Ba - O (1) #1	130.76 (15)
O (1) – Ba - O (1) #1	69.3 (2)
O (7) – Ba - O (2)	67.01 (14)
O (7) #1 – Ba - O (2)	143.79 (13)
O (8) – Ba - O (2)	59.12 (14)

O (8) #1 - Ba - O (2)	102.18 (14)
O (4) #1 - Ba - O (2)	141.71 (14)
O (4) - Ba - O (2)	103.71 (12)

Symmetry transformations used to generate equivalent atom: #1 -X+3/2, -Y+1/2, Z

Table -4: Hydrogen coordinates (×104) and isotropic displacement parameters (A<sup>2</sup> × 10<sup>3</sup>) for BBPT crystal.

	X	Y	Z	U (eq)
H (2)	7290	3442	1312	62
H (3)	6951	3622	-672	65
H (5)	5100	3157	130	66
H (6)	5447	2954	2117	66
H (8)	5011	2095	9044	61
H (9)	4671	1862	11016	59
H (12)	6590	1778	12112	71
H (12)	6933	2028	10142	68
H (6')	5004	1687	12994	140(40)
H (7B)	6760(30)	3561(9)	6140(50)	61(18)
H (7A)	6520(20)	3254(18)	7190(30)	46(14)
H (8A)	6640(40)	1564(12)	5220(90)	110(30)
H (8B)	6140(30)	1920(40)	4490(80)	130(40)

Table- 5: Hydrogen bonds for BBPT (Å and degree)

D-H...A	d (D-H)	d (H...A)	d (D...A)	< (DHA)
O (6)-H (6')...O (3) #2	0.82	1.71	2.505(5)	161.8
O (7)-H (7B)...O (6) #3	0.9299(12)	1.99(3)	2.857(5)	154 (6)
O (7)-H (7A)...O (3) #4	0.9299(12)	1.95(2)	2.836(5)	158 (5)
O (8)-H (8A)...O (3) #5	0.9300(12)	1.80(2)	2.714(6)	166 (8)
O (8)-H (8B)...O (6) #6	0.9300(12)	2.32(5)	2.172(6)	152 (9)

Symmetry transformation used to generate equivalent atoms:

#1 -X+ 3/2, -Y+1/2, Z #2 -X +1, -Y+1/2, Z+3/2 #3-X+5/4, Y+1/4, Z-3/4 #4 X,Y,Z+1 #5 -X+5/4, Y-1/4, Z+3/4 #6 X,Y,Z-1

### 3.2. DRS -UV-Vis-NIR Spectral Studies

The diffuse reflectance spectrum of grown single crystal was carried out using Perkin-Elmer Lambda 35, double beam spectrophotometer in the range of 190-1100 nm. The absorption and transmittance spectra were obtained by using Kubelka Munk (K-M) theory and the resultant spectra is shown in Fig.4. The UV-Vis lower cut-off wavelength is found to be at 208 nm. Fig.4 shows that the material posses a low absorption, indicating the BBPT single crystal as promising material for electro-optic applications. Just below 477 nm, the absorbance raises and it is due to the electronic transitions in the aromatic ring of the title material.

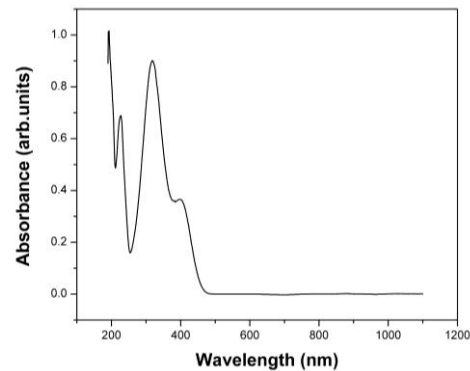


Fig-4: The UV-Vis-NIR Absorbance spectrum of BBPT single crystal.

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons. The nature of the transition is determined by using classical relation,

$$(\alpha h\nu)^2 = A (h\nu - E_g)$$

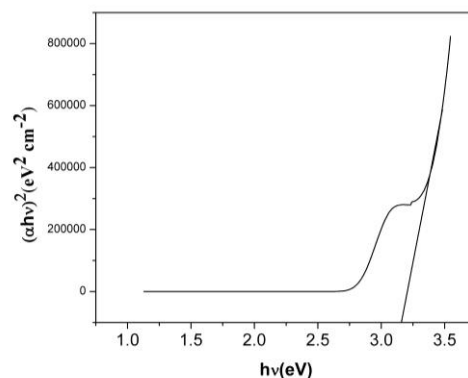


Fig -5: (αhν)<sup>2</sup> versus Photon energy hν of BBPT single crystal.

Where  $\alpha$  is the absorption coefficient,  $A$  is a constant,  $h$  is the plank's constant,  $\nu$  is the frequency of the incident beam and  $E_g$  is the optical band gap the crystal. The value of absorption coefficient in the present case is order  $10^6 \text{ cm}^{-1}$ , which supports direct band gap nature of the material. A plot of variation of  $(\alpha h\nu)^2$  versus Photon energy  $h\nu$  (eV) is shown Fig. 4. Based on the allowed direct inter band gap transition, the band gap is determined by extrapolating straight line of  $(\alpha h\nu)^2$  versus photon energy curve to the intercept on horizontal photon energy axis. The direct optical band gap value is found to be 3.17 eV.

### 3.3. FTIR Analysis

The FTIR analysis of the BBPT crystal were carried out using KBr pellet technique by a Bruker vertex 70 FTIR spectrometer and shown in Fig. 6 and the corresponding vibrations were assigned in Table 6. There is a broad envelope peak obtained at  $3247 \text{ cm}^{-1}$  may due to OH stretching vibration of water. The  $\text{NO}_2$  symmetric and asymmetric vibrations were confirmed by the peak at  $1492 \text{ cm}^{-1}$  and  $1590 \text{ cm}^{-1}$  respectively. The presence of aromatic ring skeletal vibrations was observed at  $1332 \text{ cm}^{-1}$ . A sharp and small absorption peak at  $1100 \text{ cm}^{-1}$  represented the C-OH stretching vibration. The peak at  $842 \text{ cm}^{-1}$  corresponds to C-H deformation. Small absorption peaks observed between 450 and  $500 \text{ cm}^{-1}$  arise due to the presence of the O-Ba bonds [17-18].

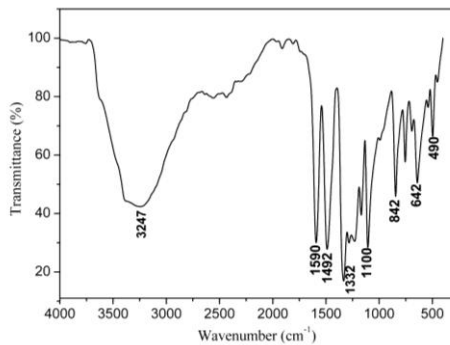


Fig -6: FTIR spectrum of BBPT

Table -6: The Vibrational modes of BBPT single crystal and their tentative assignments

Wavenumber ( $\text{cm}^{-1}$ )	Assignment
3247	O-H asymmetric stretching
1590	$\text{NO}_2$ stretching vibrations
1492	$\text{NO}_2$ vibrations
1332	Aromatic ring vibrations
1100	C-OH stretching vibration
842	C – H deformation

642	C-N stretching vibration
450-500	O - Ba stretching

### 3.4. Micro- Raman spectral analysis

Generally the unresolved peaks in the FTIR spectrum would be clearly resolved in Micro-Raman spectrum. In the present work Micro-Raman analysis was made on the BBPT crystal using in the region between  $400 \text{ cm}^{-1}$  and  $1700 \text{ cm}^{-1}$  Jobin-Yvon Horibia (LABRAM- HR) visible spectrometer.  $\text{Ar}^+$  laser ( $488 \text{ nm}$  wavelength,  $10 \text{ mW}$  power) was used as an excitation source. The resultant Micro-Raman spectrum of BBPT single crystal is shown in Fig. 7.

The Vibrational peaks at  $1465, 1518, 1591 \text{ cm}^{-1}$  represent C=C stretching vibration was observed from Figure. 7, for the same type of vibration only one peak around  $1590 \text{ cm}^{-1}$  was observed in FTIR. The para substitutions of nitro group with its symmetric vibration were observed at  $1327 \text{ cm}^{-1}$ . The bending vibration of C-H out plane of benzene ring was observed at  $854 \text{ cm}^{-1}$ .

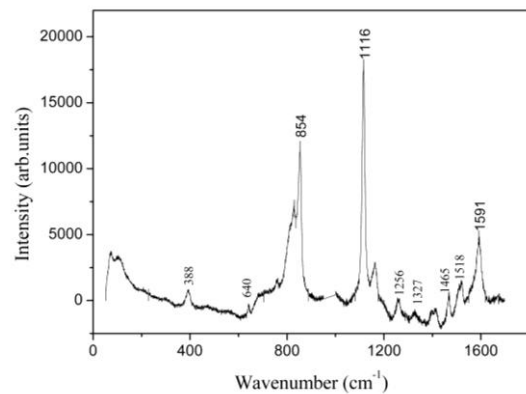


Fig -7: Micro- Raman spectrum of BBPT single crystal.

The peaks at  $1116 \text{ cm}^{-1}$  corresponds to C-H in plane bending vibration. The Micro-Raman peaks at  $640$  and  $1256 \text{ cm}^{-1}$  represented C-N stretching vibration which is also observed in FTIR spectrum. The hydrate of barium metal ion in the lattice of the crystal was evident from peaks below  $500 \text{ cm}^{-1}$  [20].

### 3.5. SHG Efficiency Of BBPT Single Crystal

The Second Harmonic Generation (SHG) conversion efficiency of BBPT single crystal was measured by Kurtz-Perry powder technique [21]. A Q-switched mode locked Nd: YAG laser was used to generate about  $6 \text{ mJ/pulse}$  at  $1064 \text{ nm}$  fundamental radiation. This laser can be operated in two modes. In the single shot mode, the laser emits a single  $8 \text{ ns}$  pulse whereas in multi shot mode, the laser produces a continuous train of  $8 \text{ ns}$  pulses at a repetition rate of  $10 \text{ Hz}$ . In this present study, a single shot

mode of 8 ns laser pulse with a spot radius of 1 mm was used. This experimental setup consists of a mirror and 50/50 beam splitter (BS) to generate a beam with pulse energies about 6 mJ. The input laser beam was passed through an IR reflector and then directed to the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm.

The photodiode detector and oscilloscope measured the light emitted by the sample. Microcrystalline powder of KDP and BBPT crystal was taken in a similar sized capillary tube and sealed at one end for comparison. The intensity of the second harmonic output from the sample was compared with KDP. Thus, the figure of merit of SHG efficiency of the sample was estimated. The KDP had been taken as a reference sample that has an output 0.260 V. The output of the BBPT grown crystal was calculated from SHG study that has an output of 4.212 V. From the above calculated result of SHG efficiency of the BBPT crystal was 16.2 times that of KDP.

#### 4. CONCLUSION

A semi-organic NLO material BBPT single crystal was grown by slow evaporation technique. Single X-ray diffraction study was carried out to find the unit cell parameter and the crystal structure of the material. The optical study shows that the crystal was optically transparent in the entire visible and near infrared region with lower cut-off wavelength of 208 nm. The functional groups were confirmed by FTIR and Micro-Raman spectra. The SHG efficiency of the grown single crystal was found to be 16.2 times greater than that of KDP crystal. Owing to its transparency, molecular strength and non-centrosymmetric structure the grown crystal may consider to be a promising material for NLO applications.

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