

Crystal growth, spectral and thermal analyses of a semi organic nonlinear optical single crystal: L-tyrosine hydrochloride

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L-tyrosine hydrochloride have been synthesized by chemical route and grown as single crystals by slow evaporation method from a supersaturated solution prepared from the solvent of 2 Normal hydrochloride (HCl) at ambient temperature. In addition to the single crystal and powder X-ray diffraction analyses FTIR, FT-Raman, NMR spectral analyses also have been done to study the structural properties. Linear and nonlinear optical characteristics have been studied by using UV-Visible spectral analysis and Kurtz Perry powder technique respectively. The second harmonic generation conversion efficiency of the grown crystal has been confirmed by the emission of green light. Thermo gravimetric (TG), Differential thermal analysis (DTA) and differential scanning calorimetric studies have also been employed to study the thermal behavior of the crystal sample and reported in this paper.

(Received July 24, 2012; accepted October 30, 2012)

Keywords: Semi organic, Optical materials, Crystal growth, X-ray diffraction, Thermo gravimetric analysis, NMR

1. Introduction

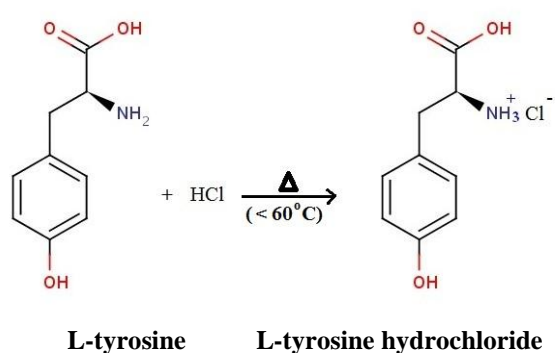
In recent few decades, much interest is focused on the growth of non linear optical materials because of their potential applications towards opto-electronics, photonics, Laser spectroscopy etc., [1,2]. The development of highly efficient non linear optical (NLO) crystals for visible and ultraviolet (UV) regions is most important for both laser spectroscopy and laser processing. Organic crystals possess sufficiently large nonlinear co-efficient, are transparent in ultraviolet region, have a lower laser damage threshold power and are easy to grow with large dimensions. However, most organic NLO crystals have poor mechanical and thermal properties and are at risk to damage during processing. On the other hand, inorganic crystals are having higher mechanical and thermal properties but, poor NLO property. Hence to achieve the desirable properties in one material the semi organic materials are derived from organic and inorganic materials. Owing to this, it is desired to find new NLO crystal materials which have a shorter cutoff wavelength [3-5]. Petroysan et al., have derived some semi organic nonlinear optical crystals of amino acids salts and reported the interaction with various acids [6]. Recently our team has reported the effect of solvent normality on the growth of L-tyrosine bromide single crystals [7]. Natarajan et al.,

has reported the growth and some of the properties of L- tyrosine hydrochloride crystals [8]. However, sufficient characterization has not been observed in our literature survey. In this paper, the growth of L-tyrosine hydrochloride (LTHC) structural and thermal characterization of the grown crystal have been discussed elaborately.

2. Experimental techniques

2.1 Synthesis of L-tyrosine hydrochloride (LTHC)

The analytical grade L-tyrosine and hydrochloric acid (HCl) were taken as starting materials to synthesize L-tyrosine hydrochloride (LTHC) in 1:1 molar ratio. The calculated amount of hydrochloric acid was dissolved first in excess of milli pore water of resistivity 18.2 MΩcm. The measured amount of L-tyrosine was added to the solution slowly with stirring. After the solution attained the homogeneous state it was kept in a hot plate which was maintained bellow 60 °C and allowed to evaporate in order to synthesize the LTHC salt according to the following reaction.



2.2 Bulk growth of LTHC

Bulk growth of LTHC single crystal has been carried out in aqueous solution by slow evaporation technique, using a constant temperature bath controlled to an accuracy of $\pm 0.01^\circ\text{C}$. The saturated solution was prepared from the 2N solvent at 30°C and then filtered to remove insoluble impurities. The seed obtained from slow evaporation method was used for the bulk growth. The solution was maintained at 30°C for 2 days before seeding. After the seed was mounted properly, the solution was covered by a thin plastic cover and a few holes were made in order to induce the evaporation of solvent so as to enable the growth process. The microbes have not been observed during the growth of the crystal, which may probably due to the presence of hydrochloric acid, which acts destructively on the growth of microbes. Bulk crystals of dimension around $10 \times 10 \times 8 \text{ mm}^3$ have been harvested after a period of fifteen days. The grown crystals are stable at ambient temperature and non hygroscopic. The as grown crystals are shown in Fig. 1.



Fig. 1. Photograph of as grown crystals of L-tyrosine hydrochloride.

2.3. Characterization techniques

As grown seed crystals were used to study the properties. Single crystal X-ray diffraction analysis was carried out using an ENRAF CAD-4 diffractometer with

MoK_α ($\lambda = 0.7107 \text{ \AA}$) radiation to identify the crystal system and to estimate the lattice parameters. Powder x-ray diffraction pattern was also obtained by Bruker D8 advanced model diffractometer and the lattice parameters were verified using monoclinic crystallographic equation and the diffraction pattern is indexed. The FTIR spectrum of L-tyrosine hydrochloride crystal was recorded in the range $400\text{--}4000 \text{ cm}^{-1}$ using a Perkin-Elmer spectrometer by KBr pellet method in order to verify the presence of various functional groups. FT-Raman spectrum was also recorded by using Bruker RFS 27 spectrometer and various modes of vibrations have been assigned [9]. The ^{13}C and ^1H NMR spectra of the grown crystal were recorded using JEOL GSX 400 instrument at 30°C to confirm the functional groups identified [10]. To confirm the nonlinear optical property, the powder of the grown crystal was subjected to Kurtz powder SHG test [11]. Thermo gravimetric (TG), Derivative thermo gravimetric (DTG), Differential thermal analysis (DTA) for the grown crystals were carried out at nitrogen atmosphere by NETZSCH thermal analyzer to study the thermal property of the as grown crystal. Differential scanning calorimetric curve (DSC) was also obtained using scanning calorimeter to find the thermal stability more precisely.

3. Results and discussion

3.1 Single crystal X-ray diffraction analysis

Single crystal x-ray diffraction analysis was carried out to determine the lattice parameters. The data were collected at 293 K using MoK_α ($\lambda = 0.71069 \text{ \AA}$) radiation. From the single crystal XRD analysis, it has been observed that the grown crystal possess monoclinic structure. The lattice parameter values are listed in Table 1. The single crystal data are in good agreement with reported values [8].

Table 1. Crystal data of LTHC in the present study.

Identification code	Single crystal data
Chemical formula	$\text{C}_9\text{H}_{12}\text{O}_3\text{NCl}$
Temperature	293(K)
Wavelength	0.7107 \AA
Crystal system	monoclinic
Unit cell dimension	$a = 5.091 \text{ \AA}$ $b = 9.024 \text{ \AA}$ $c = 11.065 \text{ \AA}$
β	91.80°
Volume \AA^3	508.339
Density (ρ) g/cm^3	1.44

3.2 Powder X-ray diffraction analysis

The grown crystal was made as powder and subjected to powder x-ray diffraction study. The data were collected at 298 K from two theta value of 10° to 80° with the source wave length of 1.5460 \AA . The step size of 2θ and the scan step time were fixed as 0.05° and 10 seconds respectively. The prominent well resolved Bragg's peaks at specific diffraction angles reveal the high crystalline nature of the grown crystal. Using the cell parameters, 2θ values and corresponding d spacing the miller indices (hkl) of prominent peaks have been identified and indexed for monoclinic system. The indexed powder x-ray diffraction pattern of LTHC is shown in Fig. 2.

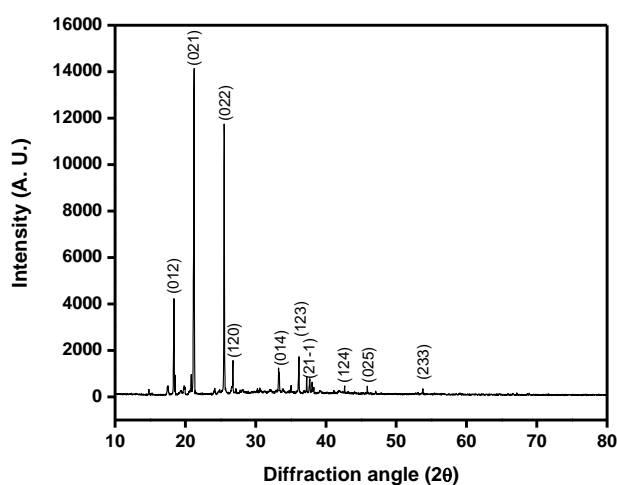


Fig. 2. Powder x-ray diffraction pattern of L-tyrosine hydrochloride.

3.3 FTIR and FT-Raman spectral analysis

In order to analyze the presence of functional groups in LTHC qualitatively, Fourier transform infrared (FTIR) and FT-Raman spectra were recorded in the range of $400\text{--}4000 \text{ cm}^{-1}$ and $50\text{--}5000 \text{ cm}^{-1}$ as shown in Fig. 3 and 4 respectively. In FTIR spectrum the broad envelop between 2000 and 3500 cm^{-1} includes overlap of absorption peaks due to O–H stretch of $-\text{COOH}$ and phenolic O–H, and N–H stretch of NH_3^+ . The CH_2 vibrations which generally lie just below 3000 cm^{-1} are not clearly resolved. The broadening of peak in this region is due to hydrogen bonding. Overtones and combination bands with prominent peaks near 2500 and 2000 cm^{-1} are due to hydrochlorides in FTIR spectrum. These bands are also almost continuous in the range 3030 to 2500 cm^{-1} . Most of these vibrations are clearly resolved in FT-Raman spectrum. The sharp spectral lines observed between 2800 and 3070 cm^{-1} includes the lines due to O–H stretch of $-\text{COOH}$ and phenolic O–H, and N–H stretch of NH_3^+ . The CH_2 vibrations which generally lie just below 3000 cm^{-1} are clearly resolved in the Raman spectrum. In the finger print region of FTIR spectrum, the C=O vibration of $-\text{COOH}$ lies at 1735 cm^{-1} and the same is observed at 1724 cm^{-1} in Raman spectrum. The bending modes of

NH_3^+ occurs close to 1598 and 1475 cm^{-1} in infrared (IR) spectrum, whereas these modes occur nearly at 1613 and 1558 cm^{-1} in Raman spectrum. The CH_2 bending modes appear at 1475 and 1351 cm^{-1} in IR spectrum and at 1458 and 1328 cm^{-1} in Raman spectrum. The intense band at 1235 cm^{-1} is due to phenolic C–O stretch in both spectra. The groups of peaks associated with it are due to $-\text{COO}-$ vibrations. The para substitution in the aromatic ring is confirmed by the peak at 839 cm^{-1} in the IR spectrum. As the IR spectrum does not carry peak close to 1630 cm^{-1} , the crystal must be devoid of any water of crystallization. It is also confirmed by the absence of weight loss due to water in the TGA trace. The strong line at 125 cm^{-1} is due to the torsion oscillation of $\text{NH}_2 - \text{C} - \text{COOH}$ and the bending mode due to C– NH_2 is observed at 279 cm^{-1} in Raman spectrum. The important and prominent wave numbers of vibrations and their assignments are presented in the Table 2.

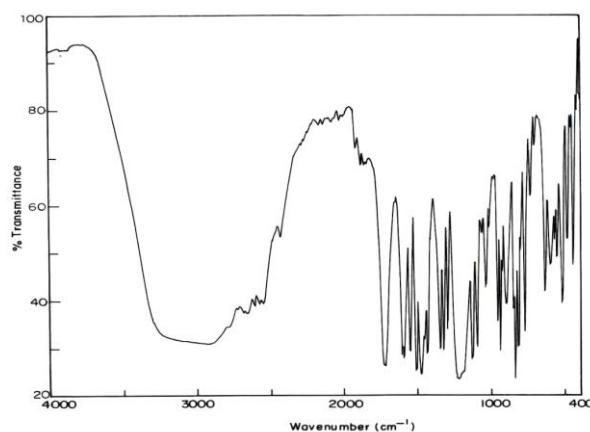


Fig. 3. FTIR Spectrum of L-tyrosine hydrochloride crystalline powder.

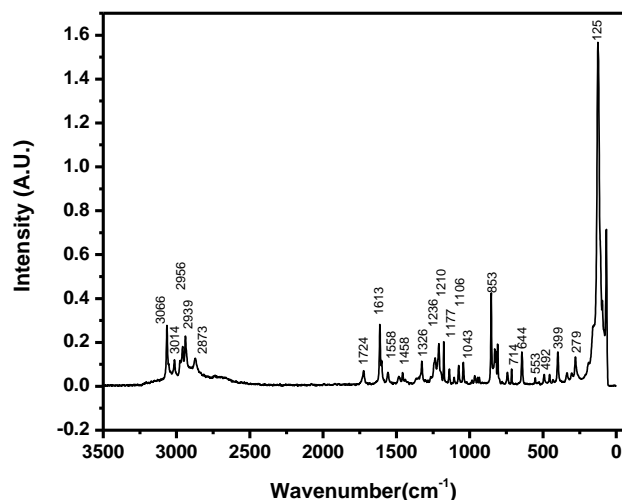


Fig. 4. FT-Raman spectrum of L-tyrosine hydrochloride.

Table 2. Wavenumbers (cm^{-1}) of FTIR absorption peaks and FT - Raman lines in the spectra of LTHC crystal samples and their assignments.

Wave number (cm^{-1})		Assignment
FTIR	FT-Raman	
3058	3066	C - H asym. stretching (aliphatic)
--	3014	C - H asym. stretching in ring
--	2958	C - H stretching and CH_2 asym. stretching
2922	2939	CH_2 sym stretching
--	2873	CH_2 asym stretching
2141	--	C-H stretching
1734	1724	C=C stretching
1598	1613	NH_2 scissoring
1556	1558	C-C-C stretching
1475	1458	C-H in plane bending in ring
1438	--	CH_2 scissoring
1330	1326	Combination of C-C-C stretching and Phenolic OH
1235	1236	Phenolic OH stretch with ring carbon
--	1210	in plane bending of C - H and OH of COOH
--	1177	C - C stretching
1136	1139	O - H in plane bending of COOH
1104	1106	C - N stretching
1041	1043	C - H in plane bending
898	853	CH_2 torsion/ Para Substitution
838	829	Ring breathing
820	821	NH_2 wagging
777	743	NH_2 wagging + O - H opb + C-C-C bending
739	714	O - H opb of COOH + opb of C-C-C
637	644	Combination of Vibrations
525	553	C-C-C out of plane bending
492	492	C-H bending + C-C-C out of plane bending
--	399	C-C-C out of plane bending
--	336	O-H out of plane bending of phenolic group
--	279	C- NH_2 bending
--	125	Torsional oscillation of NH_2 -C-COOH

3.4 NMR spectral analysis

NMR spectrum has been used to identify the carbon and hydrogen atoms present in various chemical environments and to confirm the functional groups in the grown crystal. The ^{13}C NMR spectrum of the grown crystal of LTHC is shown in Fig. 5. The carboxyl carbon gives its signal at 172.6 ppm. The aliphatic carbon carrying NH_3^+ and aromatic ring gives their signals at 55.4 ppm and 35.9 ppm respectively. The aromatic ring carbon

produces their characteristic signal between 110 and 140 ppm. The aromatic ring carbon carrying the alkyl position gives its signal at 126.8 ppm. The ortho and meta carbon of the ring with alkyl substituent gives their signals at 132 and 117.2 ppm respectively. The para carbon carrying on substituent shows its signal at 156.4 ppm. Since no other peaks are observed, the compound has been synthesized as pure L-tyrosine hydrochloride and used for large size crystals.

Proton NMR spectrum of the purified LTHC sample was recorded using D_2O as solvent and is shown in Fig. 6. The spectrum shows six different peaks at different chemical shift position. The ortho hydrogen (proton) in the aromatic structure can see each other as aligned (parallel) or opposed (antiparallel) and come to resonance twice. Thus the ortho protons appear as doublet. These doublets have been seen at $\delta = 6.86$ and $\delta = 7.16$ ppm with the splitting factor of $J = 8.4$. The aliphatic CH proton has given its signal as triplet at $\delta = 4.27$ ppm with the splitting factors of $J = 5.6$ and 7.2 . The doublet signal at $\delta = 3.2$ ppm is due to CH_2 . The multiple splitting is due to presence of NH_3 in the molecular structure.

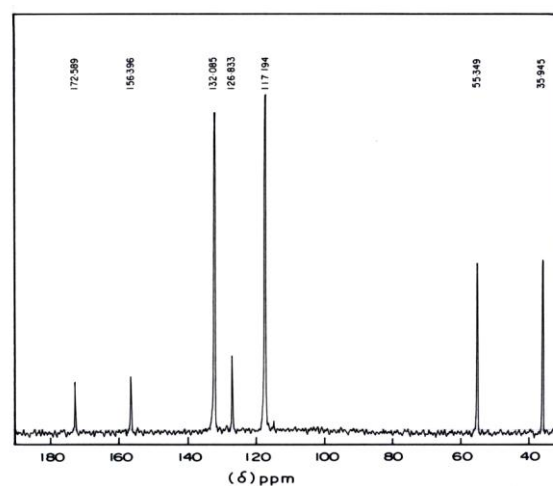


Fig. 5. ^{13}C NMR spectrum of L-tyrosine hydrochloride.

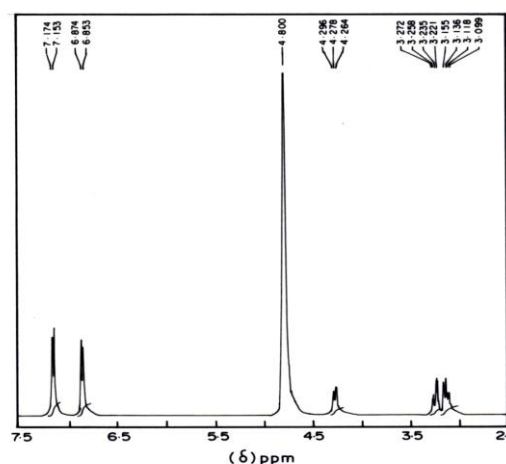


Fig. 6. ^1H NMR spectrum of L-tyrosine hydrochloride.

3.5 UV-Vis spectral analysis

Since the absorption, if any in the NLO material near the fundamental or second harmonic will lead to loss of conversion efficiency, it is necessary to have good optical transparency in an NLO crystal in the UV and visible region. Optical absorption spectrum was recorded in the range between 200 to 800 nm and the spectrum is shown in the Fig. 7. LTHC crystals have UV cutoff at 250 nm and no absorption of light has been observed to any appreciable extent in the visible range of the electromagnetic spectrum. Hence, LTHC is useful for optoelectronic applications and the second harmonic generation or other applications in the UV and visible region.

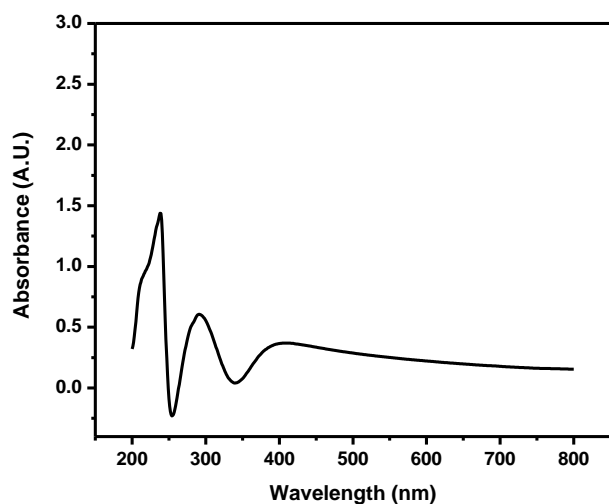


Fig. 7. UV-Vis absorption spectrum of L-tyrosine hydrochloride.

3.6 NLO property test

The NLO efficiency of the grown crystal was found by Kurtz and Perry powder technique [11]. The fundamental beam of 1064 nm from Q switched Nd: YAG laser was used to test the second harmonic generation (SHG) property of the crystal in powder form. Pulse energy 405 mJ/pulse and pulse width 8 ns and repetition rate 10 Hz was used. The output light was made to fall on the photomultiplier tube to measure the intensity of radiation. The generation of SHG signal in the sample and NLO property have been confirmed from emission of green radiation from the sample.

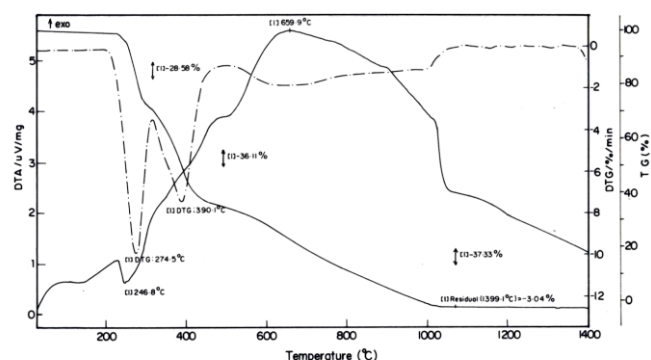


Fig. 8. TG, DTG and DTA curves of L-tyrosine hydrochloride powder sample.

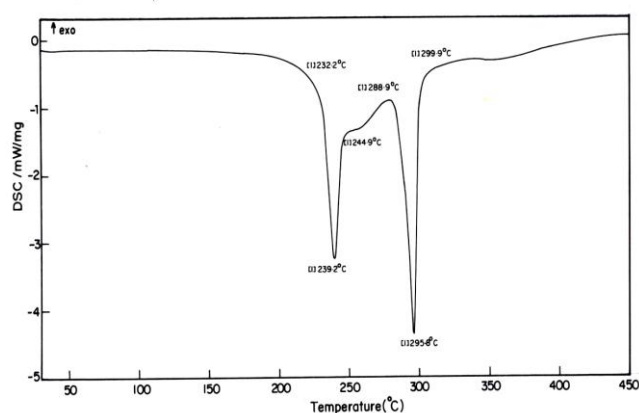


Fig. 9. DSC curve of L-tyrosine hydrochloride.

3.7 Thermal analysis

TG and DTA analyses are of immense importance as far as fabrication technology is concerned, as they provide the information about the thermal stability of the material for fabrication where a considerable amount of heat is generated during the cutting process and laser irradiation. Thermal analysis was performed on the grown crystals to study the thermal stability and melting point. The thermo gravimetric analysis (TGA) of LTHC was carried out between room temperature (28 °C) and 1400 °C at a heating rate of 10 °C per min. The experiment has been performed in nitrogen atmosphere and the TG, DTG & DTA plot is as shown in Fig. 8. Although the TGA trace appears nearly straight up to 250 °C, a careful examination of differential thermal analysis (DTA) reveals a minor endothermic peak around 115 °C, which could be due to physically adsorbed water. But from 250 °C onwards, a steady decrease in weight has been observed (64.69 %) in two steps up to 500 °C which signifies the decomposition of the sample. At temperatures above 500 °C, the final stage of decomposition has occurred, giving a total loss equal to 37.33 %. The DTA trace indicates a weak endotherm starting at about 115 °C which may also be assigned to isomorphous transformation, as there is no corresponding weight loss in TGA trace or in DTG. This is

followed by an endothermic peak at about 246.8 °C due to its melting. This is accompanied by mild endotherms at 659.8 °C resulting in heavy weight loss in TGA due to decomposition of the sample in this stage. However, from the DSC (Differential scanning calorimetric) curve shown in Fig. 9, it is observed that the melting is started at 232 °C and the process completed at 244.9 °C. Hence, from this study, it can be said that the crystal can retain texture up to 230 °C.

4. Conclusion

Bulk single crystals of L-tyrosine hydrochloride have been grown using the slow evaporation of solvent technique. XRD analysis revealed the crystal system and the values of lattice parameters. FTIR, FT-Raman spectral studies and NMR spectra confirmed the synthesized material as pure LTHC. Thermal analysis reveals that the crystal is thermally stable up to 230 °C. The studies on the NLO property confirmed the second harmonic conversion efficiency of the crystal. From the present investigation the optical and thermal properties of the grown crystal indicate the suitability of L-tyrosine hydrochloride crystal for device fabrications.

Acknowledgements

One of the authors (P A) is grateful to Mr. A. Ganesh Kumar, Vice-Chairman, Thiruvalluvar College of Engineering and Technology, Vandavasi - 604505, India, for his constant encouragement and support. The authors are thankful to SAIF, Indian Institute of Technology-Madras, Chennai-600 036 for providing the structural characterization facilities like NMR, FT-Raman and Single crystal x-ray diffraction studies.

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