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# Structural, spectroscopic and nonlinear optical studies on a new efficient organic donor-acceptor crystal for second harmonic generation: L-Threoninium picrate

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#### ABSTRACT

A new and efficient organic nonlinear optical (NLO) crystal from the amino acid family, viz., L-threoninium picrate (LTHP), has been grown by solvent evaporation technique from aqueous solution. The structure of LTHP was elucidated using single crystal X-ray diffraction data. The compound crystallized in the non-centrosymmetric space group  $P_{2_1}$  and the unit cell contains two L-threoninium cations and two picrate anions. The backbone conformation angles  $\Psi^1$  and  $\Psi^2$  are in *cis* and *trans* configurations for both the picrate and the threoninium residues. An intra-molecular hydrogen bond between the amine N atom and the nearby oxygen atom, viz., N1–H1B···O3 is observed, with a graph set motif  $R_1^{-1}(5)$ . The second harmonic generation (SHG) efficiency of this material was measured using Kurtz and Perry method and found to be about 43 times that of standard potassium dihydrogen phosphate (KDP) crystals. Fourier transform infrared (FTIR) and ultraviloet–visible–near infrared spectral studies were also carried out. The details are discussed.

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#### 1. Introduction

Recent advances in organic nonlinear optical (NLO) materials have invoked a large revival of interest in this area of research on account of their widespread industrial potential applications. In particular, studies have concentrated on second harmonic generation (SHG), viz., the first-order NLO effect. Results have shown that an inherent relationship exists between the structure of these materials and their observed properties. On the molecular scale, the extent of charge transfer is assumed to dominate the SHG output while on the supramolecular scale, a high SHG output requires non-centrosymmetry, strong intermolecular interactions and good phase-matching ability [1–4]. The NLO process requires materials that manipulate the amplitude, phase, polarization and frequency of optical beams. Although a variety of materials including inorganic, organometallic, organic and polymeric have been studied for their NLO activity, it is the organic materials which have been receiving the maximum attention. In addition to the advantage in synthesis, organic materials have ultra fast response time, photo-stability and large first hyperpolarizability ( $\beta$ ) values. In particular,  $\pi$ -conjugated systems linking a donor (D) and

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an acceptor (A) show large NLO response and hence have been well studied. One way of designing such type of systems is synthesizing complexes of amino acids with picric acid. Picric acid [5] and its complexes with amino acids, viz., L-prolinium picrate, L-valinium picrate and L-asparaginium picrate show very high second harmonic generation efficiency [6–8]. In the present work, another such new compound, L-threoninium picrate (LTHP) is reported. The synthesis, elucidation of structure, details of the hydrogen bonding, possible structural features leading to the SHG efficiency, FTIR and UV-vis-NIR studies of the title compound are discussed.

#### 2. Experimental procedures

LTHP crystals were grown by solvent evaporation technique. L-Threonine (Loba, 99% purity) and picric acid (Sd. fine, 99% purity) were dissolved in distilled water in 1:1 stoichiometric ratio to get a saturated solution. This was filtered into a clean glass beaker and covered by a clean polythene sheet with few holes on it, so as to reduce the rate of evaporation of solvent. Small yellow-coloured crystals of size  $3.0 \text{ mm} \times 1.0 \text{ mm} \times 1.0 \text{ mm}$  were obtained within few days. The density of the single crystal was determined by the floatation technique using a liquid-mixture of bromoform and carbon tetrachloride and it is  $1.64(2) \text{ g/cm}^3$ . The melting point of the crystal was determined using a melting point apparatus and the value is  $132(2)^{\circ}$ C.

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#### Table 1

Crystal data, experimental conditions and structure refinement parameters.

Identification code	LTHP
Empirical formula	$C_{10}H_{12}N_4O_{10}$
Formula weight	348.24
Temperature	293(2)K
Wavelength (MoK $\alpha$ )	0.71069 Á
Crystal system, space group	Monoclinic, P21
Unit cell dimensions	a=9.235(5) Å
	$b = 6.265(5)$ Å, $\beta = 108.42(5)^{\circ}c = 12.727(5)$ Å
Volume	698.6(7) Å <sup>3</sup>
Z, Calculated density	2, 1.655 g/cm <sup>3</sup>
Absorption coefficient	0.151 mm <sup>-1</sup>
F(000)	360
Crystal size	$0.24mm\times0.21mm\times0.18mm$
Theta range for data collection	2.32-24.91°
Limiting indices	$0 \le h \le 10, -1 \le k \le 7, -15 \le l \le 14$
Reflections collected/unique	1685/1584 [ <i>R</i> (int)=0.0190]
Completeness to theta = 24.91	99.9%
Absorption correction	$\psi$ -Scan
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data/restraints/parameters	1584/1/219
Goodness-of-fit on F <sup>2</sup>	1.053
Final R indices [I > 2sigma(I)]	R1 = 0.0281, wR2 = 0.0769
R indices (all data)	R1 = 0.0289, wR2 = 0.0773
Absolute structure parameter	0.0(14)
Extinction coefficient	0.099(7)
Largest diff. peak and hole	0.298 and $-0.274e({\rm \AA})^{-3}$

#### 2.1. Characterization

Nonius CAD-4 MACH 3 diffractometer with MoK $\alpha$ (0.71073Å) radiation was used to obtain the accurate unit cell parameters. The crystal structure was determined from the single crystal Xray intensity data, collected at room temperature (293 K). The data reduction was done using XCAD4 [9]. The absorption correction was given using the method of  $\psi$ -scan [10]. The structure solution and refinement were performed using SHELXTL [11]. The structure was solved by direct methods and full-matrix least-squares refinements using  $F^2$  taking all the unique reflections. The crystal data, experimental conditions and structure refinement parameters, are presented in Table 1. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms which participated in the H-bonds were located from the difference Fourier and refined with isotropic thermal parameters. All the other H atoms (-CH) were positioned geometrically and refined using a riding model with C-H=0.97 (-CH) or 0.98 (-CH<sub>2</sub>)Å with  $U_{iso}$ (H)=1.2 $U_{eq}$  (parent C atom). The SHG efficiency was measured using the Kurtz and Perry method. The FTIR spectra of the sample were recorded using a FTIR Spectrometer (SHIMADZU FTIR, model 8400S), in KBr phase in the frequency region of 400–4000 cm<sup>-1</sup>, under a resolution of  $4 \,\mathrm{cm}^{-1}$  and with a scanning speed of  $2 \,\mathrm{mm/s}$ . The transmission spectra were recorded using an AGILENT (8453) UV-vis-NIR spectrophotometer in the range of 190-1100 nm covering the entire near ultraviolet, visible and NIR regions.



Fig. 1. Molecular structure of LTHP.

#### 3. Results and discussion

#### 3.1. Structural features

The loss of proton in the picrate anion is confirmed by the C–C distances near the phenolic group (C5–C6 and C5–C10). The picrate anion plays a vital role in forming hydrogen bonds with the threonine residue. The picrate anion forms a strong asymmetric O–H...O hydrogen bond and an N–H...O hydrogen bond with the threonine residue. Of the three nitro groups, two (N2/O5/O6 and N4/O9/O10) are twisted from the plane of the ring. This twisting does not depend upon the C–N bond distances [12]. The molecular structure of LTHP with 50% probability displacement ellipsoids is shown in Fig. 1.

#### 3.1.1. Conformational features

The amino acid exists in the cationic form with a positively charged amino group and a protonated carboxylic acid group. The torsion angles  $\Psi^1(N1-C2-C1-O1)$  and  $\Psi^2(N1-C2-C1-O1)$  describing the torsions of the two C-O bonds around C1-C2 are  $-29.8(3)^\circ$  and  $151.5(2)^\circ$ , indicating that the carboxylic acid and the amino group are twisted with respect to each other. Such deviation from the planarity of these groups is observed in the crystal structures of bis(L-threoninium) sulfate monohydrate [13], Ophospho-L-threonine and O-phospho-DL-thereonine [14]. The side chain conformation is described by the torsion angles  $\chi^{11}$ ,  $\chi^{12}$  and  $\chi^{13}$  of  $-54.0(2)^\circ$ ,  $-175.3(2)^\circ$  and  $-172.1(2)^\circ$ , respectively.

#### 3.1.2. Hydrogen bonding interactions

Intermolecular N1–H1C...O1 interaction form a linear zigzag head-to-tail chain of amino acid. Such a linear chain running along the *b*-axis is flanked by picrate anions on either side through O2–H2...O4 interaction. An intra-molecular hydrogen bond between the amine N atom and the nearby oxygen atom, viz., N1–H1B...O3 is observed, with a graph set motif  $R_1^{1}(5)$  (Fig. 2). In addition to these marked H-bond interac-



Fig. 2. Stacking of L-threoninium cations and picrate anions.

Table 2		
Hydrogen-bond	geometry	(Å,°).

D–H…A	d(D-H) (Ấ)	d(H…A) (Å)	d(D…A) (Å)	∠(DHA)(°)
O(2)-H(2)-O(4)i	0.82	1.85	2.660(3)	169
O(2)-H(2)-0(5)i	0.82	2.41	2.714(3)	103
O(3)-H(3)-0(2) <sup>ii</sup>	0.82	2.28	3.015(3)	150
N(1)-H(1A)-0(4)iii	0.89	2.30	2.904(3)	125
N(1)-H(1A)-0(10)	0.89	2.06	2.884(3)	153
N(1)-H(1B)O(3) <sup>iii</sup>	0.89	2.37	2.680(3)	101
N(1)-H(1B)O(7) <sup>iv</sup>	0.89	2.24	2.063(3)	153
N(1)-H(1B)O(9)	0.89	2.52	2.898(3)	106
$N(1)-H(1C)-O(1)^{v}$	0.89	1.98	2.868(3)	173
C(2)-H(2A)-0(3)vi	0.98	2.47	3.412(3)	162
C(3)-H(3A)-O(4)	0.98	2.53	3.416(3)	151

Symmetry transformations used to generate the equivalent atoms: (i) x, -1+y, z; (ii) x, 1+y, z; (iii) 1-x, -1/2+y, 1-z; (iv) x, y, 1+z; (v) 1-x, 1/2+y, 1-z; (vi) -x, 1/2+y, 1-z; (vi) -x, 1/2+y, 1-z.

tions, a variety of other zigzag interactions are also found in the structure (Table 2). [CCDC 752510 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, by e-mailing data\_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033].

#### 3.2. Second harmonic generation

Since LTHP has crystallized in a non-centrosymmetric space group, a preliminary study of the powder SHG was made using a beam of wavelength 1064 nm, using Kurtz and Perry method [15]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm was used with an input power of 3.5 mJ, pulse width of 10 ns and the repetition rate being 10 Hz. The crystals of LTHP were ground to a uniform particle size of about 125–150 µm and then packed in capillaries of uniform bore and exposed to the laser radiation. A powder of KDP, with the same particle size was used as a reference. The output from the sample was monochromated to collect only the second harmonic ( $\lambda$  = 532 nm), eliminating the fundamental and the intensity was measured using a photomultiplier tube. It is seen that the SHG efficiency of LTHP is about 43 times higher than that of KDP. Second harmonic signal of 690 mV was obtained for LTHP while the standard KDP samples gave a SHG signal of 16 mV per pulse, for the same input energy.

## 3.2.1. Structural features responsible for the high SHG efficiency of LTHP

The level of SHG response of a given material is inherently dependent upon its structural attributes. On a molecular scale, the extent of charge transfer (CT) across the NLO chromophore determines the level of SHG output, the greater the CT, the larger the SHG output. The presence of intermolecular interactions, such as hydrogen bonds, can extend this level of CT into the supramolecular realm, owing to their electrostatic and directed nature, thereby enhancing the SHG response [16,17]. In the present material, the large SHG efficiency possibly arises due to the following reasons: (i) large number of hydrogen bonds; the threoninium cation and the picrate anion are linked through O-H-O hydrogen bonding. The amino N atom of threoninium cation forms N-H--O hydrogen bonds with the oxygen atoms of picrate anion. Also, O-H--O intramolecular hydrogen bonds are available. Hence, the intermolecular hydrogen bonding between phenolate and nitro group of picric acid with L-threoninium residue enhances the SHG value, which is the required property for a system to exhibit nonlinear optical processes. (ii) The  $\pi$ - $\pi$  stacking of picrates anion; the picrates are arranged as parallel arrays (Fig. 3) and the nearest separation



**Fig. 3.** The  $\pi$ - $\pi$  stacking of picrate anions.

between two picrate planes is 3.275 Å, which falls in the category of  $\pi$ - $\pi$  stacking. It will promote the charge transfer between the anion and the cation in the presence of electromagnetic fields. (iii) The presence of strong electron acceptors and strong electron donors; in this case, the picrate anion is acting as the acceptor (nitro group) and the threonine cation is acting as donor (amino group). These donors and acceptors are bridged by the intermolecular hydrogen bonding (N-H…O). The magnitude of optical nonlinearities depends on the strength of the donor-acceptor groups. With nitro acceptor group, the relative efficiency of various donor groups in an increasing order is:  $OCH_3 < OH < OC_6H_5 < OCH_3 < N_2H_3 < NH_2$  [18]. Hence in the present case, the donor-acceptor strength would be considerably high. (iv) The linear zigzag head-to-tail chain; intermolecular N-H-O interaction form a linear zigzag head-totail chain of amino acids (see Table 3). All the above, are in part, the reasons for the large SHG efficiency possessed by this material.

## 3.3. Fourier transform infrared (FTIR) and UV-vis–NIR spectroscopic studies

The recorded FTIR spectra (Fig. 4) were compared with the standard spectra of the functional groups [19] and tentative assignments made for the absorption peaks. All the absorption frequencies and their tentative assignments are listed in Table 3. For optical device applications, the transparency in the near-IR region is significant rather than that in the visible region

Table 3			
FTIR spectral	data	for	LTHI

Wave number (cm <sup>-1</sup> )	Tentative assignments
3400 s	O–H stretching
3238 m	N–H symmetric stretching
2914 b	C–H stretching
1745 s	C=O Asymmetric stretching
1612 b	NH3 <sup>+</sup> asymmetric deformation
1570 m	NO <sub>2</sub> asymmetric stretching
1541 m	NH <sub>3</sub> symmetric stretching
1493 b	CH <sub>3</sub> asymmetric deformation
1425 m	NO <sub>2</sub> stretching
1273 b	CH <sub>3</sub> deformation
1163 m	C=O stretching
1098 s	C=C stretching
918 m	C–C stretching
787 m	C–C skeletal stretching
743 m	NO <sub>2</sub> scissoring
706 s	C–H bending
542 m	C-C-N deformation

s-strong, m-medium, b-broad.



Fig. 5. Transmittance spectrum of LTHP.

because 1.3 and 1.5  $\mu$ m wavelengths are used in optical telecommunication systems. But for medical and industrial applications, visible and IR regions are used. Hence, a good NLO material should be transparent in the optical as well as near-IR regions. The absorbance spectrum has been recorded for the diluted solution (water). The absorption increases rapidly around 200 and 356 nm (Fig. 5), which are due to  $\pi$ - $\pi$ \* and n- $\pi$ \* transitions, respectively. The absorbance coefficient was estimated as  $1.176 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 356 nm. The absence of absorption in the region between 450 and 1100 nm shows that these crystals are useful for the second harmonic generation of Nd:YAG laser ( $\lambda$  = 1064 nm).

#### 4. Conclusions

The crystals of a new NLO material from the amino acid family, viz., L-threoninium picrate (LTHP) were grown using slow evaporation technique. The crystal structure of LTHP was elucidated using single crystal X-ray diffraction data. The proton in the picric acid migrated to the L-threonine forming L-threoninium picrate. The SHG efficiency of this material was measured using Kurtz and Perry method and found to be about 43 times that of standard KDP crystals. Large number of hydrogen bonds, the  $\pi$ - $\pi$  stacking of picrate anions, the presence of strong electron acceptors and electron donors and the linear zigzag head-to-tail chains are, in part, the reasons for the large SHG efficiency possessed by this material. The FTIR spectrum shows the presence of the functional groups and the mode of vibrations. The absorption increases rapidly around 200 and 357 nm, which are due to  $\pi - \pi^*$  and  $n - \pi^*$  transitions, respectively. The absence of absorption in the region between 450 and 1100 nm shows that these crystals are useful for the second harmonic generation of Nd:YAG laser ( $\lambda = 1064 \text{ nm}$ ).

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2010.04.044.

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