Synthesis and electronic structure studies of a novel nonlinear optical crystal L-leucinium squarate monohydrate: A spectroscopic view

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ABSTRACT

Nonlinear optical active L-leucinium squarate monohydrate single crystals were grown using the slow evaporation technique. The crystal structure was determined using the single crystal X-ray diffraction technique. FT-IR and FT-Raman spectra were recorded and analyzed. Meanwhile, the thermal characteristics of the sample were analyzed using TGA-DTA techniques. In addition, the equilibrium geometry, vibrational wavenumbers and first-order hyperpolarizability were calculated with the aid of the density functional theoretical method. The red-shift of NH_3^+ stretching wavenumbers indicates the formation of inter- and intra-molecular hydrogen bonding in the molecule. Similarly, the blue-shift in the C-H stretching wavenumbers is due to the presence of C-H···O hydrogen bonding. The natural bond orbital analysis confirms the occurrence of a strong intermolecular hydrogen bonding that is responsible for the stabilization of the molecule. Molecular electrostatic potential maps help to predict the electrophilicity and nucleophilicity groups in the molecule. The HOMO-LUMO energy gap value suggests the possibility of charge transfer within the molecule. The SHG conversion efficiency was investigated using the Kurtz and Perry method and was found to be higher than that of urea. The intercontacts in the crystal structure were analyzed using the Hirshfeld surfaces analysis method. The thermodynamic properties at different temperatures were also calculated.

1. Introduction

Nonlinear optical (NLO) materials have attracted the attention of researchers for tailor-made device applications which have been increasing in the past few decades because of their potential industrial applications especially in the field of photonics for optical switching, optical modulators, data storage devices, telecommunication, optical information processing, and high-density optical disk data storage [1,2]. Effective NLO single crystals with efficient optical frequency conversion are the key elements for the development of laser systems. Organic materials show remarkable properties because of their fast and large nonlinear response over an extensive frequency range, inherent synthetic flexibility and large optical damage threshold for laser power and low frequency dispersion. One of the main advantages of organic materials is that they permit users to modify the chemical structure with large physical structural diversity and properties for the desired NLO properties [3,4]. The main challenge is to find a chemical solution with a weak interlayer bonding:- however, the crystal forming should have excellent NLO properties. To solve these issues, methods are implemented to increase the interlayer interaction by introducing strong

covalent bonds or by reducing the interlayer spacing to construct a more compact structure [5–7]. Amino acid family crystals are of great interest because all amino acids have chiral symmetry and crystallize in noncentrosymmetric space groups [8,9]. They exhibit some specific features such as molecular chirality, weak van der Waals interaction, hydrogen bonds and zwitterionic nature of the molecule which favors crystal hardness [10,11]. Several new complexes incorporating amino acids have been recently crystallized, and their structural, optical and thermal properties have been investigated [12–15]. L-leucine is an essential amino acid that plays a role in muscle repair and blood sugar regulation. The squaric acid, which is a strong diprotic acid, interacts with bases resulting in a variety of hydrogen-bonding complexes. The present work deals with the growth, single-crystal X-ray diffraction (XRD) and the detailed vibrational spectral studies aided by density functional theoretical (DFT) calculations to elucidate the molecular structure and NLO property by investigating the intramolecular charge transfer (ICT) interaction, hydrogen bonds and first-order hyperpolarizability of the novel nonlinear optical crystal L-leucinium squarate (LLS) monohydrate.
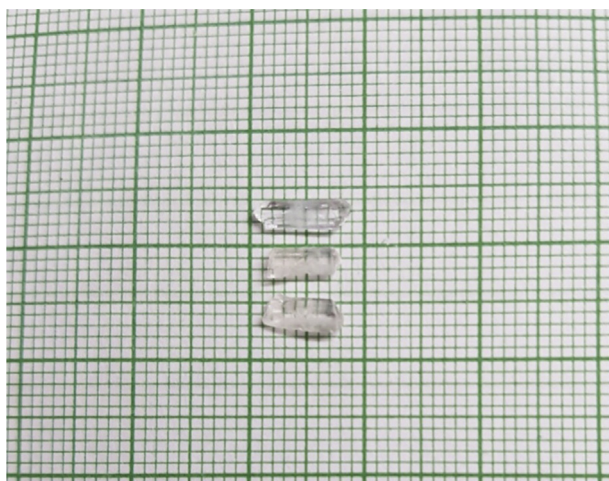

Fig. 1. Photograph of the grown L-leucinium squarate monohydrate single crystals.

2. Experimental details

2.1. Synthesis

Single crystals of LLS were grown using the slow evaporation technique at a constant temperature of an aqueous solution containing L-leucine and squaric acid in 1:1 stoichiometric ratio. The solution was kept in a constant temperature bath, and colorless transparent crystals were obtained after four weeks. The photograph of grown single crystals is shown in Fig. 1.

The single crystal XRD analysis was carried out using a Bruker AXS Kappa Apex-2 charge coupled device diffractometer with graphite-monochromated MoKα (λ = 0.7107 Å) radiation. The unit cell dimensions and intensity data were recorded at 296 K. The structure was solved using direct methods followed by Fourier synthesis and refined by full-matrix least-squares procedures using the SHELX-97 program [16].

2.2. IR and Raman measurements

The Fourier-transform infrared (FT-IR) spectrum of LLS was recorded in the range 4000–400 cm^{-1} with a Thermo Nicolet, Avatar 370 spectrometer using the potassium bromide pellet method. The FT-Raman spectrum of LLS was recorded using a Bruker RFS-27 spectrometer in the range 3500–50 cm^{-1}.

3. Computational details

Quantum chemical computations of L-leucinium squarate monohydrate were performed using the Gaussian'09 program [17] at the Becke3-Lee-Yang-Parr (B3LYP) level with 6–311 + + G(d,p) basis set [18–20]. To offset the systematic errors caused by basis set incompleteness, negligence of anharmonicity, an empirical uniform scale factor of 0.9763 was used [21,22]. Molecular geometries were fully optimized with Berny's optimization algorithm using redundant internal coordinates and were confirmed to be minimum energy conformations. The Raman activities (S_i) calculated by the Gaussian'09 program were converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [23,24].

$$I_i = \frac{f\left(\nu_o - \nu_i\right)^4 S_i}{\nu_i \left[1 - \exp\left(\frac{-hc\nu_i}{kT}\right)\right]} \tag{1}$$

where ν_o is the exciting wavenumber; ν_i is the vibrational wavenumber

Table 1
Crystallographic data and structure refinement parameters of LLS single crystal.

Parameters	Values
Empirical Formula	$(C_6H_{14}NO_2)\cdot(C_6HO_4)\cdot H_2O$
CCDC deposit no.	948844
Color	Colorless
Chemical formula weight	524.48
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	$a = 14.21(15)$ Å, $b = 6.08(7)$ Å, $c = 15.05(17)$ Å, $\alpha = 90°$, $\beta = 95.26\ (4)°$, $\gamma = 90°$
Volume	1295.1(2) Å^3
Z	2
Calculated density	1.345 Mg m^{-3}
Absorption coefficient	0.115 mm^{-1}
F(000)	556
Crystal size	$0.30 \times 0.25 \times 0.20$ mm^3
Theta range for data collection	1.36–28.30°
Index ranges	$-18 \leq h \leq 18$, $-6 \leq k \leq 8$, $-20 \leq l \leq 18$
Reflections collected	9999
Independent reflections	5966 [R(int) = 0.0264]
Completeness to theta = 28.29°	98.9%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9774 and 0.9663
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5966/1/351
Goodness-of-fit on F^2	1.033
Final R indices[$I > 2\sigma(I)$]	$R_1 = 0.0569$, $wR_2 = 0.1528$
R indices (all data)	$R_1 = 0.0875$, $wR_2 = 0.1817$
Largest diff. peak and hole	0.359 and -0.445 e Å^{-3}
Flack parameter	0.14(3)

of the ith normal mode; h, c and k are universal constants; and f is the suitably chosen common scale factor for all peak intensities. The Lorentzian band shapes were used for plotting simulated infrared and Raman spectra with a full width half-maximum of 10 cm^{-1}.

4. Results and discussion

4.1. Structural geometry study

The LLS crystallizes in the monoclinic space group $P2_1$ with two formula units in a unit cell ($Z = 2$). The cell dimensions are $a = 14.21(15)$ Å, $b = 6.08(7)$ Å, $c = 15.04(17)$ Å; $\alpha = 90°$, $\beta = 95.26(4)°$, $\gamma = 90°$; and $V = 1295.08$ Å. The molecule consists of L-leucinium anion and a squarate cation linked to each other with hydrogen bonds. The crystallographic data and structure refinement parameters are given in Table 1.

Anisotropic displacement parameters were applied to non-hydrogen atoms in full matrix least square refinement based on F^2. The hydrogen atoms were assigned common isotropic displacement factors and are included in the refinement cycles through the use of geometrical restraints. The programs APEX2/SAINT, SAINT/XPERP, SHELXL-97, and SIR 92 were used for the computation [16,25,26]. The fractional atomic coordinates are listed in Table 2.

The bond length of C9-O4, C10-O5, C7-O6 and C8-O3 is 1.250, 1.299, 1.239 and 1.235 Å, respectively. Slight variations seen in bond length are due to the intermolecular interactions. Extensive hydrogen bonds are formed by coordinated water with neighboring carboxylic oxygen. The ORTEP plot and crystal packing diagram of the title molecule are shown in Fig. 2(a) and (b), respectively.

The optimized molecular structure of LLS was obtained using the DFT-B3LYP method with the 6–311 + + G(d,p) level of basis set. The optimized molecular structure with the atom numbering scheme is