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## Structural and nonlinear optical studies of a salt with an octupolar chromophore: Guanidinium cyclopropanecarboxylate

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## ABSTRACT

A new organic compound, guanidinium cyclopropanecarboxylate, has been synthesized and characterized by single crystal X-ray diffraction, infrared spectroscopy and nonlinear optical measurements. The infrared spectrum was calculated with density functional theory (DFT). The second-order NLO response was evaluated with the Kurtz and Perry powder method. From the molecular structure, the molecular hyperpolarizability tensor was determined with Hartree-Fock and DFT methods. The second-order susceptibility tensor of the crystal was evaluated by the summation of the effective hyperpolarizability tensors calculated for the asymmetric unit surrounded by ESP-derived charges.

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## 1. Introduction

Guanidine is a strong base ( $pK_a = 13.5$ ) and readily reacts with all types of organic acids to give salts with good crystallinity, largely because of the presence of six potential donor sites for hydrogen-bonding interactions. The guanidinium salts of heteroaromatic carboxylic acids have proved to be a particularly useful means of generating stable hydrogen-bonded supramolecular framework structures. Some examples of the guanidinium salts structures are with the aromatic monocarboxylic acids [1,2], in the hydrated form and with 3-nitrobenzoic acid [3], 4-amino-3,5,6-trichloropicolinic acid, [4], and guanidinium 4-aminobenzoate [5], in the anhydrous form. Among these examples, high-dimensional hydrogen-bonded structures are predominant, with the guanidinium cation forming multiple cyclic hydrogen-bonding associations with carboxylate O-atom acceptors, most commonly those defined by graph sets  $R_2^2(8)$  and  $R_2^1(6)$  and, to a lesser extent,  $R_1^1(4)$  [6,7].

From the point of view of their physical properties, guanidine compounds are potentially interesting for non-linear optics applications, as demonstrated by Zyss et al. with the encapsulation of guanidinium cations between hydrogen L-tartrate anions [8]. In these guanidine salts, the extension of basic hydrogen-bonding rules [6,7] was used as guideline for predicting packing motifs, with the objective of obtaining

non-centrosymmetric structures with potential high nonlinear optical response.

The guanidinium cation, when it has a perfect trigonal symmetry, is a purely octupolar system ( $\beta = \beta_{j=3}$ ) with a central acceptor atom interacting with the surrounding donor moieties  $NH_2$ . The octupolar molecules can circumvent the disadvantages associated with dipolar molecules namely, the high tendency towards unfavorable aggregation and small off-diagonal hyperpolarizability tensor components. The guanidinium cation is completely planar and has approximately the symmetry  $D_{3h}$ , i.e., the complete symmetry of an equilateral triangle: one 3-fold axis; 3 horizontal twofold axes; one horizontal plane; 3 vertical planes containing the horizontal axes [9]. The three C—N bond lengths in the  $CH_6N_3^+$  cation are similar with values ranging from 1.313 to 1.329 Å. The usual model of electron delocalization in this species, leading to a C—N bond order of 1.33, is applicable here.

From the knowledge of the crystal structure of a material, its macroscopic nonlinear optical properties can be estimated using several methods with different levels of sophistication. In the oriented gas model, first employed by Chemla et al. [10], it is assumed the additivity of the molecular hyperpolarizabilities. In this model, the macroscopic susceptibilities are obtained from a tensor sum of the microscopic hyperpolarizabilities of the unit cell and the effects of the surrounding medium are described by appropriate local field factors. Very recently other methods were proposed for the prediction of nonlinear optical susceptibilities, namely sum over bands [11] and finite field with periodic boundary conditions [12].

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In this work the guanidine salt obtained by the reaction with carboxylic acids and the crystal structure was synthesized and characterized using experimental and computational methods. The nonlinear optical properties of the microscopic units were calculated with density functional theory (DFT), using several functionals, and with the Hartree-Fock (HF) method. We used ElectroStatic Potential (ESP) charges to simulate the electrostatic effect of the crystalline environment on the electronic structure of the chromophores. The efficiency for SHG of the non-centrosymmetric salts was investigated for SHG using the Kurtz and Perry powder method [13].

## 2. Experimental section

### 2.1. Synthesis

The title compound was prepared by adding cyclopropanecarboxylic acid (Sigma, 95%, 2.0 mmol) to guanidine carbonate (Aldrich, 99%, 1 mmol) in a water solution (100 mL). The solution was slowly warmed to the boiling point and then left to evaporate under ambient temperature and pressure. Crystals grew from the solution by slow evaporation over a period of a few weeks.

### 2.2. Single crystal X-ray diffraction

The crystal structure of guanidinium cyclopropanecarboxylate ((**I**)), was determined using the X-ray data collected on a Bruker APEX II single crystal diffractometer [14], at the room temperature with *MoK $\alpha$*  radiation. The structure was solved by direct methods as implemented in SHELXS-97 and refined by full-matrix least-squares using SHELXS-97 [15,16]. The refinement was done allowing the non H-atoms to freely refine with anisotropic displacement parameters. The H-atoms were constrained to ride on their “parent atoms” with isotropic displacement parameters. The refinement parameters are presented in Table 1. PLATON [17] was used to analyze the structure. Mercury, version 3.3 [18], was used for figure plotting. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number CCDC 1430252.

### 2.3. Infrared spectroscopy (FTIR)

The FTIR spectrum was recorded at room temperature with the KBr pellet technique using a PerkinElmer Spectrum 400 FTIR/ATR diamond/zinc selenide plate, resolution 1 cm<sup>-1</sup>, 128 scans.

### 2.4. Nonlinear optical techniques

#### 2.4.1. SHG measurements

Kurtz and Perry devised an experimental technique which allows a fast and efficient way of testing candidate NLO materials [13]. This method requires that the nonlinear optical material is a powder, which is usually easy to obtain. The Kurtz and Perry powder method can give some qualitative measure of the second-harmonic efficiency to check if a material can be useful for nonlinear optics [19].

The crystalline powder material is placed in a sample holder and it is irradiated by an high-power pulsed laser beam with a wavelength of 1064 nm that is expanded before reaching the sample. In the sample the intensity of the second-harmonic,  $I^{2\omega}$ , generated in all directions, is limited only by the sample holder geometry, then this SHG light coming from the sample is focused on a concave mirror that collimate this light. The collimated beam is focused on the photomultiplier (PMT) by a bi-convex lens.

The photomultiplier voltage and previous filters are optimized to get a good signal-to-noise relation and avoid the saturation of the photomultiplier. This voltage is measured with a digital oscilloscope

**Table 1**

The crystal details of the structure refinement and the data collected of the noncentrosymmetric structure of the Guanidinium cyclopropanecarboxylate, (**I**).

Emp. formula	C <sub>5</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub>
Formula weight	145.16
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal color	Colorless
Crystal habit	Block
Crystal size (mm)	0.64 × 0.55 × 0.31
Crystal system	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> (Å)	7.8245(11)
<i>b</i> (Å)	8.2030(12)
<i>c</i> (Å)	11.8751(17)
$\alpha$ (°)	90
$\beta$ (°)	90
$\gamma$ (°)	90
Volume (Å <sup>3</sup> )	762.20(19)
<i>Z</i>	4
Calc. dens.(g/cm <sup>3</sup> )	1.265
Abs. coef. (mm <sup>-1</sup> )	0.099
<i>F</i> (000)	312
Data collec. range	3.02–27.11 °
Index ranges:	-10 < <i>h</i> < 9, -10 < <i>k</i> < 10, -15 < <i>l</i> < 14
Reflections collected/unique:	8486/1686
<i>R</i> (int)	0.0169
Completeness ( $\theta = 25.00^\circ$ )	100%
Refin. method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data/restraints/parameters:	1686/0/91
Parameters	
<i>F</i> <sup>2</sup> Goodness-of-fit	1.275
<i>R</i> indices:	
Final [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0475
<i>wR</i> <sub>2</sub>	0.1480
All data	0.0513
<i>wR</i> <sub>2</sub>	0.1537
Largest diff. peak and hole (eÅ <sup>-3</sup> )	

which is triggered by the signal itself. The signals are exported to a computer and integrated with a script written with the software Mathematica® version 8.0. The result of the integral of the signal is proportional to the SHG intensity generated by the tested material, but the real result of SHG efficiency is obtained by comparison with a signal generated by a reference material under the same experimental conditions. The measurements were performed with a fundamental wavelength of 1064 nm and the laser pulses were produced by a Nd:YAG laser at low power, 11 mJ per pulse, with a duration of 10 ns and a frequency of 10 Hz.

## 3. Computational methods

### 3.1. Calculation of infrared spectrum

Prior to the calculation of the theoretical infrared spectrum, the geometry optimization of (**I**) was performed using the GAMESS US package [20], starting from the experimental X-ray geometry. The calculation was performed within density functional theory (DFT) using B3LYP (Becke three-parameter Lee-Yang-Parr) for exchange and correlation, which combines the hybrid exchange functional of Becke [21,22] with the correlation functional of Lee, Yang and Parr [23]. The basis set used was the 6-311++G\*\*. Each self-consistent field calculation was iterated until a  $\Delta\rho$  of less than 10<sup>-5</sup> bohr<sup>-3</sup> was achieved. The final equilibrium geometry at the minimum energy had a maximum gradient in internal coordinates of 10<sup>-5</sup> Hartree bohr<sup>-1</sup> or Hartree rad<sup>-1</sup>. At the end of the geometry optimization we conducted an Hessian calculation to guarantee that the final structure corresponds to a true minimum, using the same level of theory as in the geometry optimization. A vibrational analysis was performed for during the Hessian calculation to calculate the IR spectrum.

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