

# A synthesis, X-ray crystallographic and vibrational studies of guanidinium *o*-nitrobenzoate hydrate. New NLO crystal in guanidinium nitrobenzoate family

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## ABSTRACT

According to literature data the two crystals are known: guanidinium *m*-nitrobenzoate and guanidinium *p*-nitrobenzoate. Both compounds belong to noncentrosymmetric crystallographic systems are considered as second order generators in nonlinear optic (NLO). For each of these crystals the detailed crystallographic, theoretical calculations and vibrational studies were performed. It is interesting that nitrobenzoic acid create three variety of compounds ((2) ortho-, (3) meta- and (4) para-) what any data for third member of guanidinium nitrobenzoate crystal were not known.

The guanidinium *o*-nitrobenzoate hydrate crystal was synthesized first time. The performed X-ray crystallographic study shown that crystal belongs to space group without macroscopic symmetry center. Additionally, the vibrational spectra (intensities, frequencies and PED analysis) of investigated compound are presented. These results are compared with theoretical calculations for equilibrium geometry and vibrational properties.

Furthermore, the results of the theoretical approach include HOMO and LUMO energies and first order hyperpolarizability were obtained, also. On the basis of these data the crystal was classified as second order generator.

All obtained results are compared with previous literature data of guanidinium *m*-nitrobenzoate and guanidinium *p*-nitrobenzoate compounds. Surprisingly, each of examined crystal belongs to different crystallographic system and shows different vibrational properties.

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## 1. Introduction

A guanidine molecule with only ten atoms ( $\text{CN}_3\text{H}_6$ ) belongs to the simplest organic chemical compound, but plays a crucial role in the features of investigated compounds. The specific planar configuration with  $\text{sp}^2$  hybridization of carbon atom makes that investigated cation can be used as potential H-donor in hydrogen bonds and these weak chemical interactions play the most important role in studied compounds. On the other hand, high symmetry ( $\text{D}_{3\text{h}}$ ) of investigated molecule can be used for design of new compound with using rules of supramolecular chemistry. Many of discovered compounds based on guanidine molecule shown interesting properties as phase transition phenomena or nonlinear optical properties.

According to basic information nitrobenzoic acid can exist in three forms. In literature the ortho-, meta- and para-nitrobenzoic acids are known. For the sake of hydroxycarboxylic group plays role of metadirecting substituent during the synthesis of this compound the meta-form is strongly preferred (more than 80%). An efficiency of created during synthesis process for both ortho- and para-form of nitrobenzoic acid is significantly smaller (19% in the case of ortho-form and 1% for para-nitrobenzoic acid, only).

It is interesting, that only two complexes of guanidine with nitrobenzoic acid are known. The crystallographic structures of guanidinium *p*-nitrobenzoate and guanidinium *m*-nitrobenzoate salts are known in literature. According to x-ray crystallographic study performed by Adams and co. [1] guanidinium *p*-nitrobenzoate crystal belongs to monoclinic system with space group:  $P2_1$  or  $P2_1/m$  (where first group is centrosymmetric). The additional research shown [2] that this crystal is noncentrosymmetric and belongs to  $P2_1/m$  space group. Extended investigations made by Arumanayagam and Murugakoothan [3] indicate that this crystal

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has NLO properties. The SHG behavior was confirmed by Kurtz-Perry technique. The NLO signal is ca. 3-times stronger than that noticed for KDP standard. On the other hand, the deeper studies of electronic structure, some vibrational properties and intervening orbital interaction were studied recently by Sasikala and co. [4].

Surprisingly, investigation of guanidinium *m*-nitrobenzoate compound shown that this crystal belongs to  $P2_12_12_1$  space group of orthorhombic system [5]. The macroscopic inversion center in this space group is absent. Therefore, this compound can be used in NLO, however literature data are not available. Our TD-HF calculations [6] shows unambiguously that this compound can be used as SHG generator with efficiency much better than for *p*-nitrobenzoate guanidinium complex.

The guanidinium *o*-nitrobenzoate hydrate crystal was synthesized first time. The performed X-ray crystallographic study shown that crystal belongs to crystallographic group, without macroscopic symmetry center, similarly like noticed for both previous crystals. On the basis of these data the crystal was classified as second order generator in NLO. In this paper the detailed results of experimental and theoretical studies for new obtained guanidinium *o*-nitrobenzoate hydrate crystal are presented. The X-ray crystallographic structure is compared with theoretical DFT approach. The vibrational spectra in the frame of PED theoretical calculations are discussed, also. On the basis of this calculation the detailed computational studies of vibrational properties were performed. The theoretical IR and Raman frequencies, intensities and PED analysis are presented. Additionally, the NBO charges, HOMO and LUMO shapes and NLO properties in TD-HF formalism were calculated.

## 2. Experimental

The aqueous solution of guanidinium carbonate and *o*-nitrobenzoic acid in molecular ratio 1:1 was prepared. After two weeks at ambient temperature some transparent colorless small crystals were obtained (size  $2 \times 2 \times 2$  mm approx.). It should be noticed that two other guanidinium compounds with *m*-nitrobenzoic and *p*-nitrobenzoic acids crystallized without any problems, immediately. On the other hand, the analysis of theoretical calculation results shown that enthalpy of guanidinium *o*-nitrobenzoate hydrate compound is much lower (ca.  $-1737$  a.u.) than two other (ca.  $-1660$  a.u.). That is why that problem with crystallization of titled compound is connected with steric behavior of *o*-nitrobenzoic (adjacent two functional group) acid rather than thermodynamic processes.

The X-ray measurements were carried out on KUMA-diffraction KM-4 diffractometer with the graphite monochromator and  $\omega/2\theta$  scan mode with CCD detector. The structure was solved by the direct methods (SHELX) and refined by the full-matrix least square method using SHELX program. Anisotropic thermal factors were determined for all non-hydrogen atoms. The hydrogen atoms were located from the difference Fourier maps and their positions and isotropic thermal parameters were refined.

The infrared spectra for powder sample were measured using the Bruker IFS-88 spectrometer with the resolution of  $2\text{ cm}^{-1}$ . Samples, as suspensions in Nujol or Fluorolube were put between KBr windows. The spectral range was  $4000\text{--}400\text{ cm}^{-1}$ . For spectral range  $400\text{--}80\text{ cm}^{-1}$  the polyethylene windows were used.

The powder Raman spectra for guanidinium *o*-nitrobenzoate hydrate were measured using Bruker IFS-88 spectrometer and FT-Raman attachment (FRA-106) with resolution of  $2\text{ cm}^{-1}$  and 128 scans. Nd:YAG laser ( $1064\text{ nm}$ ) pumped by diode laser with power ca.  $180\text{ mW}$  was used.

A differential scanning calorimetric (DSC) measurements were performed on Perkin-Elmer DSC 8000 calorimeter equipped with

Controlled Liquid Nitrogen Accessory LN2 with a heating/cooling rate  $20\text{ K/min}$ . The powder samples of the mass ca.  $20\text{ mg}$  were sealed in the aluminum pans. The measurements were performed in the  $100\text{--}350\text{ K}$  temperature range, but no phase transition was found in this range of temperature.

The calculations of equilibrium geometry, theoretical IR and Raman spectra were performed with the Gaussian program (09 revision D.01) configured on the Wrocław High Performance Computer Cluster. For calculation, the structural data from X-ray investigations of crystal were used. The coordinates for particular atoms were taken from CIF crystallographic data. For better characterization of hydrogen bonds observed in real crystal a bigger cluster with formal two molecules was used in calculation. The optimized structure has been calculated by the DFT/B3LYP method. The 6-311++G (d,p) basis set was performed.

For optimized structure, the frequencies in harmonic approach and infrared intensities were calculated by the density functional triply-parameter hybrid model (DFT/B3LYP) with the 6-311++G (d,p) basis set. The obtained frequencies of vibrations were scaled by 0.93. The calculated pseudo potential energy distribution (PPED) for the investigated molecule enabled us to make detailed band assignment in infrared spectra.

The NBO charges, HOMO and LUMO orbitals energies were analyzed directly from Gaussian program log files. The mentioned properties were visualized by Gaussview program. In the case of HOMO, LUMO graphic illustrations of the isosurface the value equal to 0.01 was used.

## 3. Results

### 3.1. X-ray experimental structure

One formal molecule of investigated crystal is shown in Fig. 1. Projection of crystal structure in *cb* plane is presented in Fig. 2. The details of X-ray experiment are collected in Table 1. In Table 2 the experimental values of bond lengths are compared with theoretical data.

The investigated crystal of guanidinium *o*-nitrobenzoic hydrate acid belongs to *Aea2* space group of orthorhombic system with parameters  $a = 15.4730(2)$ ,  $b = 12.4882(2)$  and  $c = 11.4734(2)$  Å and  $Z = 4$ . It should be mentioned that space group of this crystal is different than that noticed in the cases of two guanidinium crystals with *m*-nitrobenzoic ( $P2_12_12_1$ ) and *p*-nitrobenzoic acids ( $P2_1$ ). Additionally, in the structure of titled crystal the water molecule is

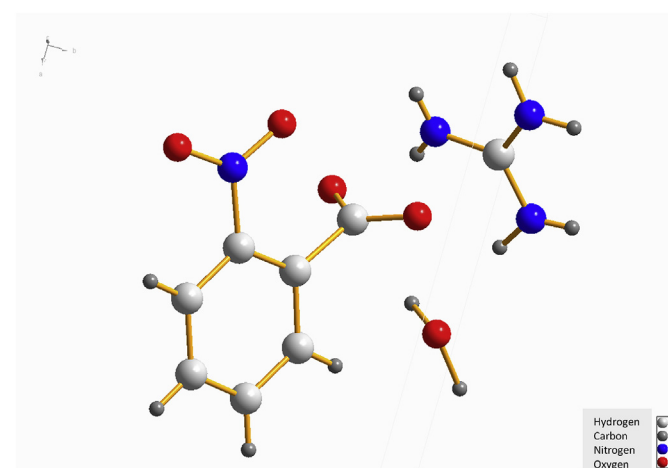


Fig. 1. One formal molecule of investigated compound.

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