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## Novel organic NLO material bis(*N*-phenylbiguanidium(1+)) oxalate – A combined X-ray diffraction, DSC and vibrational spectroscopic study of its unique polymorphism

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## ABSTRACT

Three polymorphic modifications of bis(*N*-phenylbiguanidium(1+)) oxalate are reported, and their characterization is discussed in this paper. The non-centrosymmetric bis(*N*-phenylbiguanidium(1+)) oxalate (I), which was obtained from an aqueous solution at 313 K, belongs to the monoclinic space group *Cc* ( $a = 6.2560(2) \text{ \AA}$ ,  $b = 18.6920(3) \text{ \AA}$ ,  $c = 18.2980(5) \text{ \AA}$ ,  $\beta = 96.249(1)^\circ$ ,  $V = 2127.0(1) \text{ \AA}^3$ ,  $Z = 4$ ,  $R = 0.0314$  for 4738 observed reflections). The centrosymmetric bis(*N*-phenylbiguanidium(1+)) oxalate (II) was obtained from an aqueous solution at 298 K and belongs to the monoclinic space group  $P2_1/n$  ( $a = 6.1335(3) \text{ \AA}$ ,  $b = 11.7862(6) \text{ \AA}$ ,  $c = 14.5962(8) \text{ \AA}$ ,  $\beta = 95.728(2)^\circ$ ,  $V = 1049.90(9) \text{ \AA}^3$ ,  $Z = 4$ ,  $R = 0.0420$  for 2396 observed reflections). The cooling of the centrosymmetric phase (II) leads to the formation of bis(*N*-phenylbiguanidium(1+)) oxalate (III) ( $a = 6.1083(2) \text{ \AA}$ ,  $b = 11.3178(5) \text{ \AA}$ ,  $c = 14.9947(5) \text{ \AA}$ ,  $\beta = 93.151(2)^\circ$ ,  $V = 1035.05(8) \text{ \AA}^3$ ,  $Z = 4$ ,  $R = 0.0345$  for 2367 observed reflections and a temperature of 110 K), which also belongs to the monoclinic space group  $P2_1/n$ . The crystal structures of the three characterized phases are generally based on layers of isolated *N*-phenylbiguanidium(1+) cations separated by oxalate anions and interconnected with them by several types of N–H⋯O hydrogen bonds. The observed phases generally differ not only in their crystal packing but also in the lengths and characteristics of their hydrogen bonds. The thermal behaviour of the prepared compounds was studied using the DSC method in the temperature range from 90 K up to a temperature near the melting point of each crystal. The bis(*N*-phenylbiguanidium(1+)) oxalate (II) crystals exhibit weak reversible thermal effects on the DSC curve at 147 K (heating run). Further investigation of this effect, which was assigned to the isostructural phase transformation, was performed using FTIR, Raman spectroscopy and X-ray diffraction analysis in a wide temperature range.

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## 1. Introduction

The utilization of crystal engineering approaches [1] for the preparation of novel materials exhibiting nonlinear optical (NLO) properties is very efficient, especially in the field of molecular materials based on hydrogen-bonded salts or derived from co-crystals of suitable polarizable organic molecules. The crystal structures of these materials are formed by selected organic molecules (cations), which are primarily responsible for the observed NLO properties, and counter anions or molecules interconnected via an extensive system of hydrogen bonds. The energy of existing hydrogen bonds can counteract the tendencies of the organic molecules and ions with highly delocalized  $\pi$ -electron systems to form unwanted centrosymmetric pairs. In addition, the formed hydrogen-bonded structures frequently exhibit advantageous chemical and

physical properties. Examples of NLO properties that can be employed for interesting technical applications, such as the generation of new laser frequencies, all-optical switching, optical power limiting, image manipulation and the processing or data storage of these materials, include harmonic generation (e.g., especially second harmonic generation - SHG), sum- and difference-generation, intensity dependence of the complex refractive index, light-by-light scattering, and stimulated light scattering [2,3]. A very recent application of hydrogen-bonded salts of organic molecules is based on stimulated Raman scattering. This  $\chi^{(3)}$  NLO phenomenon is used for the development of compact and efficient frequency converters of the one-micron laser emission based on neodymium or ytterbium lasants [4–6].

Many physical properties (including the optical properties) of solid-state materials are intimately related to the symmetry of their crystal structures (e.g., the absence of the center of symmetry necessary for  $\chi^{(2)}$  NLO phenomena), and the eventual phase transitions are frequently accompanied by changes in the studied physical properties. In addition

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to “classical” phase transitions (i.e., first order transitions, second order and/or lambda transitions), other rarely observed effects, such as glass and isostructural phase transitions, can occur in this family of molecular crystals. The isostructural phase transitions, i.e., a phase transformation where the newly formed phase preserves the space group and Wyckoff positions of the parent phase, were defined by Chernyshov et al. [7] and are generally characterized by the discontinuous changes of the unit-cell volume and atomic coordinates with a temperature decrease or increase. This phenomenon (also mentioned in earlier literature [8,9]) was observed and described for compounds such as diglycine perchlorate [10], anilinium sulphate [11], 4-aminotriazole - adipic acid (1/1) [12] and *m*-carboxyphenylammonium hydrogen phosphite [13].

The selection of an *N*-phenylbiguanide molecule for our efforts in the field of crystal engineering of novel NLO materials [14–16] was motivated by the promising values of the calculated first hyperpolarizability components (see Quantum chemical calculations section) for its cation, which represents an interesting moiety with a delocalized  $\pi$ -electron system.

Biguanides are generally strong  $\sigma$ - and  $\pi$ -donating ligands, which form stable complexes with transition metal ions in high or unusual oxidation states [17,18]. Biguanide complexes of boron have also been investigated for wood conservation [19]. The complexes and derivatives of biguanides can also be widely applied to the field of medicine, where they are used for the treatment of diabetes mellitus, pain, anxiety, memory disorders and malaria [20–23].

The main goal of this paper is the preparation and detailed characterization (using a combination of diffraction, calorimetric and spectroscopic methods) of novel salts of *N*-phenylbiguanide with oxalic acid as prospective NLO organic materials. Three crystal structures of the polymorphic *N*-phenylbiguanidium(1+) oxalate modifications were determined: non-centrosymmetric bis(*N*-phenylbiguanidium(1+)) oxalate (I) and centrosymmetric bis(*N*-phenylbiguanidium(1+)) oxalates (II) and (III). The phase transformation associated with the cooling of the centrosymmetric phase (II) to a low-temperature phase (III) was monitored by DSC, X-ray diffraction, IR and Raman spectroscopy, and the mechanism of this isostructural phase transformation is discussed. The quantitative determination of the SHG efficiency of the non-centrosymmetric phase (I) in powdered samples was performed with respect to promising NLO properties.

## 2. Experimental

### 2.1. Materials and methods

The crystals of bis(*N*-phenylbiguanidium(1+)) oxalates, **phbigua<sub>2</sub>ox (I)** and **phbigua<sub>2</sub>ox (II)**, were prepared from the saturated aqueous solutions of *N*-phenylbiguanide (98%, Aldrich) mixed with 2 mol·L<sup>-1</sup> solution of oxalic acid (purum, Lachema) in a 2:1 molar ratio (base:acid). The obtained solutions were kept in a desiccator over KOH at a selected temperature. The colourless crystals of **phbigua<sub>2</sub>ox (I)** were obtained as plates at a temperature of approximately 313 K. The **phbigua<sub>2</sub>ox (II)** crystallized as colourless needles at 298 K. The prepared crystals were filtered off, washed with methanol and dried in a desiccator over KOH. The reference crystals of *N*-phenylbiguanidium(1+) chloride (**phbiguaCl**) were prepared by the slow evaporation of the aqueous solution of *N*-phenylbiguanide and 2 mol·L<sup>-1</sup> solution of hydrochloric acid in a molar ratio 1:1. The colourless crystals were isolated and dried in the air.

The collection of X-ray structural data and temperature-dependent structural data (from 290 K to 110 K with a step of 20 K) was performed on a Nonius Kappa CCD diffractometer (MoK $\alpha$  radiation, graphite monochromator). The temperature of the crystal was controlled using an Oxford Cryosystems liquid nitrogen Cryostream Cooler. The phase problem was solved using direct methods (SIR-92, see the literature [24]) and the non-hydrogen atoms were refined anisotropically, using the full-matrix least-squares procedure (SHELXL97, see the literature reference [25]). The positions of the hydrogen atoms were localized

on the Fourier difference maps and were fixed during refinement using a rigid body approximation with the assigned displacement parameters equal to 1.2  $U_{iso}$  (pivot atom). The basic crystallographic data, measurement and refinement details are summarized in Table 1. The crystallographic data for **phbigua<sub>2</sub>ox (I)**, **phbigua<sub>2</sub>ox (II)** and **phbigua<sub>2</sub>ox (III)** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 970119, CCDC 970120 and CCDC 973045. A copy of the data can be obtained free of charge by applying to CCDC, 12 Union Road, Cambridge CB21, EZ, UK (fax: +44 1223 336033; e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). The bond lengths, angles and hydrogen bonds characteristics in the title compounds are presented in Tables S1 and S2, Supplementary material.

The phase purity of the prepared polycrystalline samples was also controlled by the powder X-ray diffraction method at room temperature using the Bragg-Brentano geometry on a Philips X'pert PRO MPD X-ray diffraction system equipped with an ultrafast X'Celerator detector using a Cu-anode (CuK $\alpha$ ;  $\lambda = 1.5418 \text{ \AA}$ ). The recorded diffraction patterns (see Tables S3–S5 and Fig. S1, Supplementary material) are consistent with the calculated diffraction maxima (FullProf software [26]).

The quantum chemical calculation (Gaussian 09W program package [27]) of the *N*-phenylbiguanidium(1+) cation was performed using the closed-shell restricted Density Functional Theory (B3LYP) method with 6-311G(d,p) basis set, tight convergence criteria and an ultrafine grid. The geometry optimizations were followed by calculations of the first hyperpolarizability component within vibrational frequency calculations using the same method and basis set, Table S6, Supplementary material. The calculated geometry and frequencies (scaled with 0.967 vibrational scaling factor [28]) were compared with the experimental values. The theoretical Raman intensities of the computed normal modes were calculated (RAINT program [29]) for the 1064 nm excitation wavelength, taking the Raman scattering activities from the Gaussian output. The assignment of the computed normal vibrational modes for the *N*-phenylbiguanidium(1+) cation is based on the visualization of the atom motions in the GaussView program [30] and performed PED analysis using the VEDA4 program [31] (described in detail in paper [32]), see Table S7, Supplementary material.

The infrared spectra were recorded using DRIFTS and the nujol or fluorolube mull (KBr windows) techniques on a Thermo Scientific Nicolet 6700 FTIR spectrometer with a 2 cm<sup>-1</sup> resolution and Happ-Genzel apodization in the 400–4000 cm<sup>-1</sup> region. The FAR IR spectra were recorded down to 100 cm<sup>-1</sup> (2 cm<sup>-1</sup> resolution) in the PE pellets.

The Raman spectra of the polycrystalline samples were recorded on a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with the Nicolet Nexus FT Raman module (2 cm<sup>-1</sup> resolution, Happ-Genzel apodization, 1064 nm Nd:YVO<sub>4</sub> laser excitation, 200 mW power at the sample) in the 150–3700 cm<sup>-1</sup> region.

Low-temperature FTIR measurements were carried out on the same instruments using the same parameters described above. The samples were placed in an Oxford Instruments nitrogen cryostat Optistat DN-V equipped with KRS-5 windows (MID IR) and polyethylene windows (FAR IR) and measured in the 310–77 K temperature interval. The temperature was controlled and stabilized using an ITC 503S controller. The nujol mull method with KBr windows and polyethylene pellets was used for recording the mid-IR and far-IR spectra, respectively.

The temperature-dependent Raman spectra were recorded on a Thermo Scientific DXR Raman Microscope interfaced to an Olympus microscope (objective 10 $\times$ ) in the 25–1800 cm<sup>-1</sup> spectral region with a resolution of approximately 3 cm<sup>-1</sup>. The power of the frequency-stabilized single mode diode laser (780 nm) impinging on the sample was 10 mW. The powder samples were placed in a Linkam Scientific Instruments FTIRSP600 stage controlled by LinSys32 software and measured in the 310–77 K temperature region. The spectrometer was calibrated using a software-controlled calibration procedure employing multiple neon emission lines (wavelength calibration), multiple polystyrene Raman bands (laser frequency calibration) and standardized white light sources (intensity calibration).

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