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Phase transition in polar 2-nitroanilinium nitrate. Graph-set approach of hydrogen bonding patterns and analysis of vibrational spectra

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ABSTRACT

A phase transition in new compound 2-nitroanilinium nitrate, (H2NA)NO_3, was found. A symmetry lowering from orthorhombic, *Pmn*2_1, to monoclinic one, *P*2_1, at 249 K is observed. During the phase transition, the H2NA$^+$ and nitrate ions displace from the mirror plane in high-temperature phase. As a result, hydrogen bonding network constructed by the ammonio group and NO_3^- anion is changed. Especially, a bifurcated hydrogen bond disappears. Mathematical operations using both elementary and hydrogen bond graph-set descriptors were used for the first time to describe a mechanism of phase transition. Changes in hydrogen bonding network were also studied by means of vibrational spectroscopy. Band shift associated with stretching and bending vibrations of the ammonio group indicates that the energy of intermolecular interactions rises along with temperature decrease. SHG response for the studied compound is higher than KDP, $I_{(H2NA)NO3} = 1.1 \cdot I_{KDP}$, although a decay of the signal was observed due to instability of the sample.

1. Introduction

Among three isomers 2-, 3- and 4-nitroaniline, only the 3-nitroaniline crystallizes without a center of symmetry and therefore second harmonic generation is expected for this compound [1–14]. However, since nitroanilines are Brønsted bases, their salts of various properties can be easily obtained. Therefore, a search of new functional materials can be expanded for large group of organic ionic crystals. Recently, among salts of 2-methy-4-nitroaniline, the first non-linear organic compound, two polymorphs of chloride were reported as non-centrosymmetric, *P*-42_1c and *P*$2_12_12_1$ [15]. In the case of 2-nitroaniline, it possesses the smallest dipole moment among nitroanilines. Therefore, it can be expected the biggest chance for obtaining non-centrosymmetric salt for that isomer, because there is a general tendency of molecules with large dipole moment to crystallize with a center of symmetry. More recently, hybrid organic-inorganic compounds of 2-methoxyaniline with $SnCl_3^-$ and $SnCl_6^{2-}$ were obtained [16,17], where the former compound crystallizes without a center of symmetry but the latter one is centrosymmetric. Such a result may be associated with a molecular structure of the octahedral $SnCl_6^{2-}$ anion which possesses inversion center and therefore facilitates organization of the crystal structure as centrosymmetric [18–24]. Although it is worth noting that a use of a pyramidal $SnCl_3^-$ anion in synthesis is not a sufficient condition for non-centrosymmetry [25].

Besides, 2-nitroaniline is interesting molecule that it forms N—H⋯O intramolecular hydrogen bond, which additionally stabilizes position of terminal groups (NH_2 and NO_2). If the amino group is protonated, a formation of intramolecular hydrogen bond is also energetically privileged for isolated H2NA$^+$ ion [26]. However, a rotation barrier for the NH_3^+ group is relatively small, 2.87 kcal/mol, and it depends on the position of the nitro group. Nevertheless, the position of the ammonio group can be easily changed by intermolecular hydrogen bonds as was observed for 2-nitroanilinium chloride and bromide [26,27].

In this work, we present crystal structure of room- and low-temperature phases of 2-nitroanilinium nitrate, which are non-centrosymmetric. An analysis of phase transition and especially change of hydrogen bonding patterns during this process is presented. Mathematic approach using operations on graph-set descriptors as a tool for description of molecular mechanism of phase transition is used for the first time. Additionally, non-linear properties for the studied compound were evidenced by means of SHG experiment.

2. Materials and Methods

2.1. Synthesis

The starting compounds, 2NA [Aldrich, purum, ≥98% (NT)] and nitric acid (Sigma-Aldrich, 70%), were used as supplied. The 2NA (1 mmol, 0.1381 g) was dissolved in a mixture of 5 ml of methanol and 5 ml of isopropanol, and then 0.5 ml HNO_3 was added. Colorless crystals of 2-nitroanilinium nitrate were obtained after six days by slow evaporation of the mixture.

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2.2. Single Crystal X-ray Diffraction Studies

X-ray diffraction data were collected on an Oxford Diffraction four-circle single crystal diffractometer equipped with a CCD detector using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å). The raw data were treated with the CrysAlis Data Reduction Program (version 1.171.38.34a). The intensities of the reflections were corrected for Lorentz and polarization effects. The crystal structures were solved by direct methods [28] and refined by full-matrix least-squares method using SHELXL-2014 program [28]. Non-hydrogen atoms were refined using anisotropic displacement parameters. H-atoms connected with C atoms from the aromatic rings were visible on the Fourier difference maps, but placed by geometry and allowed to refine “riding on” the parent atom with $U_{iso} = 1.2\ U_{eq}(C)$. Coordinates of hydrogen atoms of the ammonio group were refined, but $U_{iso} = 1.5\ U_{eq}(N)$. Visualizations of the structures were made using Diamond 3.2 k [29]. Low temperature X-ray diffraction experiments were carried out using OxfordCryosystems device in the ranges 300 K–100 K with $\Delta T = 10$ K and 250 K – 240 K with $\Delta T = 1$ K.

High pressure experiment was carried out using Merrill-Bassett diamond anvil cell. The pressure was measured collecting a set of approximately hundred reflections for CaF_2 which was a standard, and referring a unit cell volume to known characteristics vs. pressure. Both standard and sample crystals were placed between diamonds in a hole of stainless steel gasket. A mineral oil was used to fill the chamber.

2.3. Spectroscopic Measurements

Room temperature FT-IR spectra in the 4000–400 cm^{-1} range were measured on the Bruker IFS-88 spectrometer with 2 cm^{-1} resolution. Nujol and fluorolube mull techniques have been used in the measurements. Closed cycle helium cryostat system of APD Cryogenics INC. (DE-202 Expander, Compressor Model HC-2, Microprocessor-based Temperature Indicator/Controller Model 5500-1-25) was used for low temperature measurements (300−12 K). The temperature of the sample was maintained with an accuracy of ±0.1 K. Powder FT-Raman spectrum at room temperature was recorded with FRA-106 attachment to the Bruker IFS-88 spectrometer over the frequency range 3600–50 cm^{-1} with resolution of 2 cm^{-1}; applying Nd:YAG laser ($\lambda = 1064$ nm, power ca. 150 mW).

2.4. Second Harmonic Generation Measurements

SHG measurements for powdered samples of the non-centrosymmetric $(H2NA)NO_3$ and that of KH_2PO_4 (KDP), which was used as a reference material, were mounted between separate microscope glass slides and excited by tunable femtosecond laser pulses from the laser system consisting of a Quantronix Integra-C regenerative amplifier operating as an 800 nm pump and a Quantronix-Palitra-FS BIBO crystal-based optical parametric amplifier. This system delivers wavelength-tunable pulses of ~130 fs length and was operated at the repetition rate of 1 kHz. A detailed description of the experiment can be found elsewhere [30]. *Caution! Work with the high-power laser brings danger to the eyes, especially in spectral range in which the beam is invisible. Adequate eye protection should be used during measurements.*

2.5. Computational Details

All the computations were performed using density-functional theory (DFT) and hybrid Becke's three-parameter the Lee-Yang-Parr correlation functionals (B3LYP) [31–35] and the 6-31G(d,p) basis set was used. The calculations were carried out for the singlet electronic ground state and no symmetry restrictions were applied. All the atomic positions were taken from crystallographic data. Due to keeping preserved the $H2NA^+$ molecular structure existed the crystal structure of $(H2NA)NO_3$, dihedral angles of both the ammonio and nitro groups were constrained, but the other geometry parameters were optimized similarly to the procedure written in Ref. [26].

3. Results and Discussion

3.1. Crystal Structure of Ortho-Nitroanilinium Nitrate

Title compound crystallizes at room temperature in orthorhombic crystal system, non-centrosymmetric space group $Pmn2_1$ (Table S1). X-ray experiment at low temperature revealed change of the crystal symmetry to monoclinic one, $P112_1$ space group. Non-standard setting of the unit cell was used for low-temperature phase to inherit a setting from high-temperature phase. The crystal twinned into two domains after phase transition, which was associated with a change of lattice gamma angle (Fig. 1). Detailed diffraction experiments showed that this angle started to change at 249 K (Fig. 1b). (Changes of the other lattice parameters upon cooling were deposited as Supplementary Information.) Since the crystal symmetry was lowered during phase transition, both the mirror and *n* glide planes disappeared. Therefore, the violation of extinction rule, $h + l = 2n$, for *n* glide plane was observed (Fig. 2).

High pressure experiment was carried out at 0.3(1) GPa. Due to low quality of the diffractions pattern and small number of reflections only the lattice parameters could be determined: $a = 6{,}44(10)$ Å, $b = 8013$ (12) Å, $c = 7760(4)$ Å, $\gamma = 91{,}6\ (4)$ deg and $V = 401(3)$ $Å^3$. The values can be referred to those obtained at low temperature, 100 K.

In orthorhombic phase, $(H2NA)^+$ and NO_3^- ions lie on the mirror plane, however two hydrogen atoms of ammonio group and two oxygen atoms of the nitrate lay in general positions (Fig. 3). As a result of phase transition, the mirror plane disappears and all the ions lay in

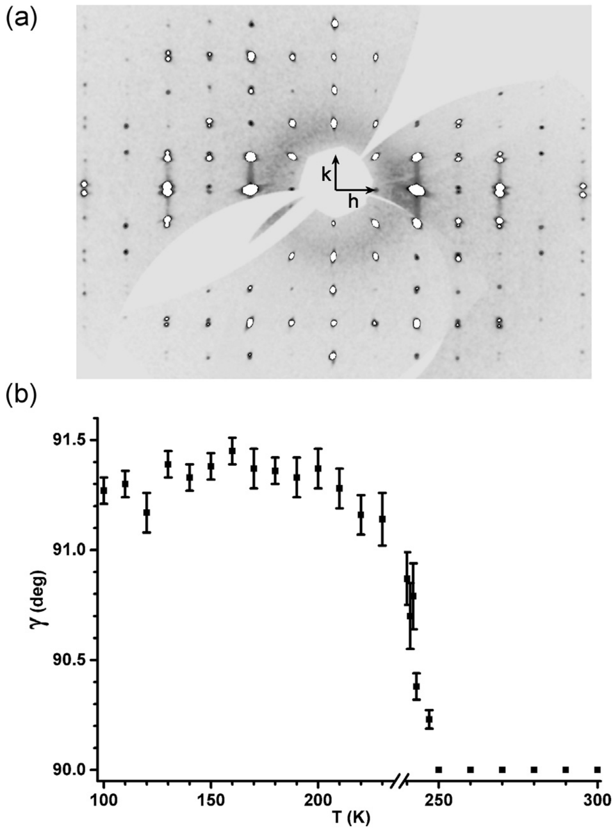

Fig. 1. (a) A section of reciprocal space with (hk0) plane for a measurement at 100 K. Large group of spots are split due to crystal twinning. (b) Changes of the γ angle with temperature indicate a phase transition at 249 K.