

„Influence of anion and substituent on structure and spectroscopic properties of the salts of nitroaniline derivatives with inorganic acids”

Volodymyr Medviediev

Summary

The subject of this doctoral dissertation mainly lays in the field of structural studies of functional materials, which belong to the group of organic-inorganic salts. The overriding goal was the searching for new compounds with nonlinear optical properties. The subject of the research was new compounds containing selected nitroaniline derivatives and inorganic anions. The main research objectives of this dissertation were the determination of the influence of the substituent in the benzene ring of the organic cation and the influence of the anion on packing of the molecules in the crystal and on the architecture of intermolecular interactions, as well as the spectroscopic properties of the obtained compounds. Four nitroaniline derivatives containing substituents at different positions (2-chloro-4-nitroaniline, 2-methyl-3-nitroaniline, 2-methyl-5-nitroaniline and 2-methyl-6-nitroaniline) and six inorganic acids (HCl, HBr, HI, HNO₃, H₂SO₄ and H₃PO₄) were selected for the syntheses. Eighteen new organic-inorganic compounds were obtained in crystalline form. In addition, a new polymorphic form of the starting compound (2-chloro-4-nitroaniline) crystallizing in the non-centrosymmetric *P1* space group was discovered during structural studies.

Since the compounds were obtained in a monocrystalline form, a thorough analysis of the crystal structures of these substances was carried out using X-ray diffraction studies methods in a wide range of temperatures and their physicochemical properties were related to the average crystal structure. Other measurement methods were also used to determine the properties of the compounds: X-ray powder diffraction, differential scanning calorimetry, infrared and Raman spectroscopy, and second harmonic generation tests for the samples crystallizing without the centre of symmetry.

Structural studies allowed to systematize the structures taking into account the diversity and dimensionality of intermolecular interactions in the crystals. It was found that the charge assisted hydrogen bonds, N–H···anion, play the most important role in the molecular packing in the crystals. In any of the examined structures, the hydrogen bond networks do not extend in the three directions, but form layers (2D), chains (1D) or 0D patterns. Algebraic relations between the hydrogen bonding patterns were described using extended approach of the graph-set method, which allowed to divide the architecture of

interaction networks into six basic groups. It was demonstrated that the anions used in synthesis of the salts have the greatest impact on the dimensionality of the hydrogen bonding networks. The bisulphate and dihydrogen phosphate salts show a strong tendency to form layers of hydrogen bonds, and the halide anions usually form networks of lower dimensionality.

An important part of the work was quantum-chemical computation using modern methods and software packages. Molecular geometry calculations and potential energy surfaces for the organic cations helped to understand the role of the weak interactions. A simulation of the theoretical spectra was necessary for the interpretation of the experimental IR and Raman spectra and band shifts, and for the potential energy distribution analysis (PED). It was shown that the nitro group takes part in the most important interactions in a view of the creation of the crystal lattice along three dimensions. They complement the 2D-0D hydrogen bonding networks. The nitro group in the studied salts interacts with neighbouring molecules mainly in two ways – perpendicular and parallel. Basing on the vibrational spectra, the relation between the frequencies of $\nu_s\text{NO}_2$ mode and type of the interactions created by the nitro group was determined.

Additionally, the practical aspect of the studied compounds were verified for the non-centrosymmetric samples. Second harmonic generation tests showed two times higher nonlinear response of new polymorph of 2-chloro-4-nitroaniline. Moreover, in the case of $(\text{H}_2\text{m}_5\text{na})\text{H}_2\text{PO}_4$, a significant decrease of SHG-signal intensity from 85% to 23% in relation to KDP was observed. This result was related to the continuous phase transition during sample cooling.

The presented results of the doctoral dissertation complement the knowledge about the synthesis, structure and properties of the salts of nitroaniline derivatives with inorganic anions. This doctoral thesis was prepared in the form of a thematically consistent series of six scientific articles published in international referred journals, which are the main part of the thesis.