Summary of the Doctoral Dissertation

TEMPERATURE AND PRESSURE EFFECT ON THE CRYSTAL STRUCTURES OF L-ARGININE HOMOLOGUES AND 1H-PYRAZOLE-1-CARBOXAMIDINE SALTS

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The primary aim of this work is to investigate the correlation between the molecular and crystal structures and physicochemical properties of the studied compounds. The author decided to synthesize L-arginine homologues with shorter carbon chain due to a number of factors. The first of these was the important biological significance of L-arginine for mammalian organisms and the unknown structures of its homologues, which also play key roles in the functioning of living organisms. Another factor was the chirality of the L-arginine homologues. In this study, only one stereoisomer was used for the synthesis, which gave confidence in obtaining crystals without a centre of symmetry, for which second-harmonic generation tests were planned. The third factor was a potential increase in the value of hyperpolarizability of L-arginine analogue molecules as a result of shortening the carbon chain and consequently reducing the distance between the carboxyl and guanidine groups possessing π electrons. The compounds obtained in this work are salts of (*S*)-2-amino-3-guanidinopropionic acid (HAmGP) and (*S*)-2-amino-4-guanidinobutanoic acid (HAmGB). The presented L-arginine homologues have very complex hydrogen bonding networks, mainly formed between the guanidine and amine groups and the anion present in the structures of salts. The analysis of the hydrogen bonding architecture was carried out by means of algebraic expressions, using descriptors of elementary graphs and obtaining descriptors of hydrogen bonding patterns - chains or rings. Infrared and Raman spectra were also measured for most of the structures, which showed high similarity to each other. Diffraction studies revealed that two of the discussed salts (H_2AmGP)Cl (**5**) and (D_2AmGP)Cl (**6**) have an isosymmetric pressure phase transition within the space group $P2_1$. Phase II is characterized by an extremely rare physicochemical property - negative area compressibility (NAC). This is the first reported occurrence of this property for an organic compound possessing such a complex three-dimensional hydrogen bonding network. It is worth mentioning that the deuterated analogue (**6**) has a higher value of the negative area compressibility coefficient, and this is connected with the occurrence of the geometrical effect of isotopic substitution (GIE). For both compounds (H_2AmGP)Cl (**5**) and (D_2AmGP)Cl (**6**), second harmonic generation tests were performed in the function of pressure. For the prototype phase, a decrease in the nonlinear response was observed up to a pressure of about 0.86 GPa and an increase in the intensity of the generated signal during further compression of the sample. This effect is probably related to the decreasing polarizability of the molecules during the compression of the crystal in phase I and to the increasing polarizability in phase II due to the occurrence of the area compressibility phenomenon. Owing to these properties, both compounds are very good candidates as pressure indicators or actuators due to having a high value of negative area compressibility coefficient.

The (*S*)-2-amino-4-guanidinobutanoic acid molecule, as for (*S*)-2-amino-3-guanidinopropionic acid, can exist in two cationic forms in salts: $(H_2AmGB)^+$ and $(H_3AmGB)^{2+}$. Compared to the propionic analogue, there is a less complex hydrogen bonding network in HAmGB acid-based compounds, although the patterns show great similarity. The main role is played by interactions between guanidine and amine groups and anions in the structures of salts. Compilation of the structural data and the generation of the second harmonic response showed that a higher nonlinear effect of the compounds can be obtained (a) by shortening the carbon chain in a series of L-arginine analogues, (b) by deprotonation of the carboxyl group and (c) for such conformers of (*S*)-2-amino-3-guanidinopropionic acid cations in which the distance of the guanidinium group from the carboxyl group is the smallest.

Due to the importance of the guanidine group in the search for stable crystals for nonlinear optics, there were attempts to obtain new compounds based on the cationic form of 1H-pyrazole-1-carboxyamidine, which is a popular substrate in the amidination of amines. In this work, the molecular and crystal structures for eight new salts of 1H-pyrazole-1-carboxyamidine were determined. The simple procedure presented in this work for the synthesis of compounds with $HPyCA^+$ cation demonstrates the ease with which a salt other than the commercially available chloride can be selected in organic synthesis when the presence of chloride ions would be undesirable. An algebraic approach was used in the topological analysis of the hydrogen bonding network in the crystals and shown a high similarity of the formed patterns. All compounds discussed in this section contain the same tautomeric form of the $HPyCA^+$ cation, in which the carboxyamidine group is protonated and the nitrogen atom N2 of the pyrazole ring is deprotonated. Theoretical calculations of the protonation route for PyCA showed that this tautomeric form of the cation is the only favored one. For 1H-pyrazole-1-carboxyamidine nitrate, a reversible, continous phase transition has been discovered The transition occurs at 174 K from the monoclinic space group $P2_1/c$ to the triclinic space group *P*-1. The mechanism of the phase transition is based on a subtle displacement of the nitrate anions, which leads to the disappearance of the screw axis 2_1 and the c-glide plane. The stability of the prototype phase up to a pressure of 1.27 GPa is shown by a series of diffraction measurements at high pressure.