

Pressure dependence of crystal and molecular structure and NLO response of L-Arg homologue salts

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Second harmonic generation (SHG) in organic crystals is a subject of extensive investigation for years. The absence of an inversion centre in such crystalline materials is mandatory in order to observe second-order non-linear response, although many other features play an important role and must be taken into account for synthesis of non-linear materials. For example, an occurrence of delocalized π electrons and intramolecular donor-acceptor charge transfer between two molecular subparts (functional groups) is necessary and it leads to large hyper-polarizability β . So, this kind of materials are good candidates for second harmonic generation studies.

In light of the above, the burning question is – in which direction one should look for materials with great SHG response? In the author's concept, conformation of molecules in crystals is a key factor to obtain high SHG signal. Generally, the most important parts of molecule in the SHG context are donor – acceptor groups. With this reason, L-arginine analogues were chosen in these studies. They have shorter carbon chain in comparison to the L-arginine. We observed that relative distance between functional groups have a key role for enhancement of the SHG signal. What is more, inorganic anions in salts have a great influence on conformation of carboxyl and guanidinium groups. Some of them make single hydrogen bond with cation, what leads to appear more degrees of freedom for donor-acceptor groups. It is possible, that more degrees of freedom for aforementioned groups causes more suitable alignment of intramolecular charge transfer vectors in the crystal, which gives higher non-linear response.

The goal of the study is to verify experimentally, how the high pressure can modulate SHG response in one phase to avoid SHG changes connected to phase transitions and juxtapose them to the results for L-arginine homologues. So, correlation of molecular conformation and crystal structure with SHG is shown. This knowledge gives us opportunity to describe theoretically which conformation can give the highest SHG response for particular materials.

We present crystal and molecular structures of 7 new salts (2Cl^- , 2Br^- , 2I^- , 2NO_3^- , Cl^- , I^- , 4NO_3^-) of (*S*)-2-amino-3-guanidinopropanoic acid, which is an analogue of L-arginine. Crystal structures were determined by X-ray diffraction at room and low-temperature conditions (100 K). Since earlier studies have shown that external pressure can tune SHG signal, diamond anvil cell was used to investigate the pressure dependence of SHG response.

The result of SHG measurements revealed that monochloride salt of (*S*)-2-amino-3-guanidinopropanoic acid has better optical non-linear properties than L-arginine chloride, $3 \cdot I_{\text{KDP}}$ vs. $0.3 \cdot I_{\text{KDP}}$. This fact can be associated with shorter carbon chain (*S*)-2-amino-3-guanidinopropanoic acid and thus closer intramolecular distance between p-electron rich carboxyl and guanidinium groups than in L-arginine. What is more, the SHG response is more than 2 times better in 2.8 GPa pressure than in standard pressure.

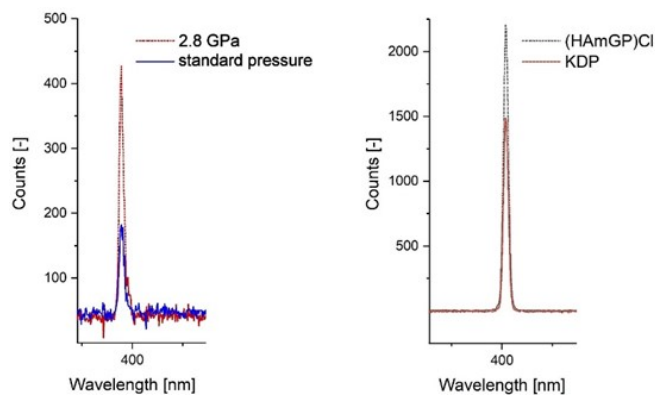


Figure 1. SHG response for monochloride salt of (*S*)-2-amino-3-guanidinopropanoic acid at various pressure conditions.

Keywords: Crystal structure, L-Arg homologue, Hydrogen bond, High pressure, SHG