Computational Investigation of Mechanical Properties of Organic Molecular Crystals

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The mechanical response of a molecular crystal to an applied force is a core material property closely connected to crystal packing and intermolecular interactions. With the advancements in crystal engineering, many flexible molecular crystals have been discovered which can be applied in the pharmaceutical industry and as nano- and micromechanical devices [1]. Some molecular systems exhibit polymorphism, allowing them to pack into crystalline structures in multiple ways, resulting in different mechanical responses. In this study, *p*-halogenated benzene-based esters are used to computationally explore the correlation between mechanical properties and crystal structure. These esters were selected based on previous experimental research on bromine derivatives that exhibit multiple polymorphs, with one being elastic and another brittle [2]. To predict and rationalize the mechanical response, we use periodic DFT methods implemented in CRYSTAL23 program. All crystal structures are optimized, and calculations of elastic constants are performed. From these calculations, mechanical properties such as Young's moduli are calculated and correlated with other computational tests, such as virtual tensile tests and interaction energies. Computational results are complemented with experimental studies to predict and explain the intermolecular interactions that lead to specific mechanical responses. By varying *para*-substituted halogens (chlorine, bromine and iodine), we investigate how subtle changes in molecular structure impact molecular packing and flexibility of synthesized materials. This work represents a step towards developing a computational methodology for predicting and understanding mechanically responsive crystalline organic materials.

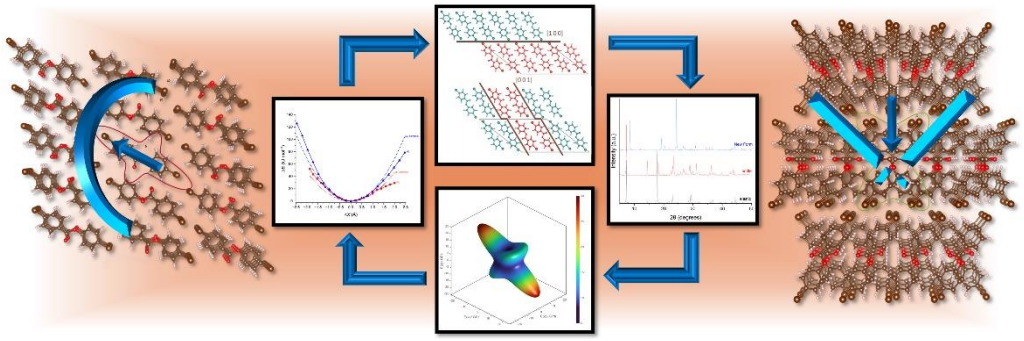

Figure 1. Computational modeling of mechanical properties of organic molecular crystals

References:

[1] S. Saha, M. K. Mishra, C.M. Reddy, G. R. Desiraju, *Acc. Chem. Res.* **51** (2018) 2957−2967.

[2] S. Saha, G. R. Desiraju, *Chem. Commun.*, **54** (2018) 6348-6351.