Computational Study of Mechanically Flexible Polymorphs of Halogenated Phenyl Benzoates

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For a long time, molecular solids have been used in various fields such as pharmaceuticals, electronics, and materials science. It was shown that molecular solids exhibit electronic and optical properties which could be utilized to make molecular semiconductors and optoelectronics. Despite their potential, molecular solids also possess negative traits that hinder their marketability, leaving room for improvement and motivating scientists to develop new molecular materials [1]. Crystal engineering plays a crucial role in synthesizing new molecular materials with desired properties. One way to accomplish that is by understanding crystal packing, which results from intermolecular interactions [2]. Crystal bending and shearing are physical properties which can be directly tied to the crystal structure. Molecular compounds of the same chemical composition can pack in different ways forming polymorphs. For instance, 4-bromophenyl 4-bromobenzoates form polymorphs with very different physical properties: one is brittle while the other is elastic [3]. This study focused on finding the relationship between intramolecular interactions in molecular crystals and their elastic properties. Various derivatives of *p*-halogenated phenyl benzoates were modeled and their crystal structures were optimized using periodic DFT methods in CRYSTAL23 program. Their elastic behavior was investigated by calculating interaction energies between molecules along specific crystal planes and performing virtual tensile tests. Additionally, different polymorphs and the influence of chemical structure by varying halogens in *para* position were examined to assess how minor structural differences affect mechanical properties. Finally, computational results were compared to experimental studies. A positive correlation between computational and experimental findings could enhance future research in designing molecular crystals with desired physical properties.

References:

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