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DFT approach to (benzylthio)acetic acid: conformational search, molecular (monomer and dimer) structure, vibrational spectroscopy and some electronic properties

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Abstract: The DFT studies were carried out with the B3LYP method utilizing the 6-31G and 6-311++G(d,p) basis sets depending on whether the aim of calculations was to gain the geometry at equilibrium, or to calculate the optimized molecular structure of (benzylthio)acetic acid (*Hbta*) in the forms of monomer and dimer. The minimum conformational energy search was followed by the potential energy surface (PES) scan of all rotary bonds existing in the acid molecule. The optimized geometrical monomeric and dimeric structures of the title compound were compared with the experimental structural data in the solid state. The detailed vibrational interpretation of experimental infrared and Raman bands was performed on the basis of theoretically simulated ESFF-scaled wavenumbers calculated for the monomer and dimer structures of *Hbta*. The electronic characteristics of *Hbta* is also presented in terms of Mulliken atomic charges, frontier molecular orbitals and global reactivity descriptors. Additionally, the MEP and ESP surfaces were computed to predict coordination sites for potential metal complex formation.

Keywords: (Benzylthio)acetic acid; DFT calculations; PES scan analysis; Molecular geometry; Vibrational analysis; HOMO–LUMO; Mulliken atomic charges, MEP and ESP surfaces

1. Introduction

In the last few decades, the carboxylic compounds containing aromatic rings are in the spotlight of numerous research activities due to the fact they are the efficient partners in various organic syntheses and they act as motif-controlling functional elements in crystal engineering [1]. The crystal engineering (supramolecular chemistry) consists in the skilful design and synthesis of new supramolecular assemblies of particular structural features that translate directly to their potential applications in many fields, like material science, inorganic and organic chemistry, biology and pharmacy [2]. The universal involvement of carboxylic compounds (containing not only the oxygen donor atoms but also the other types of donors present in the organic unit, such as nitrogen and/or sulphur) as building bricks for the construction of stable supramolecular networks due to their ability to create extended systems of various non-covalent forces including coordination bonding [3], hydrogen bonding [4], aromatic–aromatic π–π stacking interactions [5] and also the electrostatic and charge-transfer interactions [6].

The (benzylthio)acetic acid (*Hbta*) is used in synthetic chemistry. For example, it serves as an intermediate in the synthesis of a series of aryl-heteroaryl derivatives whose pharmacological action and generic structure are supposed to constitute an alternative to modafinil used as wake-fulness promoting agents in the treatment of excessive sleepiness caused by sleep apnea, narcolepsy, or shift work sleep disorder [7]. The *Hbta* also acts as an intermediate in the preparation of 3-(4-methoxy-bezylidene)-isothiochroman-4-one containing the sulphur atom