

# Structural and spectroscopic differences among the potassium 5-hydroxypentanoyltrifluoroborate salt and the furoyl and isonicotinoyl salts

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## ABSTRACT

FT-IR, FT-Raman and ultraviolet–visible spectroscopies were used to characterize the potassium 5-hydroxypentanoyltrifluoroborate salt (HTFB) while the theoretical structures of this salt in gas and aqueous solution phases were studied by using hybrid B3LYP/6-311++G\*\* calculations and the self consistent reaction field (SCRF) and solvation (SM) models because these models consider the solvent effects. Good concordance were obtained among the predicted <sup>1</sup>H-, <sup>13</sup>C and <sup>19</sup>F-NMR chemical shifts for HTFB in aqueous solution with the corresponding experimental available data for this salt in CDCl<sub>3</sub>. The corrected solvation energy by using ZPVE and non electrostatic terms is higher for this salt (−103.73 kJ/mol) than those reported for furoyl (−84.72 kJ/mol) and isonicotinoyl (−95.05 kJ/mol). Evidently, the side chain in HTFB increase the solubility of this salt in water, as compared with furoyl and isonicotinoyl. The NBO analyses show that the potassium 2-isonicotinoyltrifluoroborate salt in both media is most stable than hydroxypentanoyl and furoyl salts and, in particular, the side chain in HTFB generates a diminishing of its stability in aqueous solution. Probably, this low stability of HTFB in solution is due to the higher solvation energy and to the n → σ\* transitions no observed in the other salts. The AIM studies support the high stability of isonicotinoyl than the other two salts and, also, reveal the ionic characteristics of the K—O and K—F interactions observed in those three salts. The comparisons of the gap values for the three species suggest that the most reactive salt is isonicotinoyl while furoyl salt is the less reactive. The descriptors show the importance of study these salts in different media because the values in solution are slightly different in the three salts from those computed in gas phase. In addition, the harmonic force fields and the scaled internal force constants for the salt in both media are reported together to their complete vibrational assignments.

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## 1. Introduction

The potassium trifluoroborate salts are very interesting compounds that structurally can present different symmetries, properties and interactions due to the nature and characteristics of the B and K atoms and to the different groups to which the trifluoroborate group is linked [1–5]. For instance, in the crystal structure of triphenylphosphonium-ethylene-trifluoroborate were reported weak C—H—F hydrogen bonds between the meta-phenyl C—H groups and the trifluoroborate B—F groups [3] while

Falcicchio et al. have recently studied a first aromatic bis(trifluoroborate) dipotassium salt with 3D network where the fluorine atoms play a important role [2]. On the other side, the new crystal structures determined by Kamiński et al. for aryl-trifluoroborate potassium salts have allowed the formulation of basic rules for phenyltrifluoroborate potassium salt in the solid phase based on the type and location of the aromatic ring substituents [1]. These different studies have revealed that the final architecture of the crystal packing is a consequence of the elevated versatility of BF<sub>3</sub>K group to form different coordinations where the supramolecular chemistry became potentially of interest in the design and preparation of new materials. In the theoretical study of the potassium 3-furoyltrifluoroborate salt by using the B3LYP/6-31G\* and 6-

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311++G\*\* methods, the B and K atoms have five and four coordination numbers, respectively presenting the most stable structures  $C_s$  symmetries [4] while the presences of two different dimeric species in the gas phase and of its anion in aqueous solution were considered in the study of the potassium 2-isonicotinoyltrifluoroborate salt in order to explain some bands experimentally observed in the vibrational and ultraviolet–visible spectra [5]. In this context, the structural and vibrational characterizations of these potassium trifluoroborate salts and their properties are necessary to know how the different groups affect the reactivities and properties of these salts considering that they are broadly used as reagents in organic synthesis chemistry [6–12]. In this opportunity, we have studied the potassium 5-hydroxypentanoyltrifluoroborate salt (HTFB) where the trifluoroborate group is linked to the hydroxypentanoyl one. In this salt, it is interesting to know the influence of the short side chain connected to the trifluoroborate group on its structural and vibrational properties and, of course, then, to compare these properties with those obtained for the two furoyl and isonicotinoyl salts [4,5]. For carried out these purposes, the structure of the salt as monomer was first modeled and optimized in gas and aqueous solution phases by using calculations derived from the density functional theory (DFT) with the hybrid B3LYP/6-311++G\*\* level of theory [13,14] and, later, taking into account the layered architectures suggested for trifluoroborate potassium salts in the solid state [1–3] the dimeric structure was considered. The anionic species of this salt was also studied because the calculations were performed in aqueous solution with the integral equation formalism variant polarised continuum method (IEFPCM) [15,16] while the solvation energy at the same level of theory was calculated employing the solvation model [17]. The vibrational analyses were performed for all species combining the experimental infrared and Raman spectra with the scaled quantum mechanical force field (SQMFF) procedure [18] and the Molvib program [19]. Thus, the force fields and the force constants were computed for the monomeric species of this salt and its anion in both media. NBO and AIM calculations [20,21] were employed to study the structural properties of HTFB while the reactivities in the different media and its behaviors were studied by means of the frontier orbitals and some descriptors, as suggested in the literature for species with similar groups [22–25]. Finally, the properties calculated for HTFB were compared with those reported for the furoyl and isonicotinoyl-trifluoroborate salts [4,5] to observe the effect of the short side chain on the IR properties.

## 2. Experimental

The infrared spectrum of a pure sample of potassium 5-hydroxypentanoyltrifluoroborate salt (HTFB) in the solid state was recorded in KBr pellets by using a Perkin Elmer Spectrum GX spectrometer in the 4000 to 400  $\text{cm}^{-1}$  region while a Perkin Elmer Spectrum GX Raman equipped with an yttrium aluminum garnet crystal doped with triply-ionized neodymium laser (excitation line of 1064 nm, 1900 mW of laser power) was employed to record the Raman spectrum in solid state at room temperature between 3600 and 100  $\text{cm}^{-1}$ . The Raman spectrum was recorded with a resolution of 4  $\text{cm}^{-1}$  and 100 scans. The ultraviolet spectrum of HTFB in aqueous solution was recorded with a Beckman spectrophotometer between 200 and 800 nm.

## 3. Computational details

The initial monomeric, dimeric and anionic structures of HTFB were modeled with the *GaussView* program [26] and later they were optimized in gas phase and in aqueous solution with the *Gaussian 09* program, Revision A.02 [27] by using the hybrid B3LYP/

6-311++G\*\* method [13,14]. As was mentioned above, the calculations in solution were performed with the IEFPCM [11,12] and the solvation models [15–17]. The potential energy surfaces (PES) were studied for variations of seven different dihedral angles corresponding to the monomer of HTFB at the same level of theory, these angles are, C1–C2–F17–B18, C5–C6–C9–O14, C9–C6–C5–C1, C6–C5–C1–C2, O16–C2–B17–F18, C5–C1–C2–B17 and C6–C9–O14–H15. From the five conformers found on the PES only the conformer C1 was considered because it presents a lower energy. Thus, in Fig. 1 were presented the two PES showing these five stable structures named C1, C2, C3, C4 and C5 being C1 the most stable conformation with a global minima in both media. These monomeric structures have  $C_1$  symmetries while in Fig. 2 are presented the dimeric and anionic structures together with the atoms labeling. Here, the final energies for the dimeric form were corrected by basis set superposition error (BSSE) [28]. Only for the most stable conformer of HTFB were computed, by using NBO and AIM calculation [20,21], the atomic Mulliken and natural population (NPA) charges, molecular electrostatic potentials, bond orders, donor-acceptor energy interactions and the topological properties at the same level of theory and in the two media. To perform the vibrational study in both media for the monomeric species and its anion their corresponding normal internal coordinates and the harmonic force fields were calculated by using the SQMFF methodology [18] and the Molvib program [19]. The normal internal coordinates of  $\text{BF}_3$  group of this salt, as in furoyltrifluoroborate and isonicotinoyl-trifluoroborate salts [4,5] present  $C_{3v}$  symmetry, as in

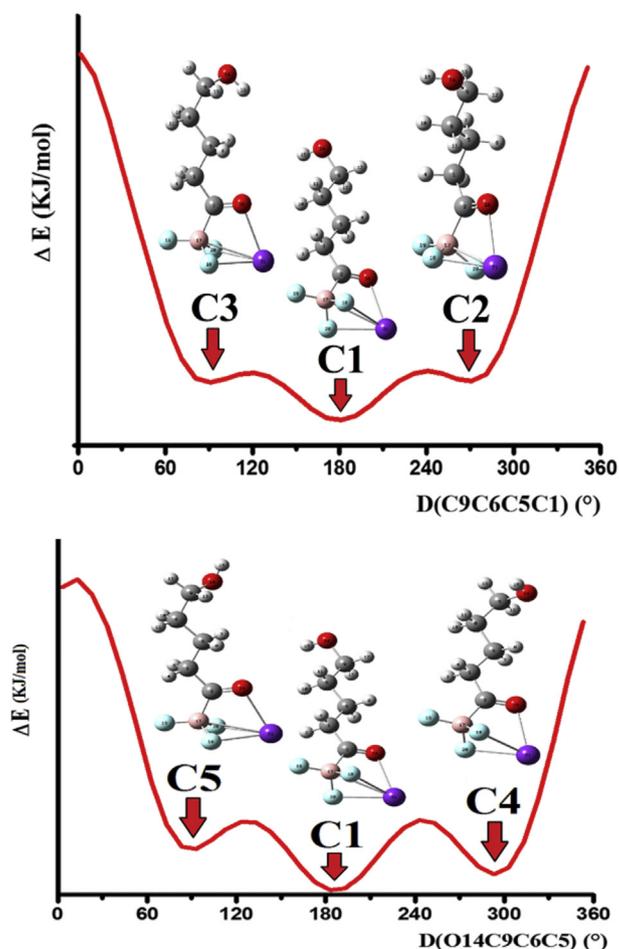


Fig. 1. Molecular structures of the more stable conformers for HTFB and their corresponding symmetries.

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