

FT-IR, FT-Raman and UV–visible spectra of potassium 3-furoyltrifluoroborate salt

Maximiliano A. Iramain^a, Lilian Davies^b, Silvia Antonia Brandán^{a,*}

^a Cátedra de Química General, Instituto de Química Inorgánica, Facultad de Bioquímica, Química y Farmacia, Universidad Nacional de Tucumán, Ayacucho 471, 4000, San Miguel de Tucumán, Tucumán, Argentina

^b Instituto de Investigaciones para la Industria Química (INIQUI, CONICET), Universidad Nacional de Salta, Av. Bolivia 5150, 4400, Salta, Argentina

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ABSTRACT

The potassium 3-furoyltrifluoroborate salt has been experimentally characterized by means of FT-IR, FT-Raman and UV–Visible spectroscopies. Here, the predicted FT-IR, FT-Raman and UV–visible spectra by using theoretical B3LYP/6-31G* and 6-311++G** calculations show very good correlations with the corresponding experimental ones. The solvation energies were predicted by using both levels of calculations. The NBO analyses reveal the high stability of the salt by using the B3LYP/6-31G* level of theory while the AIM studies evidence the ionic characteristics of the salt in both media. The strong blue colour observed on the K atom by using the molecular electrostatic potential mapped suggests that this region act as typical electrophilic site. The gap values have revealed that the salt in gas phase is more reactive than in solution, as was reported in the literature while, the F13...H6 interaction together with the K–O bond observed by the studies of their charges could probably modulate the reactivities of this salt in aqueous solution. The force fields were computed with the SQMFF methodology and the Molvib program to perform the complete vibrational analysis. Then, the 39 vibration normal modes classified as 26 A' + 13 A'' were completely assigned and their force constants are also reported.

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1. Introduction

Heteroaryl compounds containing different rings in their structures have very diverse properties according to their nature, number and different substituent groups to which they are attached. Thus, these derivatives are used in numerous syntheses, as intermediates and/or end products and are widely studied from different points of view. In particular, organometallic reagents are of interest in synthetic organic chemistry because they provide conjugation reactions by generating a new approach to the synthesis of conjugated molecules such as protein–proteins and protein–polymer [1–7]. On the other hand, the incorporation of F atoms in their structures makes these compounds can be used mainly in the pharmaceutical industry because they allow their rapid incorporation into the human body. Structural changes obviously produce changes in their properties that are of interest for the design of new drugs with fewer side effects. Here, we propose the study of the potassium 3-furoyltrifluoroborate salt, with

molecular formula: C₅H₃O₂(BF₃K), because their structural, electronic, topological and vibrational properties were not reported yet and their crystalline and molecular structure was not experimentally determined and only their synthesis and characterizations by using NMR and mass spectroscopies were recently published [3–7]. The chemical properties of this salt are of importance due to that many studies suggest that there are steric and conformational factors that modulate the reactivities of these salts especially in aqueous solution [3–7]. Thus, in this medium, it was observed that in the amide formation with hydroxyl amines, there is considerable dependence on reactivity depending on the structure of the ligand [3]. Hence, the study of the nature of the different bonds and their interactions are important taking into account those experimental observations. As in the powerful laxative sodium picosulphate [8], possibly the ionic interactions in the potassium furoyltrifluoroborate salt play an important role in their structure and in their biological properties. Thus, the purposes of this work are the structural, electronic, topological and spectroscopic study of this salt in gas phase and in aqueous solution combining DFT calculations with their experimental infrared (FTIR), Raman and electronic spectra. Here, the knowledge of the coordination modes of the B

* Corresponding author.

E-mail address: sbrandan@fbqf.unt.edu.ar (S.A. Brandán).

atoms with the three electronegative F atoms linked to the K atom is very important to understand the mechanisms of all reactions where this salt is involved. These studies were performed by using the hybrid B3LYP method with the 6-31G* and 6-311++G** basis sets in gas phase and aqueous solution [9,10]. Especially in solution, the self consistent force field (SCRF) calculations were performed considering the integral equation formalism variant polarised continuum model (IEFPCM) to analyze the solvent effects [11,12] while the solvation model was used to predict the solvation energies with both levels of theory [13]. Also, the scaled mechanical force field (SQMFF) approach [14] was employed to perform the complete assignments of their vibrational spectra while to predict the reactivities and the behaviors of the salt in both media the frontier orbitals [15,16] and some useful descriptors were also computed [17–21]. Here, the obtained values were compared with data reported in the literature for halogenated compounds with different biological properties [17–21].

2. Experimental

The infrared spectrum of the pure potassium 3-furoyltrifluoroborate salt (FTFB) in solid state was recorded in KBr pellets on a Perkin Elmer Spectrum GX spectrometer in the 4000 to 400 cm^{-1} range. The Raman spectrum of FTFB in solid state at room temperature was recorded between 3600 and 100 cm^{-1} with the optical module of the 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). The Raman spectrum was recorded with 100 scans and a resolution of 4 cm^{-1} . The ultraviolet spectrum was recorded in aqueous solution with a Beckman spectrophotometer between 200 and 800 nm.

3. Computational details

The potassium 3-furoyltrifluoroborate salt was easily modeled with the *GaussView* program [22] because it salt structurally has a furane ring linked to the trifluoroborate group (BF_3K). Then, this initial structure was optimized in gas phase by using the hybrid B3LYP and the two 6-31G* and 6-311++G** levels of theory [9,10] with the Gaussian 09 program [23]. Later, with these optimized structures were performed the potential energy surfaces (PES) considering the three dihedral C1–C2–C9–O10, C2–C9–B11–K15 and F13–B11–C9–O10 angles and both levels of theory. The two first curves mentioned are presented in Fig. 1. In each curve we observed two stable structures with the same energies, named in the first case C1 and C2, while in the other one C3 and C4 where one of them, C4 presents the lowest energy. Hence, it is easy to see that C4 is the most stable structure of FTFB which can be seen in Fig. 2. When the F13–B11–C9–O10 dihedral angle is also considered two stable structures were obtained which correspond to C2 and C4 and, for this reason, this curve was not presented here. In solution, these stable structures were optimized with the PCM/SMD models [11–13] and the Gaussian 09 program [23]. In this opportunity the atomic Mulliken and natural populations (NPA) charges were studied with both basis sets and in the two media. The NBO program [24] was used to calculate the bond orders, expressed as Wiberg indexes and the donor-acceptor interactions while the AIM2000 program was used to compute the topological properties [25]. To perform the vibrational analysis of FTFB in both media, their normal internal coordinates, the SQMFF approach [14] and the Molvib program [26] were employed to calculate the force fields with both levels of theory. The normal internal coordinates corresponding to the BF_3K group were building taking into account a C_{3v} symmetry, as in species with similar groups [8,17–19,21] while the

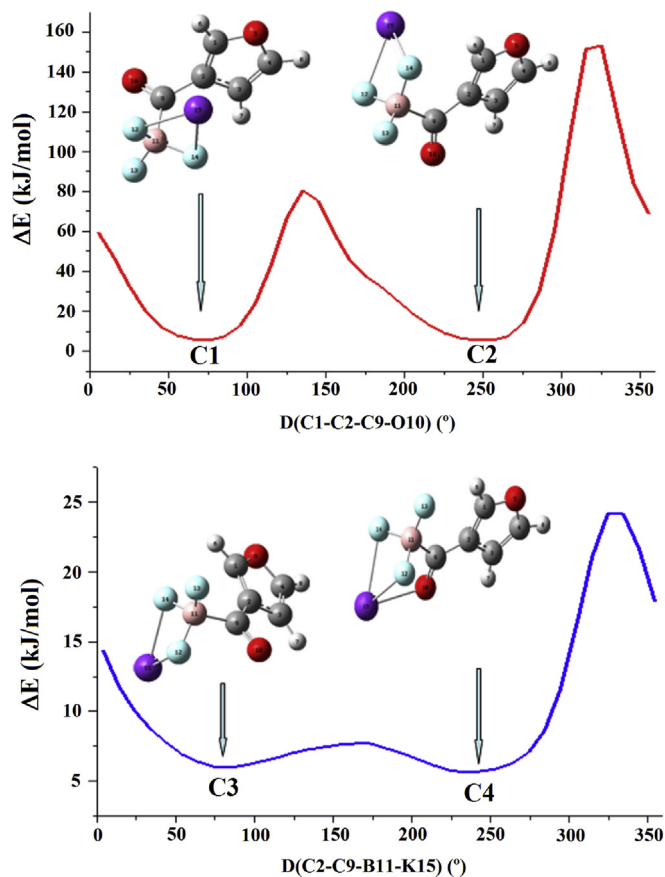


Fig. 1. Potential energy surfaces (PES) described by the dihedral C1–C2–C9–O10 (Top) and C2–C9–B11–K15 (Bottom) angles for the potassium 3-furoyltrifluoroborate salt in gas phase by using the B3LYP/6-31G* level of theory.

C4 structure was optimized with C_s symmetry. The assignments of all vibration modes were performed using the potential energy distribution (PED) contribution $\geq 10\%$. In addition, the ultraviolet–visible spectrum of FTFB in water was predicted by using Time-dependent DFT calculations (TD-DFT) with both levels of theory and the Gaussian 09 program [23]. Finally, taking into account that steric and conformational factors could modulate the

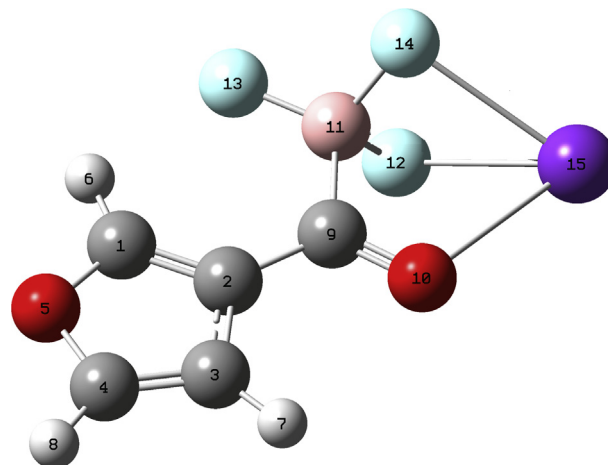


Fig. 2. Molecular structure of the most stable C4 conformer of the potassium 3-furoyltrifluoroborate salt and atoms numbering.

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