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A complete assignment of the vibrational spectra of 2-furoic acid based on the structures of the more stable monomer and dimer

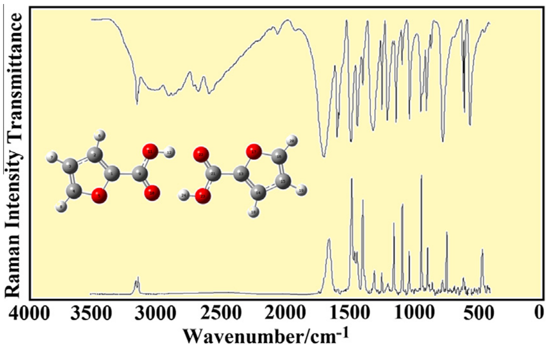
Houcine Ghalla [a], Noureddine Issaoui [a], María Victoria Castillo [b], Silvia Antonia Brandán [b],*, Henryk T. Flakus [c]

[a] Quantum Physics Laboratory, Faculty of Sciences of Monastir, Monastir 5000, Tunisia
[b] 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
[c] Institute of Chemistry, University of Silesia, 9 Szkolna Street, Pl-40-006 Katowice, Poland

HIGHLIGHTS

- The structural and vibrational properties of dimer of furoic acid were predicted.
- A complete assignment of the 66 normal vibrational modes for the dimer was performed.
- The NBO analysis reveals the high stability of the monomer and dimer *trans*.
- The electrostatic potentials have shown symmetrical structures for the two dimers.
- The calculations show that the *cis* dimer is present in the solid phase.

GRAPHICAL ABSTRACT



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ABSTRACT

The structural and vibrational properties of cyclic dimer of 2-furoic acid (2FA) were predicted by combining the available experimental infrared and Raman spectra in the solid phase and ab initio calculations based on density functional theory (DFT) with Pople's basis sets. The calculations show that there are two cyclic dimers for the title molecule that have been theoretically determined in the gas phase, and that only one of them, *cis* conformer, is present in the solid phase. The complete assignment of the 66 normal vibrational modes for the *cis* cyclic dimer was performed using the Pulay's Scaled Quantum Mechanics Force Field (SQMFF) methodology. Four strong bands in the infrared spectrum at 1583, 1427, 1126 and 887 cm^{-1} and the group of bands in the Raman spectrum at 1464, 1452, 1147, 1030, 885, 873, 848, 715 and 590 cm^{-1} are characteristic of the dimeric form of 2FA in the solid phase. In this work, the calculated structural and vibrational properties of both dimeric species were analyzed and compared between them. In addition, three types of atomic charges, bond orders, possible charge transfer, topological properties of the furan rings, Natural Bond Orbital (NBO) and Atoms in Molecules (AIM) theory calculations were employed to study the stabilities and intermolecular interactions of the both dimers of 2FA.

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Introduction

The study of compounds containing different heterocyclic rings is very important in numerous areas, such as chemistry, pharmacology, medicine and biology [1–7]. From chemical point

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* Corresponding author. Tel.: +54 381 4247752; fax: +54 381 4248169.
E-mail address: sbrandan@fbqf.unt.edu.ar (S.A. Brandán).

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of view the disposition of the rings in these compounds's type are important in relation to their structural and vibrational properties [8–22]. Thus, significant changes were observed on the geometrical parameters and bond orders of the thiophene central ring in the benzothieno[3,2-b]furan compound in relation to the isomer thieno[3,2-b]benzofuran where furan is the central ring [12]. These observations in both isomeric compounds were attributed to the calculated electronic populations of the C—O and C—S bonds of both, thiophene and furan rings. In consequence, the variations observed in the frequencies of both vibrational spectra are more significant in thieno[3,2-b]benzofuran than benzothieno[3,2-b]furan. In particular, furan and its derivatives are found in natural and synthetic products and many of them present cytotoxic, antitumor, antispamidic and anti-feeding activities [1–4]. In other heterocyclic compounds, such as the anticancer agents 1,3,4-thiadiazole derivatives, the pharmacological activities and their mechanisms of action are strongly depending on the type of modification of the 1,3,4-thiadiazole ring [5–8]. In furyl imidazole compounds, changes in the structural and vibrational properties of the different isomers are observed when the furan rings modify their position [9–12,15,16,18]. On the other hand, when the heterocyclic rings are linked to phenyl ring or other groups their properties are also modified [14,17–23]. In this context, the study of the structural properties of furan derivatives is important in relation to the pharmacological activities and to the identification of these compounds by means of vibrational spectroscopy. Thus, as a continuation of structural and vibrational studies related with heterocyclic compounds of great interest, in this work we considered the 2FA. The determination and re-determination of the crystal structure of 2FA were reported respectively by Goodwin and Thomson and, Gilmore et al. by means of X-ray diffraction [24,25]. In the first work [24], the *cis* conformation planar for the monomer was observed in the crystal structure of 2FA, it implies that the O atom of the furan ring is in a *cis* position in relation to the O atom belonging to the C=O bond of the COOH group. Those authors have reported a dimeric structure with two molecules linked in *cis* position. On the other hand, Gilmore et al. [25] have confirmed that the acidic H atoms, involved in the formation of the centrosymmetric carboxylic dimer, are disordered, as observed by Goodwin and Thomson [24]. Also, a comparative thermophysical study on the 2- and 3-furancarboxylic acids by using differential scanning calorimeter (DSC) and X-ray analysis reveals that the main differences in their supramolecular structure consist of the assembly of the carboxylic dimers into sheets [26]. Recently, the stability and the vibrational studies of the *cis* monomer of this acid were reported by Magdaline and Chithambarathanu [27] but, in that assignment the dimeric structure was not considered by these authors. So far, only a theoretical simulation of O—H and O—D stretchings band shapes of polarized infrared spectra of 2FA dimer crystals measured at liquid-nitrogen temperature were reported by Ghalla et al. [28] but, the nature of the electrostatic interactions, atomic charges, bond orders, frontier HOMO–LUMO orbitals, polarizabilities, force constants and the complete assignment for the cyclic dimer even were not published. For these reasons, the aim of this work is study the structural and vibrational properties of the cyclic dimer furoic acid combining the infrared and Raman spectra with DFT calculations using the B3LYP/6-311++G** method. The intermolecular interactions, atomic charges, bond orders and stabilization energies were calculated at the same level of theory using the NBO [29] calculations while the different topological parameters were analyzed using the Bader's Atoms in Molecules (AIM) theory [30,31]. The complete assignment of the observed bands in the vibrational spectra were performed taking into account the natural internal coordinates for the more stable monomer and cyclic dimer structures by using the harmonic force field with the Pulay's Scaled Quantum Mechanics Force Field (SQMFF) methodology [32]. In addition, the calculated properties for the two structures of each monomer and dimer were compared and analyzed between them and, with those data published by Magdaline and Chithambarathanu [27].

Experimental details

Samples of commercial 2FA were studied without posterior purification. The IR spectrum of the solid substance in KBr pellets was recorded at room temperature in the frequency range of 4000–400 cm^{-1}, with an FT-IR Perkin–Elmer spectrometer equipped with a Globar source and DGTS detector. The Raman spectrum was measured on polycrystalline sample contained in a glass capillary in the range of 4000–100 cm^{-1}, with a Bruker RF100/S spectrometer equipped with a Nd:YAG laser (excitation line of 1064 nm, 800 mW of laser power) and a liquid nitrogen cooled Ge detector. The spectra were recorded with a resolution of 1 cm^{-1} and 200 scans were applied.

Computational details

In order to compare this study with that reported by Magdaline and Chithambarathanu [27] for the *cis* monomer of 2FA using the hybrid B3LYP method [33,34] with the 6-31++G* basis set, in this case, the initial geometries for the *cis* and *trans* monomeric structures were optimized using the B3LYP/6-311++G** method, as implemented in the Gaussian 03 program [35]. The calculations were computed by using the 6-311++G** basis set due to the presence of H bond in the dimer. The initial structures of two cyclic dimers, each one with two *trans* or *cis* monomeric units were modelled using the *GaussView* program [36]. In all the calculations, the natures of the stationary points reached were checked by calculating the vibrational wavenumbers. The stable theoretical structures of the two monomers and the cyclic dimers together with the labelling of the atoms are presented in Fig. 1. The Mulliken, natural and atomic charges derived from Merz–Kollman [37] were studied for the cyclic dimers. On the other hand, the NBO calculations were carried out using the NBO 3.1 program [29], as implemented in the Gaussian 03 package program [35], while the topological analysis of the electronic charges densities for both dimers were performed using AIM methodology [30] with the AIM2000 program [31]. The B3LYP/6-311++G** method were also used to calculate the harmonic wavenumbers and the valence force fields expressed in Cartesian coordinates. Here, as in the work reported by Magdaline and Chithambarathanu [27] the resulting force fields were transformed to natural internal coordinates using the MOLVIB program [38]. The intermonomers natural internal coordinates of the cyclic dimers were defined as those reported for the cyclic dimer of monohydroxibenzoic acid [39] and, these coordinates together with the remaining ones are listed in Tables S1 and S2 (Supporting Material). Later, based on the SQMFF procedure [32], the harmonic force fields for the more stable monomer and dimer were evaluated at the same theory level, and only the Potential Energy Distribution (PED) components $\geqslant$ 10% were considered to perform the final assignment. The total energies for the *cis* cyclic dimer of 2FA were corrected for basis set superposition error (BSSE) by the standard Boys–Bernardi counterpoise method [40]. The BSSE value for that cyclic dimer of 2FA is negligible with the 6-311++G**, as observed for the dimer of monohydroxibenzoic acid [39] and, for this reasons, the corresponding value was not included in this work.

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