



Theoretical and experimental investigations on vibrational and structural properties of tolazamide



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HIGHLIGHTS

- FT-IR and Laser-Raman spectra of tolazamide were recorded in solid phase.
- Theoretical harmonic vibrational frequencies and optimized molecular structure were given for the first time.
- The complete assignments were performed on the basis of the potential energy distribution (PED).
- HOMO–LUMO energies and related molecular properties were evaluated.

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ABSTRACT

In this paper, vibrational spectra of tolazamide have been investigated by ab initio techniques in combination with experimental studies. Data on the FT-IR spectra (400–4000 cm⁻¹) and Laser-Raman spectra (100–4000 cm⁻¹) of tolazamide have been obtained in the solid phase. Assignments corresponding to the vibrational frequencies have been found and interpreted by the contribution of the potential energy distributions. The theoretical results are compared X-ray experimental data for this. Structural parameters such as bond lengths and angles, frequencies and intensities regarding Raman and IR spectra of the compound have been computed by density functional theory and Hartree–Fock methods with 6-311G++(d,p) and 6-31G(d) basis sets. They have been observed that the computed vibrational frequencies and optimized structural parameters are consistent with the corresponding experimental results. In addition, the images of frontier molecular orbitals (highest occupied and lowest unoccupied) have been presented and interpreted.

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Introduction

“Diabetes mellitus” is chronic and multifactorial disease analyzed with subheadings such as raised basal metabolic rate, damages in pancreatic beta cells, hyperglycemia. So, diabetes mellitus researches are increasing rapidly on the same rate as the increase of the disease all around the world in recent years. Drugs containing the biguanide and sulfonylurea structures for the purpose of reducing the hyperglycaemia are quite noteworthy in the field of diabetes. Because of the side effects of these drugs, the researches have been also focused on a new class of compounds. Sulfonylureas as the first-generation antidiabetic, such as tolazamide and tolbutamide, are still practiced in the treatment of diabetes but they are

less effective than the second-generation antidiabetics such as glipizide and glibenclamide. Besides, compounds with the inclusion of sulfonylurea are known for effective hypoglycemic activity. Such efficacious compounds are generally substituted on the urea groups and benzene rings. Tolazamide is an oral drug that lowers blood glucose in sulfonylurea class. The sulfonylurea derivatives are known to attract the attention on distinguishing biochemical and physical properties [1–13].

We aimed to contribute to the literature by theoretical and experimental analysis on tolazamide due to the interest in sulfonylurea groups in especially pharmaceutical industry. We have also reported a study on structural and vibrational analysis of similar anti-hyperglycemic biomolecules, gliclazide, previously [14]. Although X-ray diffraction method is one of the most frequently applied techniques for structural characterization of pharmaceutical compounds, but the utility of vibrational spectroscopy method

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has gained wide attention, due to its applicability to the short-range structure of molecular solids; rather than X-ray techniques which are being sensible to the long range order. From another perspective, we could not be reached to work on vibrational and structural characteristics of tolazamide with the help of ab initio calculation methods in literature searches. Therefore, molecular structure, frontier molecular orbitals, vibrational frequencies and related assignments of tolazamide have been investigated in detail by density functional theory (B3LYP exchange–correlation energy functional) and Hartree–Fock (HF) methods with the support of 6-311G++(*d,p*) and 6-31G(*d*) levels. Experimental peak data on Raman and FT-IR spectra of the title compounds have been also recorded in this paper.

Experimental details

Tolazamide sample was purchased from Sigma–Aldrich Co. (St. Louis, MO, USA). Fourier transforms infrared spectroscopic data (400–4000 cm^{-1}) for a KBr disk of tolazamide were recorded by a Pelkin Elmer (Waltham, MA, USA) Spectrum One Fourier transform infrared spectrometer with a resolution of 4 cm^{-1} at room temperature. The Laser-Raman spectrum data (100–4000 cm^{-1}) were recorded with the help of a spectrometer in specifications of 830 nm laser, Laser power 30 mW, and accumulation 1 and exposure time 10 s.

Computational details

Optimization steps, structure parameters, vibrational frequencies, infrared intensities, Raman scattering activities and molecular orbital visuals of tolazamide have been obtained by HF and DFT (B3LYP hybrid functional) methods with the 6-311G++(*d,p*) and 6-31G(*d*) basis set level. Gaussian 09 computer system [15] has been used for all computations. The values of 0.9051 (HF), 0.9614 (B3LYP) and 0.8929 (HF), 0.9613 (B3LYP) for 6-311G++(*d,p*) and 6-31G(*d*) basis set levels, respectively, as the scale factors [16] have been used in the computed harmonic frequencies. Vibrational Energy Distribution Analysis (VEDA 4) program [17] has been preferred to identify the stretching, in plane bending, torsional and out-of-plane local modes by potential energy distribution (PED) analysis. The studies involving vibration modes have been enriched with PED analysis by many researchers, previously [18–22].

Results and discussions

Tolazamide structure contains 42 atoms. A molecule consisting on N atoms has a total of 3N degrees freedom, corresponding to the Cartesian coordinates of each atom in the molecule. In a non-linear molecule, 3 of these degrees belong to the rotational, and 3 to the translational motions of the molecule, and so the remaining corresponds to its vibrational motions. The net number of the vibrational modes is 3N-6. Therefore, for our molecule, three Cartesian displacements of 42 atoms provide 120 normal vibration modes. The molecule has C_1 symmetry. Tolazamide electronic structures defined with atomic numbers after optimization have been presented shown in Fig. 1. The results in Table 1 contain the energies corrected for the zero point energy, dipole moments and frontier molecular orbital energies by different methods and basis set levels for the optimized compounds. Total energy values obtained by the B3LYP method are much lower than the HF method and the optimized geometry with minimal energy has resulted by B3LYP/6-311G++(*d,p*) level. Because in DFT/B3LYP, some correlation effects are taking into account through the effective exchange–correlation potential (the most stable method). In HF, each electron only sees the average electric field produced by

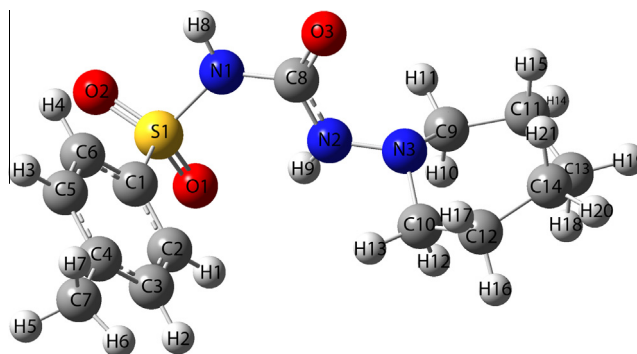


Fig. 1. Optimized structure of tolazamide by density functional theory.

all the other electrons, while DFT/B3LYP uses a more exact treatment by using functionals to describe the potential environment for each electron.

Geometric structure

Tolazamide, $C_{14}H_{21}N_3O_3S$ chemical formula, is an antidiabetic drug. Structure of the title compound consists of p-toly group, urea, sulfonyl amide and azepine group. One of the two N atoms of the urea is bounded to the azepine group while the other is bounded to the sulfonyl group which, in turn, is connected to the p-toly group. The structural parameters as bond lengths and angles resulted by using B3LYP and HF methods, 6-311G++(*d,p*) and 6-31G(*d*) basis set levels have been given in Table 2. Structure parameters of tolazamide have been compared with the experimental data from the literature [1]. They have been observed that the computed vibrational frequencies and optimized structural parameters are consistent with the corresponding experimental results. It can be said to be good agreement with the experimental data for the geometric parameters of tolazamide. Although the experimental data are obtained in the solid phase as single crystal for organics, the results of ab initio calculations are for its gas phase. Small mismatches between the structural parameters can be attributed to this situation. B3LYP hybrid functionals with 6-311G++(*d,p*) level have the highest correlations in both calculations bond lengths and angles when compared with the experimental ones.

Vibrational assignments

The experimental FT-IR and Laser-Raman spectra of the title compound have been given as Figs. 2 and 3, respectively, by combining theoretical IR and Raman spectra. Harmonic frequencies, IR intensities and Raman activities computed by B3LYP and HF approaches with 6-311G++(*d,p*) and 6-31G(*d*) basis sets are given in Table 3. Scale factors have been used in order to increase the correlations between theoretical and observed vibrational frequencies [23]. Also, the vibration modes assignments with the values higher than 10% in PED are situated in Table 3.

C–H vibrations

C–H stretching vibrations have been commonly observed as multiple weak bands in the region 3100–3000 cm^{-1} for aromatic structures [24–26]. Tolazamide has substituted aromatic system with four C–H adjacent moieties, stretching modes of C5–H3, C6–H4, C2–H1 and C3–H2, in this work. C–H stretching modes have been observed at 3108 and 3049 cm^{-1} in FT-IR spectra and 3077 and 3055 cm^{-1} in Raman spectra. These C–H modes are

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