

Conformational analysis and vibrational study of sulfanilamide

Gulce Ogruc Ildiz*, Sevim Akyuz

Istanbul Kultur University, Science and Letters Faculty, Physics Department, Atakoy Campus, 34156 Bakirkoy, Istanbul, Turkey

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ABSTRACT

The possible stable conformers of sulfanilamide molecule were searched by potential energy surface scan at both semi-empirical PM3 and DFT/B3LYP-3-21G levels of theory. Both the harmonic and anharmonic vibrational modes, the corresponding wavenumbers and IR and Raman intensities of the conformers were calculated by DFT method at B3LYP/6-31++G(d,p) level. The assignments of the fundamentals were proposed on the basis of total energy distribution (TED) calculations. The IR and Raman spectra of solid sulfanilamide were recorded and compared with the calculated ones. The dimer of the title compound were studied at DFT/B3LYP/6-31++G(d,p) level to investigate the intermolecular hydrogen bonding interactions of sulfanilamide molecule.

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1. Introduction

Sulfanilamide is the parent compound of a group of pharmaceuticals known as sulfa drugs, which are synthetic antimicrobial agents that contain the sulfonamide group. Sulfanilamides were widely used as effective chemotherapeutic agents for the prevention and cure of bacterial infections in humans [1]. It is used in treatment of meningitis, tonsillitis, gonorrhoea, pneumonia and sinus infections [2]. Since the study of polymorphism is an important issue in the pharmaceutical industry, the crystal structure of sulfanilamide has been widely investigated by many researchers so far and various polymorphs were determined [3–9]. X-ray diffraction studies of three most common polymorphs of sulfanilamide (α , β and γ) have been studied and crystal structure parameters were determined [3–6]. Lin et al. characterized the physical properties of four (α , β , γ and δ) polymorphs of sulfanilamide by X-ray diffraction measurements [8]. Although the polymorphic behaviour of the title compound has been extensively studied, there had been confusion about the stability of the polymorphs in the older studies. In the recent study of Portieri et al., β -sulfanilamide was found to be the stable form at room temperature and the α and γ forms to revert to β form on storage. The δ form was also determined by these workers but they were not able to produce sufficient amount of that form for spectroscopic characterization [7]. In a very recent

study of Gelbrich et al., the δ form was determined to be another stable form in addition to the β form [9].

Also, experimental and theoretical vibrational analysis of sulfanilamide has been reported in some studies. Varghese et al. [10] studied the molecular structure and vibrational frequencies of free sulfanilamide at HF level using 6-21G* basis set together with experimental FT-Raman and FT-IR spectra. Topaçli and Topaçli [11–14] performed IR analysis and computed the molecular structure and vibrational frequencies of free sulfanilamide and its metal complexes by both ab-initio methods employing 3-21G basis set and PM3, AM1, MINDO, MINDO3 semi-empirical methods. The RAMAN spectra of sulfathiazole and sulfanilamide were recorded by Lopez-Sanchez et al. [15].

Another vibrational study was done by Popova et al. [16] at DFT/B3LYP/6-31G++G(d,p) level of theory in which two stable conformers of sulfanilamide molecule were determined. Up to now, no systematic conformational analysis studies have been reported. In previous studies, assignments of the fundamentals were based on approximations rather than TED calculations. Furthermore, there were no theoretical vibrational studies reported on dimer and hydrogen bonding interactions of sulfanilamide molecule.

Since the differences between the polymorphic forms are associated with the existence of different conformers of the sulfanilamide molecule in the crystal lattice, the complete theoretical conformational analysis of free sulfanilamide molecule was done and four conformers were obtained. The effects of conformational changes were investigated through the optimized structure and the vibrational spectra of each conformer were obtained by DFT calculations. Since the crystal structure of α , γ and δ sulfanilamide is formed

* Corresponding author. Tel.: +90 2124984319.

E-mail address: g.ogruc@iku.edu.tr (G. Ogruc Ildiz).

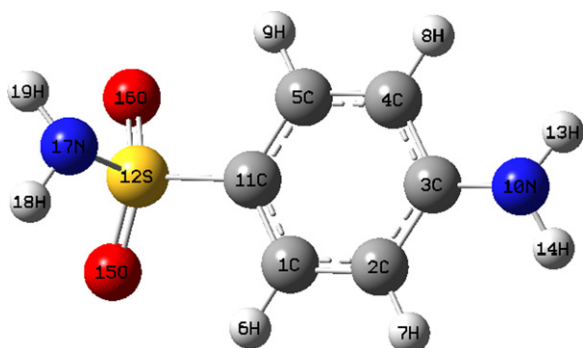


Fig. 1. Molecular model and numbering of atoms of free sulfanilamide molecule.

by joining of dimers together [9], in order to model H-bonding between the sulfanilamide molecules in the crystal structure, the dimer of the title compound is studied.

2. Methods and calculations

2.1. Experimental

The FT-Raman spectrum of the sulfanilamide was obtained from powdered sample placed in a Pyrex tube using the Bruker RFS 100/S spectrometer in the 4000–20 cm^{-1} range. The 1064 nm line, provided by a near infrared Nd:YAG air-cooled laser was used as excitation line. The output laser power was set to 100–120 mW.

The IR spectrum of solid sulfanilamide was recorded by KBr disc technique in the range 4000–400 cm^{-1} with 2 cm^{-1} resolution on a Jasco 300 FT-IR spectrometer by accumulating 200 scans.

2.2. Computational details

The theoretical conformational analysis of free sulfanilamide was done by single point energy calculations at both semi-empirical PM3 and DFT/B3LYP/3-21G theory levels. The dihedral angles around the 17N-12S, 12S-11C and 3C-10N bonds (see in Fig. 1) were altered by 30° in each iteration. The obtained structures were optimized at the same level of theory used in single point energy calculations to check the structures that correspond to local minima. The structures corresponding to real minima are reoptimized, their harmonic and anharmonic force fields, vibrational frequencies and IR and Raman intensities were calculated at DFT/B3LYP/6-31G++(d,p) theory levels. The calculations were performed by means of the Gaussian 03 software package [17]. The molecular model of free sulfanilamide is given in Fig. 1. The total energy distribution (TED %) calculations were done by the scaled quantum mechanical (SQM) force field method using the Parallel Quantum Solutions (PQS) program [18]. In order to investigate the hydrogen bonding interactions in the crystal structure, dimer of the title compound were formed and studied at DFT/B3LYP/6-31++G(d,p) level of theory.

3. Results and discussion

3.1. Conformational changes and polymorphism

The theoretical conformational analysis shows that the free sulfanilamide molecule has four conformers, two of them stable at room temperature (see in Fig. 2). Considering the energy differences between the global minimum (lowest energy) conformer and the other three conformers (see Table 1), it is seen that the energy of the first two conformers are less than kT energy (0.6 kcal/mol at room temperature and 1 atm pressure) indicating that these

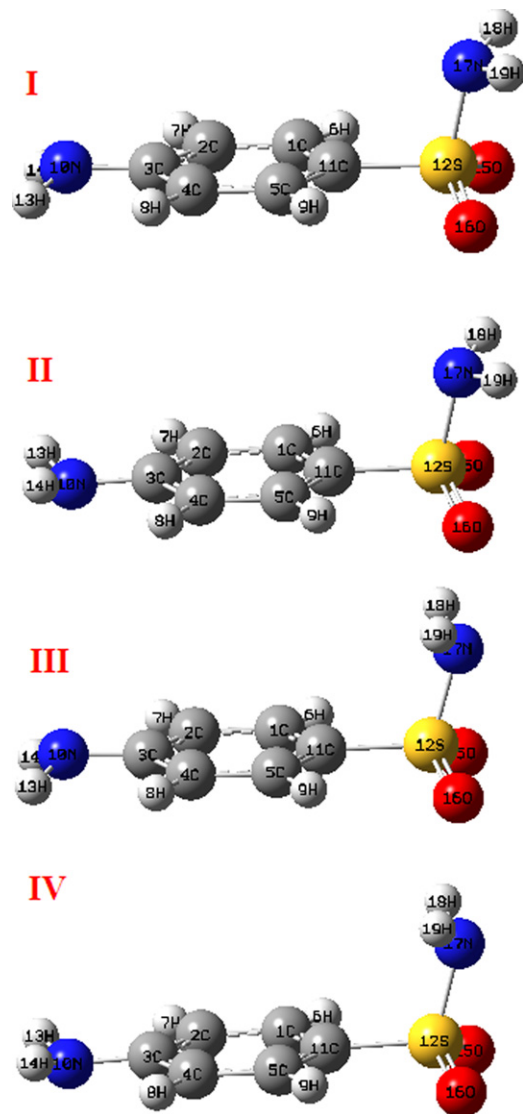


Fig. 2. The four low energy stable conformers of free sulfanilamide molecule: Global minimum conformer (I), second (II), third (III) and fourth (IV) lowest energy conformers.

two conformers have considerable population at room temperature. The energy difference of the third and fourth conformer with respect to the lowest energy conformer is calculated as 0.92 and 1.03 kcal/mol, respectively, which shows that these conformers are energetically less favourable than the first two conformers at room temperature. The optimized geometrical parameters of the global minimum conformer (I) and four stable conformers (I–IV) of sulfanilamide molecule and the optimized dihedral angles of

Table 1

The SCF energies of four conformers of free sulfanilamide molecule.

Conformers	Calculated SCF energies ^a		Relative energies ^c	
	(hartree)	(hartree) ^b	(hartree)	(kcal/mol)
Conf. I	–891.572888	–891.429399	0	0
Conf. II	–891.572733	–891.429266	0.000133	0.08346
Conf. III	–891.571868	–891.427939	0.001460	0.91616
Conf. IV	–891.571588	–891.427756	0.001643	1.03100

^a Calculated at DFT/6-31G++(d,p) level.

^b Corrected for zero-point vibrational energy.

^c The relative energies of the conformers are given with respect to the global minimum conformer (Conf. I).

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