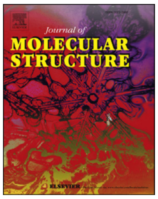
Journal of Molecular Structure 1103 (2016) 70–81

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc



Infrared, Raman and NMR spectral analysis, vibrational assignments, normal coordinate analysis, and quantum mechanical calculations of 2-Amino-5-ethyl-1,3,4-thiadiazole

Ibrahim A. Shaaban [a], Ahmed E. Hassan [a, 1], Ahmed M. Abuelela [a], Wajdi M. Zoghaieb [b], Tarek A. Mohamed [a, *]

[a] Department of Chemistry, Faculty of Science (Men's Campus), Al-Azhar University, Nasr City 11884, Cairo, Egypt
[b] Department of Chemistry, Sultan Qaboos University, P.O. Box 36, Al Khod, Oman

ARTICLE INFO

Article history:
Received 16 June 2015
Received in revised form
4 September 2015
Accepted 7 September 2015
Available online 9 September 2015

Keywords:
2-Amino-5-ethyl-1,3,4-thiadiazole
Infrared
Raman and NMR spectra
Vibrational assignment
Quantum mechanical calculations

ABSTRACT

Raman (3500–55 cm^{-1}) and infrared (4000–300 cm^{-1}) spectra of 2-Amino-5-ethyl-1,3,4-thiadiazole (AET; $C_4H_7N_3S$) have been recorded in the solid phase. In addition, the ^1H and ^{13}C NMR spectra of AET were obtained in DMSO-d_6. As a result of internal rotations of either methyl and/or ethyl groups around the C–C bonds with NH_2 moiety being planar (sp^2) and/or non-planar (sp^3) eight structures are theoretically proposed (**1**–**8**). The conformational energies and vibrational frequencies have been calculated using Density Functional Theory (DFT) with the methods of B3LYP and B3PW91 utilizing 6-31G (d) and 6-311++G(d,p) basis sets. And then **S-4** (the only conformer with real frequencies) was optimized, to yield **S-9**, however the Thiadiazole ring slightly twisted (*tilt* angle is 0.9°). The ^1H and ^{13}C NMR chemical shifts were also predicted using a GIAO approximation at 6-311++G(d,p) basis set utilizing B3LYP and B3PW91 methods with solvent effects using PCM method. The computational outcomes favor **S-9**; the methyl group being staggered to the *lone pair of* N_4 and reside *trans* position to the S atom, whereas NH_2 is non-planar in good agreement with the current study. Aided by the above mentioned DFT computations, a complete vibrational assignment of the observed infrared and Raman bands along with NMR chemical shifts has been proposed. The vibrational interpretations have been supported by normal coordinate analysis and potential energy distributions (PEDs). Finally, NH_2, CH_3 and C_2H_5 barriers to internal rotations were carried out using B3LYP/6-31G(d) optimized structural parameters (**S-9**). The results are reported herein and compared with X-ray structural parameters.

1. Introduction

Thiadiazole compounds is a five-membered ring system, which have four isomeric forms; 1,2,3-; 1,2,5-; 1,2,4- and 1,3,4-thiadiazoles. Members of 1,3,4-thiadiazole in particular has diverse applications as pharmaceuticals, oxidation inhibitors, cyanine dyes, and metal complexing agents, anticancer, antiviral, antimicrobial, anti-inflammatory, anticonvulsant, antidepressant, antioxidant, anti-tuberculostatic, analgesic and antipyretic [1–8]. Particularly, 2-Amino-5-ethyl-1,3,4-thiadiazole (AET) has been evaluated as a corrosion inhibitor [9]. To the best our knowledge, the ^1H NMR ($CDCl_3$) and infrared spectra of AET have been recorded earlier, however only few infrared frequencies have been briefly described [10]. Accordingly, 2-Amino-5-ethyl-1,3,4-thiadiazole (AET) molecule deserves more attention regarding its structure. Thus, we have initiated the current comprehensive vibrational and NMR spectral analysis supported by theoretical calculations.

We have carried out geometry optimizations, vibrational frequencies, infrared intensities and Raman activities using Gaussian 98 quantum mechanical (QM) computations [11]. Density Functional Theory (DFT) calculations were employed using the methods of B3LYP [12,13] and B3PW91 [14–16] up to 6-311++G(d,p) basis set to include the polarization and diffuse functions. Moreover, normal coordinate analysis (NCA) and potential energy distributions (PEDs) were carried out to support the vibrational

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* Corresponding author.
E-mail addresses: tarek_ama@hotmail.com, tarek_ama@azhar.edu.eg (T.A. Mohamed).

[1] Taken from the MSc Thesis of Mr. Ahmed E. Hassan to be submitted to the Chemistry Department, Faculty of Science, Al-Azhar University, Nasr City, Cairo 11884, Egypt.

http://dx.doi.org/10.1016/j.molstruc.2015.09.007

assignments provided herein. Additionally, the Gauge Invariant Atomic Orbitals (GIAO) [17,18] was used to predict ^{1}H and ^{13}C NMR chemical shifts with the hybrid B3LYP and B3PW91 functional at 6-311++G(d,p) basis set in the gaseous state and in solution by applying the polarization continuum model (PCM) [19]. Moreover the NH_2, CH_3 and C_2H_5 internal rotation barriers were evaluated with published results [20–22]. All results are reported herein and compared to similar molecules whenever appropriate.

2. Experimental

2.1. Materials

The solid sample of 2-amino-5-ethyl-1,3,4-thiadiazole (99%) were purchased from Sigma–Aldrich Chemical Company, Germany and it was used without further purification. CsI and/or KBr, dimethyl sulfoxide (DMSO-*d*$_6$) were of spectroscopic grade from Aldrich chemical company.

2.2. Spectroscopic measurements

The infrared and Raman spectra of the sample were carried out at the Egyptian Petroleum Research Institute (EPRI). The mid-infrared spectrum (4000–300 cm^{-1}; Fig. 1A) of the solid 2-amino-5-ethyl-1,3,4-thiadiazole was recorded on a Bruker FT-IR Spectrometer using KBr disc technique. To improve the S/N ratio, forty scans were collected utilizing 4 cm^{-1} resolution. The Raman spectrum of the solid sample (Fig. 1B) were obtained using dispersive Raman spectroscopy, Senterra, Bruker Optics, and the laser spot size was 1.0 μm. Raman shifts of the sample were obtained as powders deposited on glass microscope slides at ambient temperature (295 K), followed by analysis of different regions to ensure sample homogeneity and reproducibility. The laser excitation wavelength was 532 nm with the following operating conditions: scan range of 3500–55 cm^{-1} using laser power 100 mW, Aperture Setting 50 × 1000 μm, 30 s detection times, 4 cm^{-1} resolution and 25 accumulative scans. The observed IR and Raman vibrational bands are reported in (Tables 1 and 2).

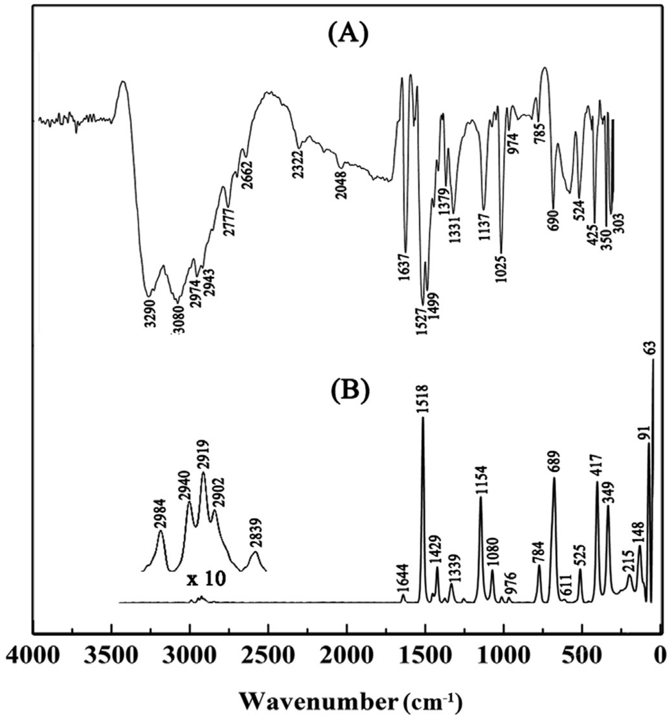

Fig. 1. Experimental vibrational spectra of 2-Amino-5-ethyl-1,3,4-thiadiazole (AET) in the solid phase; (A) IR spectrum (4000–300 cm^{-1}); (B) Raman spectrum (3500–55 cm^{-1}) using laser line ($\lambda_{ex} = 532$ nm).

^{1}H (Supplement Fig. S-1A) NMR spectrum of AET was acquired on the existing 400 MHz BRUKER BioSpin NMR Spectrometer equipped with an AVANCE magnet in DMSO-d$_6$ as solvent at ambient temperature. Trace TMS in DMSO-d$_6$ was assigned at 0 ppm and chemical shift (δ) values was measured relative to TMS standard. ^{13}C NMR spectrum (Supplement Fig. S-2A) was acquired at 100.61 MHz on the same NMR Spectrometer.

3. Computational procedures

3.1. Ab initio and DFT calculations

To study conformational stabilities of AET molecule, LCAO-MO-SCF calculations were performed using Gaussian-98 [11,23] with hybrid Density Functional Theory (DFT) whilst applying the methods of B3LYP and B3PW91 [12,24] at 6-31G (d) and 6-311++G(d,p) basis sets. As a result of the rotation of methyl and ethyl groups around the C–C bond with planar or non-planar NH_2, a total of *nine* possible conformers have been proposed for AET molecule (Fig. 2). Initially, geometry optimizations and frequency calculations of all the proposed structures for the isolated molecule were carried out by means of B3LYP/6-31G(d) using the gradient method of Pulay [25]. Structural optimization strategies were pursued until reaching the full convergence criteria for the Gaussian-98 calculations [11,23] without any constrains except particular dihedral angles to keep the symmetry of the proposed structures (**1**–**9**).

Structure (**9**; Fig. 2) has the lowest energy as predicted from the B3LYP and B3PW91 calculations at 6-31G(d) basis set, it is the lowest energy conformer with real vibrational frequencies which found to be consistent with single crystal X-ray data [26]. Therefore, the computed structural parameters (SPs) of AET molecule (**9**) are listed together with those obtained from X-ray [26] in Table 3. Correlation coefficients were also calculated to compare theoretical and experimental values [26], excellent agreement were found for bond lengths (R^2; 0.991) and deviations of about 8% for bond angles (R^2; 0.922–0.923).

The energy of structure (**4**; *planar ring*) was predicted higher than (**9**; *twisted ring and* τ *is 0.9°*) by 3121 cm^{-1} (8.92 kcal/mol) using G98 program. It is worth mentioning that, this energy difference is reduced to 57.0 cm^{-1} (0.16 kcal/mol) using G09 [27] which seems to be more reasonable (Fig. 2). Nevertheless, the predicted vibrational frequencies for **S-4** and **S-9** were similar within ±10 cm^{-1} according G09, however G98 predicts an imaginary wavenumber for **S-4**. Other proposed structures (**1**–**8**) were excluded owing to their high energies and the prediction of at least an imaginary wavenumber, as they are transition states.

3.2. Normal coordinate analysis

Normal coordinate analysis (NCA) provides an accurate description of the calculated normal modes which aid in the vibrational assignment of the observed IR and Raman bands to their respective vibrational transitions. Therefore, NCA were carried out for the most stable conformer (**9**; C_1 symmetry) by utilizing B3LYP and B3PW91 at 6-311++G(d,p) basis set. Aided by the traditional method of Wilson, Decius and Cross [28], 50 internal coordinates (Fig. 3; eleven of which are redundant) were used to construct 39 symmetry coordinates for AET (Table 4). Thereafter, the unscaled force constants in the chosen internal coordinates were calculated using a force field program similar to that described by