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Quantum chemical computational studies on 5-(4-bromophenylamino)-2-methylsulfanylmethyl-2H-1,2,3-triazol-4-carboxylic acid ethyl ester

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ABSTRACT

The optimized molecular geometry, vibrational frequencies, and gauge including atomic orbital (GIAO) ^{1}H and ^{13}C NMR shift values of 5-(4-bromophenylamino)-2-methylsulfanylmethyl-2H-1,2,3-triazol-4-carboxylic acid ethyl ester have been calculated by using Hartree–Fock (HF) and density functional method (DFT/B3LYP) with 6-31G(d), 6-31G(d,p) and LANL2DZ basis sets. The optimized molecular geometric parameters were presented and compared with the data obtained from X-ray diffraction. In order to fit the calculated harmonic wavenumbers to the experimentally observed ones, scaled quantum mechanics force field (SQM FF) methodology was proceeded. Correlation factors between the experimental and calculated ^{1}H chemical shift values of the title compound in vacuum and in $CHCl_3$ solution by using the conductor-like screening continuum solvation model (COSMO) were reported. The calculated results showed that the optimized geometry well reproduces the crystal structure. The theoretical vibrational frequencies and chemical shifts are in very good agreement with the experimental data. In solvent media the energetic behavior of the title compound was also examined by using the B3LYP method with the 6-31G(d) basis set, applying the COSMO model. The obtained results indicated that the total energy of the title compound decreases with increasing polarity of the solvent. Furthermore, molecular electrostatic potential (MEP), natural bond orbital (NBO) and frontier molecular orbitals (FMOs) of the title compound were performed by the B3LYP/LANL2DZ method, and also thermodynamic parameters for the title compound were calculated at all the HF and B3LYP levels.

1. Introduction

The chemistry and structure of heterocyclic compounds has been an interesting field of study for a long time. The synthesis of 1,2,3-triazoles and the investigation of their chemical and biological behavior have gained more importance in recent decades for biological and medicinal reasons. In this framework some compounds containing 1,2,3-triazole were investigated for biological activities such as antibacterial, hypoglycemic, antihypertensive, analgesic, antiparasitic, antiviral, anti-inflammatory, antitumor, and anti-HIV properties [1–10]. Also, 1,2,3-triazole compounds containing sulfur have been found to possess for a moderate degree fungicidal activity and better pesticidal activities in agricultural applications [11].

On the other hand it is well-known that the vibrational spectroscopy is a versatile and readily available tool for the structural studies. Since of the difficulties in the interpretation of IR spectra, quantum chemical computational methods have been used to wide its applications [12]. These computation methods give systematic errors mainly due to limited basis sets, harmonic approximation and remaining deficiencies in describing electron correlation [13] although the density functional theory (DFT) produces surprisingly accurate vibrational frequencies [14]. In order to overcome most of these errors some theoretical methods have been developed for fitting of calculated vibrational frequencies to experimentally observed ones. One of the most common used techniques is the scaled quantum mechanics force field (SQM FF) method developed by Pulay et al. [15,16]. In the SQM FF method the molecular geometry was expressed in terms of a full set of nonredundant natural internal coordinates [17,18]. Natural internal coordinates use individual bond displacements as stretching coordinates, and localized linear combinations e.g., bond angles and torsions, as deformational coordinates. On the basis of chemical intuition the natural internal coordinates of all molecules under consideration – there can be more than one – are sorted into groups sharing a common scale factor, and factors for each group which are determined by a least squares fit of well known and reliable experimental vibrational fundamentals [19].

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Recently, studies on chemical shift calculations employing quantum chemistry methods have showed that geometry optimization is a crucial factor for an accurate determination of computed NMR chemical shifts [20–25]. The improvements verified on electron correlation functions made it possible to calculate many molecular properties with comparable accuracies to traditional correlated ab initio methods, with more favorable computational costs [26]. In this framework, the DFT (B3LYP) has been a popular method in theoretical modeling, and possesses a great accuracy in reproducing the experimental values of geometry, NMR chemical shift, vibrational frequency, etc. [27–33].

Although several different methods for calculating magnetic shielding tensors have been developed, the gauge-including atomic orbital (GIAO) method [34,35] is most commonly used due to providing better results with the similar basis set size [36]. In the most cases, in order to take into account correlation effects, post-Hartree–Fock calculations of organic molecules have been performed using (i) Møller–Plesset perturbation methods, which are very time consuming and hence applicable only to small molecular systems, and (ii) density functional theory (DFT) methods, which usually provide significant results at a relatively low computational cost [26,37]. For this reason, the GIAO ^{13}C chemical shift calculations [36] within the DFT methods which take into account electron-correlation contributions have been preferred for the studies of large organic molecules [38], metal complexes [39], organometallic compounds [40].

The literature concerning 1,2,3- and 1,2,4-triazoles is rich and the papers published cover subjects such as crystal structure determination [41–43], ab initio and DFT calculations on the tautomerism and protonation sites [44–48], vibrational characteristics and photochemical transformations [49–53]. In a previous publication, IR and ^1H NMR spectra (in the $CDCl_3$ solution) and crystal structure of the 5-(4-bromophenylamino)-2-methylsulfanylmethyl-2H-1,2,3-triazol-4-carboxylic acid ethyl ester ($C_{13}H_{15}BrN_4O_2S$) have been studied by Wang and Dong [54]. To the best of our knowledge, theoretical calculation on this compound has not been published, yet. So, at the present study, the geometrical parameters, fundamental frequencies, and GIAO ^1H and ^{13}C NMR chemical shifts both in vacuum and in solvent media of this compound in the ground state have been calculated by using the HF and DFT (B3LYP) method with 6-31G(d), 6-31G(d,p) and LANL2DZ basis sets. For the study of its energetic behavior in solvent media the B3LYP method with the 6-31G(d) basis set was used by applying the conductor-like screening continuum solvation (COSMO) model. In addition, molecular electrostatic potential (MEP), natural bond orbital (NBO), frontier molecular orbitals (FMOs) of the title compound were performed by the B3LYP/LANL2DZ method, and ab initio HF and B3LYP methods with their corresponding basis sets were used to calculate several thermodynamic parameters of the compound. At the same time we also have compared all the calculations with to the corresponding experimental data. Thus, the obtained results from our calculations can be valuable for providing insight into molecular analysis.

2. Computational details

All calculations reported in this paper have been performed with the *PQS* ab initio package [55]. The molecular structure of the title compound in the ground state (in vacuum and in $CHCl_3$ by using COSMO model) was optimized by using the HF and B3LYP methods with 6-31G(d), 6-31G(d,p) and LANL2DZ basis sets. For modeling, the initial guess of the title compound was first obtained from X-ray coordinates [54]. Then, the vibrational frequencies for the optimized molecular structures in vacuum have been calculated. In order to obtain an accurate prediction, the theoretical vibrational frequencies were scaled using SQM FF method. The calculated frequencies verified that the structures were stable (no imaginary frequencies). For the ^1H and ^{13}C NMR chemical shift calculations both in vacuum and in solvent media of the title compound the GIAO approach by applying the same methods and basis sets used for the geometry optimization was used. Its geometry, together with that of tetramethylsilane (TMS) is fully optimized. The theoretical chemical shift ^1H and ^{13}C values were obtained by subtracting the GIAO isotropic magnetic shielding (IMS) values [56,57]. For instance, the average ^{13}C IMS value of TMS was taken into account for the calculation of ^{13}C chemical shift of any X carbon atom by considering the following equation $CS_x = IMS_{TMS} - IMS_x$. For the evaluation of the energetic and dipole moment behavior of the title compound in solvent media we have carried out the optimization calculations in three kinds of solvents (DMSO, ethanol and chloroform) by using COSMO [58,59] model.

3. Results and discussion

3.1. Geometrical structure

The atomic numbering schemes for the crystal [54] and theoretical geometric structure of the title compound are shown in Fig. 1a and b. The crystal structure of the title compound is monoclinic and its space group is $P2_1/n$. The crystal structure parameters are $a = 5.5220(1)$ Å, $b = 26.996(5)$ Å, $c = 10.596(2)$ Å, $\beta = 103.83(3)^\circ$ and $V = 1533.8(5)$ Å^3 [54]. The optimized geometric parameters (bond lengths and angles) of the compound calculated by HF and B3LYP methods are listed in Table 1 and compared with the experimental crystal geometry. As seen in Fig. 1a and b the molecular structure of the compound is non-planar. An intramolecular N4–H6···O2 hydrogen bond [N4–H6 0.90 Å, H6···O2 2.22 Å and N4–H6···O2 130°] exists between the amino group and carboxylic acid O2 atom [54]. The bond distances and angles have been calculated as 2.164 Å and 130.132° (HF/6-31G(d)), and 2.060 Å and 132.897° (B3LYP/6-31G(d)), respectively.

The different substitutions depending on 1,2,3-triazole ring are defined by the bond lengths C3–N4 [1.367(6) Å], C4–C5 [1.453(7) Å] and N2–C2 [1.443(6) Å] [54]. Herein these bond lengths have been calculated as 1.362, 1.466 and 1.443 Å for the HF/6-31G(d) level, and 1.366, 1.462 and 1.450 Å for the B3LYP/6-31G(d) level, respectively. In previous works, the N2–C2 bond length for 1,2,3-triazole ring depending on the different substituent was found to be 1.459(3) Å [60] and 1.416 Å [61]. In the triazole ring, the bond lengths for the N1–C3 and N3–C4 are 1.330(6) Å and 1.343 (6) Å, respectively [54]. These bond lengths were found to be 1.326 and 1.330 Å for the HF/LANL2DZ level, and 1.338 and 1.341 Å for the B3LYP/6-31G(d) level. The N1–C3 double bound distance is significantly shorter than the N3–C4 double bond, which result from the electronic factors associated with substituents the large electron density. In this relation, these obtained results are consistent with the respect to the different 1,2,3-triazole derivatives [60,61]. Also, the N1–C3 and N3–C4 bond lengths were found to be much shorter than average value for a C–N single bond (1.47 Å), but significantly longer than a C=N double bond (1.22 Å) [62], suggesting that some multiple bond character is presented. A similar trend becomes available for the C3–C4 bond (1.409(7) Å), which is significantly shorter than a C–C single (1.54 Å), but longer than the C=C double bond (1.33 Å) [62]. This supports the presence of a delocalized π-system in the triazole ring of the title compound. Furthermore, the N1–C3–N4 and N3–C4–C5 bond angles for the title compound were observed to be 125.7(4)° and 124.8(4)° [54], they were calculated as 127.0, 126.9 at HF 6-31G(d) level, 125.3°, 126.2° at B3LYP 6-31G(d) level, respectively. All the optimized geometric parameters of the title compound are shown in Table 1.