



Experimental and computational studies of 4-(Trifluoromethyl)pyridine-2-carboxylic acid



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ABSTRACT

The vibrational spectrum of 4-(Trifluoromethyl)pyridine-2-carboxylic acid was recorded using Fourier transform infrared spectrometer in the range 4000–400 cm^{-1} . The optimized geometric structure of 4-(Trifluoromethyl)pyridine-2-carboxylic acid was searched by B3LYP, CAMB3LYP, and PBEPBE levels of density functional theory (DFT). The vibrational wavenumbers of the title molecule in the ground state were computed by using B3LYP, CAMB3LYP, and PBEPBE methods with the 6-31G (d) basis set. NMR chemical shifts of the title compound were calculated using the gauge-independent atomic orbital (GIAO) method. The solvent effect on the UV–Vis absorption spectrum of the molecule was also examined using the B3LYP method by applying the integral equation formalism–polarized continuum model (IEF-PCM). The nonlinear optical (NLO) properties were measured by means of hyperpolarizability calculation. The electric dipole moment, the mean polarizability and the mean first hyperpolarizability were calculated by using the DFT method with B3LYP, CAMB3LYP, and PBEPBE levels.

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1. Introduction

Pyridine is a basic heterocyclic compound, structurally related to benzene, with one C–H group replaced by a nitrogen atom. Pyridine and its derivatives are used extensively in the synthesis of various pharmacologically and biologically active compounds. Pyridine-2-carboxylic acid (picolinic acid) has gathered great attention due to their many potential applications in the chemical and pharmaceuticals industry [1,2]. Additionally, Pyridine-2-carboxylic acid has been extensively studied in view of their interesting magnetic properties [3,4]. Picolinic acid is significant from the industrial point of view; for instance, in nuclear reactor decontamination [5,6]. It is a metabolite derived from tryptophan of humans and animals. The acid plays an important role in zinc transport [7,8]. Its complexes are reported to possess antiviral [9], antifungal [10] and antibacterial [11] activities.

DFT computations have been increasingly used for calculating a wide variety of molecular properties that includes stability structure, charge distribution, and vibrational frequencies. The advancement of ever better exchange–correlation functional has made it possible to calculate many physicochemical properties with accuracies comparable to those of traditionally correlated ab initio

methods. The goal of this study is to investigate the quantum chemical properties of the 4-(Trifluoromethyl)pyridine-2-carboxylic acid, using DFT calculations.

In this work, the molecular structure, vibrational spectra, electronic, NMR, NBO and NLO properties have been investigated on the 4-(Trifluoromethyl)pyridine-2-carboxylic acid. The optimized geometric parameters and vibrational frequencies have been calculated using B3LYP, CAMB3LYP and PBEPBE with 6-31G (d) basis set. The NMR chemical shifts of 4-(Trifluoromethyl)pyridine-2-carboxylic acid have been computed by the gauge-independent atomic orbital (GIAO) method using DFT/B3LYP method with 6-31 G (d) basis set. The energetic behaviour of the title molecule in different solvent media (methanol, ethanol, and water) has been examined using TD-DFT/B3LYP the 6-31G (d) basis set by applying the integral equation formalism–polarized continuum model (IEF-PCM). The electronic structures of stationary points have been obtained by the natural bond orbital (NBO) analysis.

2. Experimental

2.1. General

4-(Trifluoromethyl)pyridine-2-carboxylic acid was purchased from Sigma–Aldrich Company with a stated purity 97%. The IR spectrum of the title molecule was recorded in the range of

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4000–400 cm^{-1} using a Vertex 80v Bruker FTIR spectrometer using KBr disc.

3. Computational details

The DFT was applied using the B3LYP [12], CAM-B3LYP (Coulomb-attenuating method applied to B3LYP) [13] and PBEPBE (generalized-gradient-approximation exchange-correlation functional of Perdew, Burke, and Ernzerhof) [14] functional with 6-31G (d) basis set. Calculations were performed the GAUSSIAN 09W program [15]. The output files were visualized by means of GaussView tool [16]. The optimized structures and vibrational frequencies of 4-(Trifluoromethyl)pyridine-2-carboxylic acid were carried out using B3LYP, CAM-B3LYP, PBEPBE with 6-31G (d) basis set. No imaginary frequencies were found, indicating that the stationary points correspond to a true energy minimum. Electronic spectra of the title molecule were computed with the TD-DFT method starting from the ground-state geometry optimized. The integral equation formalism-polarized continuum model (IEF-PCM) dealing with solvent effect was chosen in electronic transition calculations. ^1H and ^{13}C NMR chemical shifts have been calculated within Gauge-independent atomic orbital (GIAO) approach. DFT method was also used to calculate the polarizability, dipole moment and first hyperpolarizability. A detailed interpretation of the theoretical vibrational spectra was done on the basis of the Potential Energy Distribution (PED) using VEDA4 [17] program. The NBO analysis was performed at the B3LYP level by means of the NBO 9.5 program. Fig. 1 was drawn by DIAMOND 3.0 (demonstrated version) program using arbitrary [18].

4. Result and discussion

4.1. Optimized geometry

The geometry optimization was carried out using B3LYP, CAM-B3LYP, and PBEPBE with 6-31G (d) basis set (Fig. 1). The calculated geometric parameters of 4-(Trifluoromethyl)pyridine-2-carboxylic acid for the three different levels are shown in Table S1. The C2–C10 bond length has been computed as longer than other C–C bond distances because the substitution of electron donating carboxyl group increases the electron density C–C bonds. The C10=O11 bond length has been calculated at 1.208 Å for B3LYP, 1.209 Å for CAMB3LYP and 1.225 Å for PBEPBE level, respectively. The C10–O12 bond length has been calculated 1.341 Å, 1.339 Å and 1.355 Å for B3LYP, CAMB3LYP, and PBEPBE levels, respectively. The B3LYP and CAMB3LYP hybrid schemes show better performance to calculate the bond lengths, and angle values than PBEPBE. Therefore, it can be said that DFT-calculated results are in good agreement with the literature [19].

4.2. IR assignment

Fig. 2 illustrates the infrared spectra of the 4-(Trifluoromethyl)pyridine-2-carboxylic acid in the frequency range from 4000 to 400 cm^{-1} . The FT-IR spectra of the molecule have been calculated by using B3LYP, CAM-B3LYP and PBEPBE levels with 6-31G (d) basis set. The calculated frequencies have been scaled with 0.96 for B3LYP, 0.97 for CAM-B3LYP and 0.98 for PBEPBE [20,21]. The experimental and calculated vibration frequencies are compared in Table 1.

The aromatic compounds show the presence of C–H stretching vibration in the region 3100–3000 cm^{-1} , which is the characteristic region for the ready identification of $\nu(\text{CH})$ vibrations [22]. The infrared spectrum of the molecule shows a weak band in the 3095 cm^{-1} region due to symmetric stretching vibrations of the $\nu(\text{CH})$. The broad band at 2821 cm^{-1} belonging to $\nu(\text{CH})$ asymmetric stretching vibrations of the pyridine ring. The calculated $\nu(\text{CH})$ vibrations are slightly larger than experimental values.

Most carbonyl complexes have a very intense and narrow peak in the range of 1800–1600 cm^{-1} [23,24]. The appeared bands at 1700 and 1173 cm^{-1} are assigned to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$ stretching vibrations, respectively (Fig. 2). The $\nu(\text{C}=\text{O})$ stretching vibration is calculated at 1747 cm^{-1} for B3LYP, 1819 cm^{-1} for CAM-B3LYP and 1726 cm^{-1} for PBEPBE level. As for $\nu(\text{C}-\text{O})$ stretching vibration, it is computed at 1106 cm^{-1} for B3LYP, 1143 cm^{-1} for CAM-B3LYP and 1090 cm^{-1} for PBEPBE level. Therefore, it can be said that DFT-calculated frequencies are in good agreement with experimental data.

The experimental $\nu(\text{C}-\text{F})$ vibration is observed at 1148 cm^{-1} in the FT-IR spectrum. The calculated bands at 1152, 1145 and 1159 cm^{-1} are assigned to $\nu(\text{C}-\text{F})$ vibrations for B3LYP, CAM-B3LYP and PBEPBE levels, respectively. It can be said that DFT-computed wavenumbers are in good agreement with experimental results.

The band at 1008 cm^{-1} in IR spectrum is assigned to ring breathing mode of 4-(Trifluoromethyl)pyridine-2-carboxylic acid. In pyridine and substituted pyridines, the ring breathing mode is near 995 cm^{-1} [25,26]. The ring breathing mode of the pyridine ring in the molecule is computed at 973–1000–962 cm^{-1} for the three levels, respectively. As shown in Table 1, the calculated vibrational frequencies at CAM-B3LYP level are a good agreement with experimental data.

The in-plane C–H bending vibration of 4-(Trifluoromethyl)pyridine-2-carboxylic acid is observed at 1262 cm^{-1} . The in-plane C–H bending vibration is calculated at 1293 cm^{-1} for B3LYP level, 1219 cm^{-1} for CAM-B3LYP level and 1249 cm^{-1} for PBEPBE level.

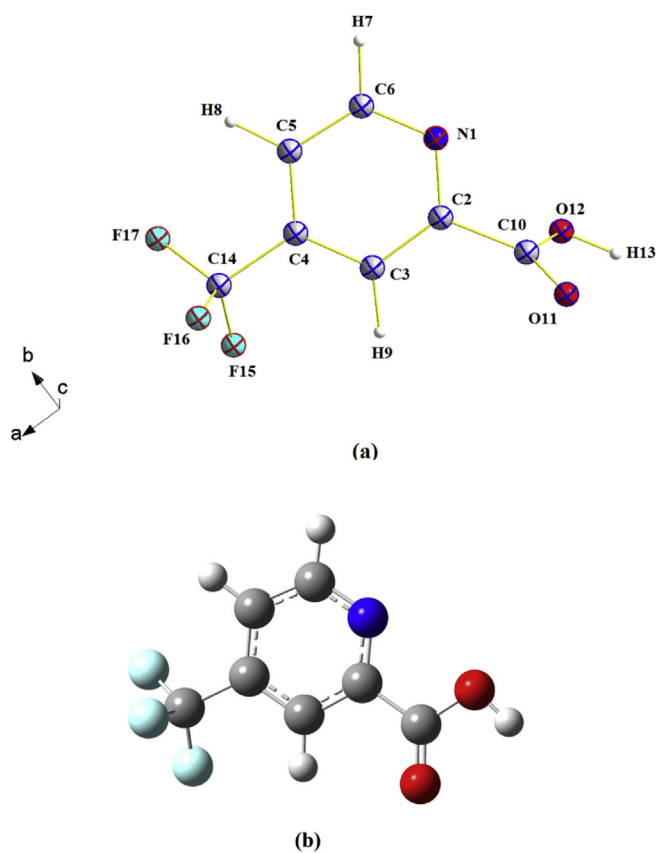


Fig. 1. (a) The molecular structure of 4-(Trifluoromethyl)pyridine-2-carboxylic acid, showing the atom-numbering scheme and (b) the optimized (obtained from DFT/B3LYP) geometric structure of 4-(Trifluoromethyl)pyridine-2-carboxylic acid.

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