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Ab initio/DFT electronic structure calculations, spectroscopic studies and normal coordinate analysis of 2-chloro-5-bromopyridine

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ABSTRACT

FT-IR (4000–400 cm^{-1}) and FT-Raman (3500–50 cm^{-1}) spectral measurements of solid sample of 2-chloro-5-bromopyridine have been done. *Ab initio* and DFT calculations have been performed giving energies, optimized structures, harmonic vibrational frequencies, depolarization ratios, IR intensities, Raman activities and atomic displacements. Furthermore, force field calculations have been performed by normal coordinate analysis. A complete assignment of the observed spectra, based on spectral correlations, electronic structure calculations and normal coordinate analysis, has been proposed. The results of the calculations have been used to simulate IR and Raman spectra for the molecule that showed good agreement with the observed spectra. The SQM method, which implies multiple scaling of the DFT force fields, has been shown superior to the uniform scaling approach. The energy and oscillator strength calculated by Time-dependent DFT results are in good agreement with the experimental results.

1. Introduction

Many substituted pyridines are involved in bioactivities with applications in pharmaceutical drugs and agricultural products [1–3]. Pyridine derivatives act as anesthetic agents, drugs for certain brain diseases, and prodrugs for treating neuronal damage caused by stroke, to name a few. They also underpin analgesics for acute and chronic pain, treatment for tinnitus, depression, and even diabetic neuropathy. The picoline derivatives prepared from aminopyridine derivatives have been shown to have cholesterol lowering properties, anticancer and anti-inflammatory agents [1]. The ring nitrogen of most pyridines undergoes reactions typical of weak, tertiary organic amines such as protonation, alkylation and acylation [2]. Pierrat et al. [3] synthesized pyridine-based derivatives from a 2-chloro-5-bromopyridine scaffold, resulting in pyridine-based libraries of synthons and chromophores.

The halogen-substituted pyridines have been subjected to various spectroscopic studies [4–11]. Green et al. [4] proposed complete assignment of the observed frequencies for monosubstituted halo and methyl-pyridines. A complete assignment of the vibrational spectra of 2-iodopyridine, aided by the *ab initio*, DFT and MP2 methods has been reported by Sortur et al. [5]. Mohan and Murugan [6] reported the assignment of frequencies for various fundamental modes of 2,6-dichloropyridine on the basis of normal coordinate calculations. Vibrational spectra and normal coordinate analysis of di-, tri-halopyridines were studied by Krishnakumar and Xavier [7,8]. Vibrational assignments and DFT studies of 5-bromo-2-nitropyridine was done by Sundaraganesan et al. [9]. Medhi and Medhi [10] analyzed the UV absorption spectrum in the range 340–185 nm in the vapour state and in solution in some solvents for 2-chloro-5-bromopyridine. They also presented UV absorption and complete vibrational assignment of the observed frequencies of 2-fluoro-5-bromopyridine [11].

In general, the DFT methods yield sufficiently good and consistent results at moderate computational costs. Due to some systematic errors, such as the neglect of anharmonicity and electron correlations, however, empirical corrections of the force field are required to obtain an acceptable agreement between the observed and calculated frequencies. In simpler molecules, uniform scaling, i.e., *global scaling* of the theoretical force field may prove satisfactory [12,13]. However, it has been shown, that application of multiple scale factors, i.e., the *selective scaling* of force fields developed by Pulay and co-workers [14–16], may lead to better results. It appears that only a few halopyridines have been subjected to a systematic investigation of the structure and vibrational assignments using *ab initio*/DFT calculations and normal coordinate analysis. Therefore, in the present study FT-IR and FT-Raman spectral measurements as well as *ab initio*/DFT electronic structure

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calculations, normal coordinate analysis and vibrational assignments of 2-Chloro-5-bromopyridine (hereafter, it is referred to as CBP) have been carried out.

2. Experimental

A solid sample of CBP was purchased from Aldrich Chemical Co. and used as received. The IR spectral measurement was carried out on a *Nicolet's Model Impact 410 FT-spectrometer*. The FT-spectrometer consisted of a Globar Mid IR source, a DTGS solid-state detector and a KBr beam splitter. The absorption spectrum of the sample was measured in KBr pellet with 100 interferograms at an interval of 1 cm^{-1}. A *Bruker Model FRA 106/RFS 100* FT-spectrometer was used for the Raman spectral measurement. The spectrometer was provided with a Quartz beam splitter and a high sensitive germanium detector. The detector was cooled to the liquid N_2 temperature. The Raman spectrum was excited in the 180° geometry with 1064 nm laser line from a diode pumped-air cooled-cw Nd:YAG laser. The optical power necessary for the measurement was varied in the range 75–100 mW. The spectrum was obtained by the co-addition of 300 interferograms at the interval of 1 cm^{-1}.

3. Computational

In order to model the structure and to compare the performance of *ab initio* and DFT methods on CBP, geometry optimization followed by vibrational frequency calculations was performed at the RHF/6-311G*, B3LYP/6-311G* and B3PW91/6-311G* using the *Gaussian 03W* [17]. Molecular electronic energies, equilibrium geometries, IR and Raman spectra have been computed. The unscaled theoretical IR spectrum was generated using frequencies calculated by Gaussian 03W in Gauss view 4 [18], and the same programs were used to visualize the normal modes. All the computed harmonic frequencies have been scaled with the factor 0.904 at RHF/6-311G*, with 0.966 at B3LYP/6-311G* and with 0.963 at B3PW91/6-311G* [13]. As an aid in the assignments, potential energy distributions (PED) have been calculated in terms of simple internal coordinates from unscaled B3LYP/6-311G* results, using the program MOLVIB [19]. Using the same program, we have also carried out normal coordinate analysis by multiple scaling of the force field in the natural internal coordinate representation described by Pulay and co-workers [14] to calculate potential energy distributions (PED) for the B3LYP/6-311G* results. The UV–vis spectrum was calculated by Time-dependent density functional theory (B3LY/6-311G* TD). The calculations have been used to determine the low- lying excited states of CBP.

4. Results and discussion

4.1. Geometry optimization

The geometrical structure of the molecule with the numbering scheme for the atoms is presented in Fig. 1. The optimization of the geometry was performed at the B3LYP/6-311G*. The molecular electronic energy of the optimized structure, C_s symmetry is −3281.5055481 hartree. We performed optimizations also at the RHF/6-311G* and B3PW91/6-311G*. The results are presented in Table 1 and are compared with the available experimental data of similar systems [20–22].

The CH and CC bond lengths computed with RHF are within 1% error and those at B3LYP/B3PW91 are in excellent agreement with the experimental data. The C–Br bond length is predicted within ∼2% at B3LYP and within ∼1% error of the experimental value at RHF/B3PW91; C–Cl bond length is predicted within ∼1% error at B3LYP and that at RHF/B3PW91 is in excellent agreement with the experimental value. The C–N bond length is predicted within ∼3% error at RHF and within ∼2% error of the experimental value at B3LYP/B3PW91. Similarly, all the bond angles are predicted within ∼1% of experimental results. However, the pyridine ring

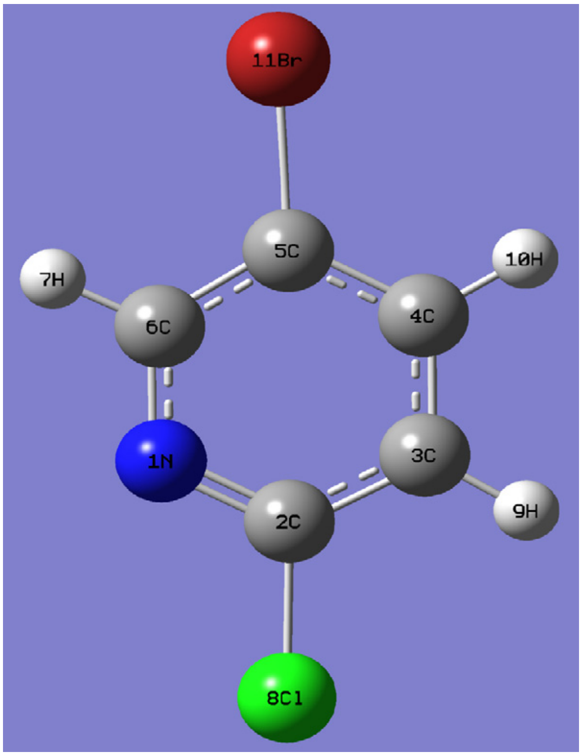

Fig. 1. Molecular structure of 2-chloro-5-bromopyridine.

Table 1
Optimized geometry parameters with 6-311G* basis set.

	Experimental[a]	RHF	B3LYP	B3PW91
Bond length (Å)				
C_4–H_{10}	1.082	1.073	1.083	1.084
C_4–C_5	1.392	1.384	1.393	1.391
C_4–C_3	1.392	1.378	1.389	1.386
C_5–C_6	1.394	1.380	1.391	1.390
C_5–Br_{11}	1.867	1.891	1.908	1.893
C_3–C_2	1.394	1.386	1.395	1.393
C_3–H_9	1.083	1.072	1.083	1.083
C_6–N_1	1.338	1.321	1.336	1.332
C_6–H_7	1.087	1.074	1.085	1.086
C_2–N_1	1.338	1.301	1.316	1.315
C_2–Cl_8	1.739	1.740	1.761	1.746
Bond angles (°)				
H_{10}–C_4–C_5	120.8	120.9	120.9	120.8
H_{10}–C_4–C_3	120.8	120.7	120.7	120.7
C_5–C_4–C_3	118.4	118.5	118.4	118.4
C_4–C_5–C_6	118.5	118.9	119.3	119.2
C_4–C_5–Br_{11}	121.4	120.9	120.7	120.8
C_6–C_5–Br_{11}	120.1	120.2	120.0	120.0
C_4–C_3–C_2	118.5	117.5	117.5	117.6
C_4–C_3–H_9	121.4	121.6	121.4	121.4
C_2–C_3–H_9	120.1	120.9	121.0	121.0
C_5–C_6–N_1	123.8	122.5	122.2	122.4
C_5–C_6–H_7	120.2	121.0	121.1	121.0
N_1–C_6–H_7	116.0	116.5	116.6	116.6
C_3–C_2–N_1	123.8	124.4	124.5	124.5
C_3–C_2–Cl_8	120.2	118.7	118.6	118.6
N_1–C_2–Cl_8	116.7	116.9	116.9	116.9
C_6–N_1–C_2	116.9	118.2	118.0	118.0

[a] Refs. [20–22].