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Anharmonic vibrational analysis of 3,4-diaminopyridine and 3-aminopyridine by density functional theory calculations

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ABSTRACT

In this work, we will report a combined experimental and theoretical study on molecular structure and vibrational analysis of 3,4-diaminopyridine (3,4-DAP) and 3-aminopyridine (3-AP). The Fourier transform infrared and Fourier transform Raman spectra of 3,4-DAP were recorded in the solid phase. The molecular geometry, harmonic vibrational wavenumbers of 3-AP and 3,4-DAP in the ground-state have been calculated by using MP2 and density functional methods (B3LYP) using 6-311++G(d,p) as basis set. Predicted electronic absorption spectra 3,4-DAP from TD-DFT calculation have been analyzed comparing with the experimental UV–vis spectrum. The calculated HOMO and LUMO energies show that charge transfer occur in the molecule. A detailed interpretation of the infrared spectra of 3-AP and 3,4-DAP is reported. The theoretical spectrograms for FTIR and FT-Raman spectra of the title molecules have also been constructed. Comparison of the experimental spectra with anharmonic vibrational wavenumbers indicates that B3LYP results are more accurate.

1. Introduction

The pyridine derivatives have an important position among the heterocyclic compounds because they can be used as nonlinear materials and photo chemicals. In particular, some of these crystals have been reported as wavenumber converters from NIR to the visible wavelength region [1]. Aminopyridines are widely used in pharmacological and medical applications. Some of them show anesthetic properties and have been used as drugs for certain brain diseases [2–4]. 2-Aminopyridine tagged oligosaccharides have been widely used for sensitive qualitative and quantitative analysis by high performance liquid chromatography with fluorescence detection [2]. 2-Aminopyridine is used in preparation of cytidine analogs [4], it is also immensely used as a reagent in analytical chemistry.

Mohan and Ilangoven [5] carried out the normal co-ordinate analysis of 2-aminopyridine, using valence force field. However, they assumed the NH_2 group of the molecule as a single mass point. The normal co-ordinate analysis of the 2-aminopyridine and ND_2–pyridine was performed in valence force field approximation. IR and absorbance intensities were calculated and electro-optical parameters (EOP) were refined in order to produce experimental IR spectrum [6]. The vibrational spectra of 3-methylpyridine have been investigated by several authors [7–9]. Generally, its molecular vibrations were assigned to the normal modes of benzene [10] which, however, may not be justified in the case of the non-symmetrical benzene derivatives [11]. Draegar performed a normal co-ordinate analysis [12] using experimental data from the early sixties [13]. Although this study resulted in a good agreement between the experimental and calculated wavenumbers, new experimental data and developments in the normal co-ordinate analysis method justify a reinvestigation of the vibrational spectra of this important molecule.

Sharma and Medhi [14] recorded the laser Raman and Infrared absorption spectra of 2-chloro-3-nitropyridine in the region 4000–500 cm^{-1}. The vibrational assignment was reported on the basis of the polarization study and by comparison with the related molecules. Medhi et al. [15] attempted to interpret the infrared and polarized laser Raman spectra of 2-chloro-5-nitropyridine. A tentative vibrational assignment of the observed wavenumbers were also given by assuming C_s point group symmetry, without performing normal co-ordinate analysis. Berezin and Elkin [16] determined the force constants for the nitro groups in 2-, 3- and 4-nitropyridine by theoretical calculations. The characteristic features of the influence of the nitro substitution on the force field of benzene and pyridine have been established. A normal mode analysis was carried out for 3-aminopyridine using force field refinement method together with ab initio (6-31G(d)) and semi empirical (AM1) quantum chemical calculations [17]. Recently, 3,4-diaminopyridinium hydrogentartarate dihydrate has been synthesized and its structure and properties elucidated in detail spectroscopically, thermally and structurally, using single crys-

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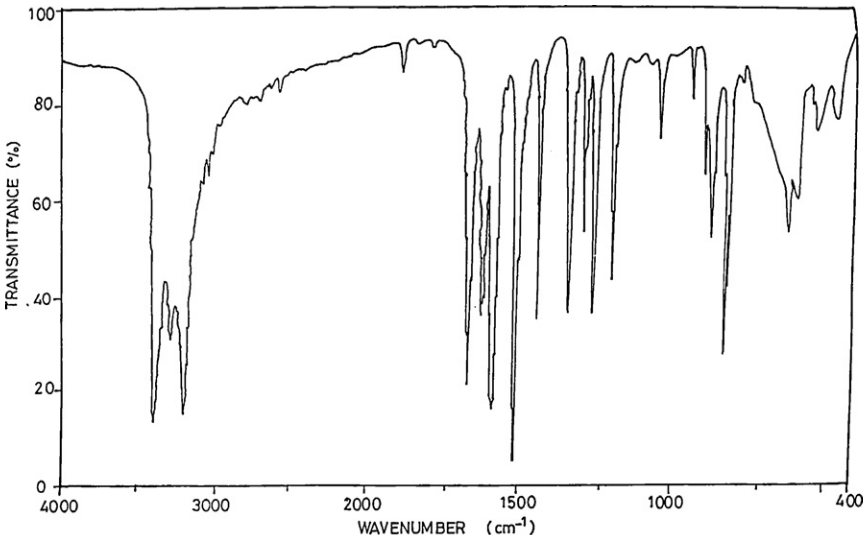

Fig. 1. FT-IR spectrum of 3,4-diaminopyridine.

tal X-ray diffraction, linear polarized solid state IR-spectroscopy, UV-spectroscopy, TGA, differential scanning calorimeter (DSC), differential thermal analyzer (DTA) and positive and negative (mass spectra with electroscope ionization) ESI-MS by Koleva et al. [18]. Therefore the present investigation was undertaken to study the FT-IR and FT-Raman spectra of these molecules completely and to identify the various normal modes with greater wavenumber accuracy. Density functional theory anharmonic wavenumber (DFT/B3LYP) and MP2 harmonic wavenumber calculations have been performed to support our wavenumber assignment.

2. Experimental

The compound 3,4-diaminopyridine (3,4-DAP) in the solid form was obtained from Sigma–Aldrich Chemical Company, USA with a stated purity of greater than 99% and it was used as such without further purification. The FT-Raman spectrum of 3,4-DAP has been recorded using 1064 nm line of Nd:YAG laser as excitation wavelength in the region 50–3500 cm^{-1} on a Brucker model IFS 66V spectrophotometer. The FT-IR spectrum of this compound was recoded in the region 400–4000 cm^{-1} on IFS 66V spectrophotometer using KBr pellet technique. The spectrum was recorded at room temperature, with the spectral resolution of 2.0 cm^{-1}. The IR spectral data for 3-AP are taken from Ref. [17] in the present study. The observed experimental FT-IR and FT-Raman spectra of the title compound is shown in Figs. 1 and 2 and theoretically constructed FT-IR and FT-Raman spectra by DFT method are shown in Figs. 3 and 4. The UV spectrum was measured in the ethanol solution in the region 200–400 nm as shown in Fig. 5. The spectral measurements were carried out at Central Electro Chemical Research Institute (CECRI), Karaikudi, Tamil Nadu.

3. Computational details

DFT and MP2 calculations were performed using GAUSSIAN 03W [19] program package on a personal computer without any constraint on the geometry [20]. Geometries of the model 3-AP and 3,4-DAP, have been first optimized with full relaxation on the potential energy surfaces at HF/6-311++G(d,p) and the resultant geometries have been used as inputs for further calculations at DFT and MP2 level. Polarization functions have been added for the better treatment of the amino groups. The optimized structural parameters were used in the harmonic vibrational wavenumber calculations at DFT and MP2 level to characterize all stationary points as minima. We have utilized MP2 and DFT/B3LYP/6-311++G(d,p) approach for the computation of molecular structure, harmonic vibrational wavenumbers and energies of optimized structures, in the present work. Anharmonic calculations (B3LYP) have been performed using the vibrational self-consistent field (VSCF) method which computes the vibrational wavenumbers including anharmonic effects. This type of calculation requires input from a previous harmonic vibrational calculation. The wavenumbers obtained from the second order perturbation theory (PT2) have been used in this investigation. By the use of GAUSSVIEW program [21] with symmetry considerations along with available related molecules, vibrational wavenumber assignments were made with a high degree of accuracy.

3.1. Prediction of Raman intensities

The Raman scattering activities (S_i) calculated with Gaussian 03 program converted to relative Raman intensities (I_i) using the following relationship derived from the intensity theory of Raman scattering [22,23]:

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i[1 - \exp(-hc\nu_i/kt)]}$$

where ν_o is the exciting wavenumber in cm^{-1}, ν_i the vibrational wave number of the ith normal mode, h, c and k fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities. For simulation of calculated FT-Raman spectra have been plotted using pure Lorentizian band shape with a bandwidth of (FWHM, full width and half maximum) of 10 cm^{-1} as shown in Fig. 4.

4. Results and discussion

On the basis of C_s symmetry the 39 fundamental vibrations of 3,4-DAP can be distributed as 27A′ + 12A″. The vibration of the A′ species are stretching and in-plane bending and those of the A″ species are out-of-plane bending. If we take in to account C_s symmetry of this molecule, there is one imaginary wavenumber corresponds to NH_2 wagging perpendicular to the ring plane. The structure at any level was not a minimum energy structure. One possessed imaginary wavenumbers of irreducible representation belong to A″. But if the