Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 124 (2014) 277–284

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Thermal and magnetic properties and vibrational analysis of 4-(dimethylamino) pyridine: A quantum chemical approach

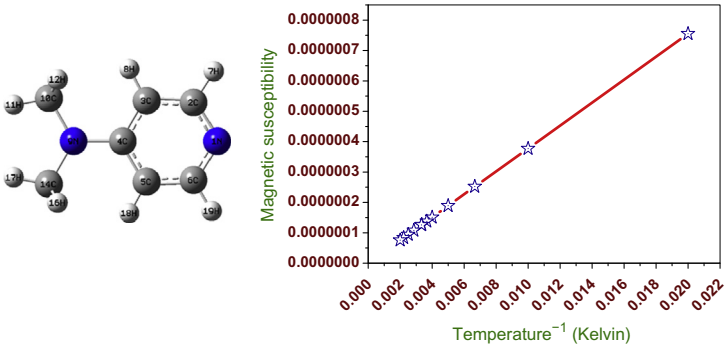
V. Balachandran [a,*], S. Rajeswari [b], S. Lalitha [b]

[a] Centre for Research, Department of Physics, A A. Government Arts College, Musiri 621 211, India
[b] P.G. & Research Department of Physics, Periyar EVR College(Autonomous), Tiruchirappalli 620 023, India

HIGHLIGHTS

- The FT-IR and FT-Raman spectra of 4-(dimethylamino) pyridine were recorded and analyzed.
- The complete vibrational assignments and spectroscopic analysis were made.
- The HOMO, LUMO energy gap were theoretically predicted.
- Temperature dependence thermodynamic parameters and magnetic properties have been analyzed.
- The magnetic susceptibility for various temperatures are predicted.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 16 November 2013
Received in revised form 9 December 2013
Accepted 10 January 2014
Available online 18 January 2014

Keywords:
4DMAP
HOMO–LUMO
Vibrational spectra
NBO
FT-IR
FT-Raman

ABSTRACT

The FT-IR and FT-Raman spectra of 4-(dimethylamino) pyridine (4DMAP) have been recorded in the region 4000–500 $cm^{-1}$and 3500–100 cm^{-1}. Quantum chemical calculations of energy, geometry and vibrational wavenumbers of 4DMAP were carried out by using ab initio HF and density functional theory (DFT/B3LYP) with complete relaxation in the potential energy surface using 6-311++G(d,p) basis set. The harmonic vibrational wavenumbers were calculated and the scaled wavenumbers have been compared with the experimental FT-IR and FT-Raman spectra. The quantum chemical parameters have been computed from the HOMO–LUMO energy values. Temperature dependence thermodynamic parameters and magnetic properties of the title compound have been analyzed. Using NBO analysis the stability of the molecule arising from hyper-conjugative interactions, charge delocalization has been analyzed. The first-order hyper-polarizability (β) values of the title molecule were computed by B3LYP method. Finally the theoretically spectrograms for FT-IR and FT-Raman spectra of the title molecule have been constructed which show good agreement with recorded spectra.

Introduction

Pyridine, also called azobenzene and amine, is a heterocyclic aromatic tertiary arnine characterized by a six-member ring structure composed of five carbon atoms and one carbon–hydrogen unit in the benzene ring being replaced by a nitrogen atom. The simplest member of the pyridine family is pyridine itself. It is colorless, flammable, toxic liquid with an unpleasant odor, miscible with water and with most organic solvents, boils at 115 °C. It is made from crude coal tar or from other chemicals based on acetaldehyde and ammonia. Aminopyridines are obtained from pyridine, when an amino group is replaced a hydrogen attached to the ring. Aminopyridines find wide application in pharmacological industry and in analytical chemical laboratories. They serve as good anesthetic agent and hence used in the preparation of drugs for certain brain disease, particularly 4-aminopyridines is an effective medicine in the treatment for multiple sclerosis [1]. The 3,4-diaminopyridine

* Corresponding author. Tel.: +91 431 2591338; fax: +91 4326 262630.
E-mail address: brsbala@rediffmail.com (V. Balachandran).

1386-1425/$ - see front matter Crown Copyright © 2014 Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.saa.2014.01.023

plays an effective role in the symptomatic treatment of multiple sclerosis fatigue like 4-aminopyridine [2]. Pyridine derivatives are used as non-linear materials [3]. Many substituted pyridines are involved in bioactivities with applications in pharmaceutical drugs and agricultural products [4–6]. Pyridine derivatives act as anesthetic agents, drugs for certain brain diseases, and prodrugs for treating neuronal damage caused by stroke. The picoline derivatives prepared from aminopyridine derivatives have been shown to have cholesterol lowering properties, anti-cancer and anti-inflammatory agents [4]. The various studies on monosubstituted halo and methylpyridines [7], 2-iodopyridine [8], 2,6-dichloropyridine [9], di-, tri-halopyridines [10,11], 5-bromo-2-nitropyridine [12], 2-chloro-5-bromopyridine [13], 2-fluoro-5-bromopyridine [14] and 2-chloro-6-methoxypyridine [15] were reported. FT-IR and FT-Raman spectra and ab initio DFT vibrational analysis of 2-chloro-5-aminopyridine was reported by Sundaraganesan et al. [16]. The FT-Raman and infrared spectra of 2-hydroxy-4-methyl-3-nitropyridine and 2-hydroxy-4methyl-5-nitropyrdine were reported by Balachandran et al. [17]. Arjunan et al. [18] discussed a comparative study on vibrational, conformational and electronic structure of 2-(hydroxymethyl) pyridine and 3-(hydroxymethyl) pyridine.

Literature survey reveals that to the best of our knowledge, no ab initio HF and DFT method of the vibrational analysis of 4DMAP have been reported so far. Therefore, the present investigation is undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wavenumber accuracy. Ab initio HF and density functional theory (DFT) calculations have been performed to support our wavenumber assignments. The redistribution of electron density (ED) in various bonding and antibonding orbital and energies have been calculated by natural bond orbital (NBO) analysis by DFT method to give clear evidence of stabilization originating from the hyperconjugation of various intra-molecular interactions. The HOMO and LUMO analysis have been used to elucidate information regarding charge transfer within the molecule.

Experimental details

The crystalline sample of 4DMAP is purchased from Sigma Aldrich Chemical Suppliers with the stated purity of 98%. Then the compound is used for spectral measurements without further purification. In the present study, the Fourier transform infrared spectrum (FT-IR) of the title compound is recorded in the wavenumber region 4000–400 cm^{-1} on a NEXUS 670 spectrophotometer equipped with an MCT detector in a KBr pellet technique. The FT-Raman spectrum is recorded in the wavenumber region 3500–100 cm^{-1} on a NEXUS 670 spectrophotometer equipped with Raman module accessory operating at 1.5 W power with Nd:YAG laser of wavelength 1064 nm is used as an excitation source. The spectral measurements were carried out at Sree Chitra Tirunal Institute for Medical Sciences and Technology, Poojappura, Thiruvanathapuram, Kerala, India.

Computational details

The entire calculation was performed at the HF and DFT level of theory using the 6-311++G(d,p) basis set on personal computer using Gaussian 09W [19] program package, invoking gradient geometry optimization [20]. Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at Hartree–Fock level, adopting the standard 6-311++G(d,p) basis set. The optimized structural parameters were used in the vibrational frequency calculations at the HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of 4DMAP were used for harmonic vibrational frequency calculations, IR and Raman intensities and Raman depolarization ratios. We have utilized the gradient corrected density functional theory (DFT) [21] with the three-parameter hybrid functional (B3) [22] for the exchange part and the Lee–Yang–Parr (LYP) correlation function [23], accepted as a cost-effective approach, for the computation of molecular structure, vibrational wavenumbers and energies of optimized structures. Vibrational wavenumbers computed at DFT level have been adjusted to be more reliable than those obtained by HF method. Finally, the calculated normal mode vibrational wavenumbers provide thermodynamic properties also through the principle of statistical mechanics.

By combining the result of the GAUSSVIEW program [24] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. The natural bonding orbitals (NBO) calculation [25] were performed using NBO 3.1 program as implemented in Gaussian 09W [19] package at B3LYP/6-31++G(d,p) level in order to understand various second-order interactions between the filled orbitals of one subsystem and vacant of another subsystem, which is a measure of the intermolecular delocalization or hyper-conjugation.

Prediction of Raman intensities

The Raman activities (S_i) calculated by the Gaussian 09W program were converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [26–28].

$$I_i = \frac{f(\upsilon_0 - \upsilon_i)^4 S_i}{\upsilon_i[1 - \exp(-hc\upsilon_i/kT)]} \quad (1)$$

where υ_0 is the exciting frequency in cm^{-1}, υ_i the vibrational wave number of the ith normal mode, h, c and k are the universal constants and f is the suitably chosen common scaling factor for all the peak intensities.

Potential energy distribution

To check whether the chosen set of symmetric coordinates contribute maximum to the potential energy associated with the molecule, the PED has been carried out. The vibrational problem was set up in terms of internal and symmetry coordinates. The Cartesian representation of the theoretical force constants has been computed at the fully optimized geometry by assuming Cs point group symmetry. The symmetry of the molecule was also helpful in making vibrational arrangement. The transformation of force field, subsequent normal coordinate analysis and calculation of the PED were done on PC with the MOLVIB program (versionV7.0–G77) written by Sundius [29,30].

First-order hyper-polarizability

The first hyper-polarizability (β_0) of this novel molecular system and related properties (β, α_0 and $\Delta\alpha$) of 4DMAP are calculated using HF/6-311++G(d,p) and DFT/6-311++G(d,p) method based on the finite-field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. First hyper-polarizability is a third rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry [31]. It can be given in the lower tetrahedral format. It is obvious that the lower part of the $3 \times 3 \times 3$ matrices is a tetrahedral. The components of β are defined as the coefficients in the Taylor series