



Barrier potentials, molecular structure, force field calculations and quantum chemical studies of some bipyridine di-carboxylic acids using the experimental and theoretical using (DFT, IVP) approach

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ABSTRACT

FT-IR and FT-Raman spectra of 2,2'-bipyridine-3,3'-dicarboxylic acid (B3DA), 2,2'-bipyridine-4,4'-dicarboxylic acid (B4DA) and 2,2'-bipyridine-5,5'-dicarboxylic acid (B5DA) were recorded and analysed. The quantum chemical calculations of the title compounds begin with barrier potentials at different rotation angles around the C-C' and C-Ca bonds in order to arrive conformation of lowest energy using DFT employing B3LYP functional with 6-311++G(d,p) basis set. This confirmation was further optimised to get the global minimum geometry. The vibrational frequencies along with IR, Raman intensities were computed, the rms error between observed and calculated frequencies were 11.2 cm⁻¹, 10.2 cm⁻¹ and 12.2 cm⁻¹ for B3DA, B4DA, and B5DA. An 87-element modified valence force field is derived by solving the inverse vibrational problem using Wilson's GF matrix method. This force field is refined using 163 observed fundamentals employing in overlay least-squares technique. The average error between computed and experimental frequencies was found as 12.85 cm⁻¹ using potential energy distribution (PED) and eigenvectors. By using the gauge-independent atomic orbital (GIAO) method calculate the ¹H and ¹³C NMR chemical shifts of the molecules and compared with experimental results. The first-order hyperpolarisability, HOMO and LUMO energies, molecular electrostatic potential (MESP) and natural orbital analysis (NBO) of titled compounds were evaluated using DFT.

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1. Introduction

In recent years, the chelate ligands of the type N-N have captured chemists notice due to the adaptability of its applications. This is true in the area of supramolecular chemistry, crystal engineering and coordination chemistry, where these are often used as blocking ligands and the study of their metallic derivatives in the solid state have revealed the tremendous importance of advanced reactivity and non-covalent interactions of these species [1,2]. Nitrogen-containing pyridine carboxylic acids as one kind of great bridging ligands can bind transition metal ions to build coordinate polymers. 2,2'-bipyridine and its derivatives can form complexes with many different metals, especially those having d³, d⁶, d⁸ or d¹⁰ electron configurations [3]. The title species exhibits a plethora of interesting photo physical and redox properties due to a strong σ -donating chelate coupled with its π acid nature allows the polypyridyl unit to stabilise transition metals in a wide range of oxidation states [4]. Bipyridyl derivatives being used in optoelectronic devices aimed at light harvesting and energy storage due to the chromophoric nature of these species [5-7]. These are typical examples of multidentate ligands. The nitrogen atom of bipyridyl moiety and the oxygen atom of dicarboxyl functional group can act not only as hydrogen bond donor but also as an acceptor in this molecule, which makes it a wonderful candidate for the construction of supra

molecular networks [8]. They also are suitable ligands for the formation of 1D, 2D and 3D network structures [9]. For cisplatin derivatives, bidentate carboxylate ligands have given to resistance to hydrolysis and high aquatic solubility. Moreover, it has also been proved that an appropriate attachment of the carboxylic acid group in coordination complexes could modulate the solubility of the complex, cell transport, anticancer and antioxidant activity [10,11]. 2,2'-bipyridyl and dicarboxyl functional groups exhibits bis(monodentate) [12], tridentate [13] bis(bidentate) [14], pentadentate or even hexadentate [15] bridge-connector, which can facilitate and direct the formation of metal-organic frameworks. The crystal structure of 2,2'-bipyridine-5,5'-dicarboxylic acid (B5DA) was reported by Chongchen Wang [16] by investigating the intermolecular hydrogen bonds.

Keeping in the view of review of the literature on the chosen molecules, it can be found that the complete analysis of vibrational spectra in the region 4000-50 cm⁻¹, vibrational properties and molecular characteristics of these molecules are not yet reported so far.

The purpose of this investigation is to

- (i) record FTIR and Raman spectrum of the titled molecules in order to get complete information on their vibrational frequencies,