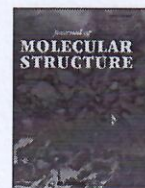




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Investigation of torsional potentials, hindered rotation, molecular structure and vibrational properties of some biphenyl carboxaldehydes using spectroscopic techniques and density functional formalism

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ABSTRACT

Fourier Transform infrared spectra and Fourier Transform Raman spectra, of biphenyl-4-carboxaldehyde (B4A), biphenyl-3-carboxaldehyde (B3A), and biphenyl-2-carboxaldehyde (B2A), were recorded in the spectral range 4000–450 cm⁻¹ and 4000–50 cm⁻¹, respectively. ¹H NMR and ¹³C NMR spectra of the three samples were also measured. Quantum chemical calculations were performed using density functional theory (DFT) and B3LYP functional in conjunction with 6–311++G(d,p) basis set in order to determine torsional potentials, barrier to hindered rotation around C–C inter-ring bond and C–C_α aromatic-carbonyl bond, optimized structure parameters, general valence force field, harmonic vibrational frequencies, potential energy distribution (PED) and infrared and Raman intensities. Its time-dependent variant (TD-DFT) was used to simulate ¹H NMR and ¹³C NMR spectra of the three molecules under investigation. Observed and calculated frequencies agreed with an rms error 11.4, 10.4, and 11.4 cm⁻¹ for B4A, B3A, and B2A, respectively. Further, measured infrared and Raman spectra agreed with their computed counterparts with fair degree of accuracy. Unambiguous vibrational assignments were made for all fundamentals using PED and eigenvectors. Experimental chemical shifts agree well with their theoretical counterparts. Geometry optimization was made for dimers of the three molecules at the same level of theory as employed for the monomers. Existence of intra-molecular and inter-molecular hydrogen bonds was predicted.

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1. Introduction

Derivatives of biphenyl attracted the attention of several researchers for good reasons. The biphenyl (BP) moiety is a constituent of ever growing number of known biologically active natural products, such as michellamine, steganon and Vancomycin [1,2]. In the synthesis of most prominent chiral ligands such as BINAP [3] and MeO-BIPHEP [4], by means of asymmetric synthesis [5] the stereogenic axes of biaryl system provides rigid molecular frameworks that makes the process highly efficient. In the field of liquid-crystals the derivatives of BP have found commercial applications [6]. In pharmaceutical research compounds containing biphenyl unit are preferred due to its privileged structure that guarantees

versatility and high success rates [7]. For example, this aromatic unit plays a pivotal role in the sartan family of drugs used for treating high blood pressure: valsartan from Novartis (Diovan), Candesartan from Astra (Atacand), losartan from Merck, Sharpe and Dhome (cozaar, Lorzaar), and irbesartan from Bristol-Myers squibb (Aprovel) [8]. Some substituted biphenyls, such as polychlorinated biphenyls (PCBs) and polybrominated biphenyls (PBBs) are useful as plasticizers and industrial flame retardants [9]. PCBs and PBBs are also known for their toxic properties [10–13]. Biphenyl derivatives are interesting from structural point of view also. The torsional angle, barrier to internal rotation, and resulting conformer depend critically on the balance of two competing interactions: the delocalization of π-electrons (i.e. π–electron conjugation) between the two phenyl rings favours a coplanar structure, whereas the repulsion between atoms in ortho position favours a non-coplanar structure. Hence, experimental and

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