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SPECTRAL ANALYSIS OF ACETYLCHOLINE HALIDES BY DENSITY FUNCTIONAL THEORY CALCULATIONS

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The optimized molecular structures, vibrational frequencies and ^1H and ^{13}C NMR chemical shifts of acetylcholine halides (F, Cl and Br) have been investigated using density functional theory (B3LYP) method with 6-311G(d) basis set. The comparison of their experimental and calculated IR, R and NMR spectra of the compounds has indicated that the spectra of three optimized minimum energy conformers can simultaneously exist in one experimental spectrum. Thus, it was concluded that the compounds simultaneously exist in three conformations in the ground state. The calculated optimized geometric parameters (bond lengths and bond angles), vibrational frequencies and NMR chemical shifts for the minimum energy conformers were seen to be in a good agreement with the corresponding experimental data. All the assignments of the theoretical frequencies were performed by potential energy distributions using VEDA 4 program.

Keywords: acetylcholine halide, vibration, DFT, IR, Raman, NMR.

INTRODUCTION

Acetylcholine [$\text{CH}_3\text{COOCH}_2\text{CH}_2\text{N}^+(\text{CH}_3)_3$] plays a central role in neurotransmission. Within the last decades, choline and acetylcholine derivatives attract many research teams to analyze their vibrational frequencies using various computational levels, including medium and/or large basis sets because of the molecular complexity, the computational costs or hardware performance [1–3]. The determination of the minimum energy conformers on the potential energy hypersurface of acetylcholine has been subject by many theoretical works.

These studies have showed that low energy conformations appear corresponding to the orientation of the acetoxy group with respect to the rest of the molecule. The different minima on the hypersurface have been related to the muscarinic and nicotinic activity of acetylcholine [4]. Marino and et al. have investigated the conformational behavior and molecular motion of acetylcholine *in vacuo* and aqueous solution [5]. They have calculated five low lying conformations by molecular mechanics computing. The *ab initio* data of acetylcholine have indicated that the most stable conformation is the *trans-gauche* arrangement of the two essential torsion angles (τ_1 ; C—C—O—C and τ_2 ; N—C—C—O) [6, 7]. The observed conformation of acetylcholine is *trans-gauche* ($\tau_1 = -166.9$ and $\tau_2 = 84.7^\circ$) in the crystal of its chloride, [8, 9] *gauche-gauche* ($\tau_1 = 78.9$ and $\tau_2 = 78.4^\circ$) in the crystal of its bromide [10] and *gauche-gauche* ($\tau_1 = \pm 83$ and $\tau_2 = \pm 89^\circ$) in the crystal of its iodide [11]. Theoretical study of acetylcholine bromide has denoted that the experimental *gauche-gauche* conformation corresponds only to a local energy minimum about $2 \text{ kcal}\cdot\text{mol}^{-1}$ above the global one associated with a different *gauche-gauche* conformation [12].