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Synthesis, crystal and molecular structure, and characterization of 2-((2-aminopyridin-3-yl)methylene)-*N*-ethylhydrazinecarbothioamide using spectroscopic (^{1}H and ^{13}C NMR, FT-IR, FT-Raman, UV–Vis) and DFT methods and evaluation of its anticancer activity

K. Ramaiah [a], K. Srishailam [b], K. Laxma Reddy [a, *], B. Venkatram Reddy [c], G. Ramana Rao [c]

[a] Department of Chemistry, National Institute of Technology, Warangal, 506004, Telangana, India
[b] Department of Physics, S R Engineering College (Autonomous), Warangal, 506371, Telangana, India
[c] Department of Physics, Kakatiya University, Warangal, 506009, Telangana, India

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ABSTRACT

2-((2-aminopyridin-3-yl)methylene)-*N*-ethylhydrazinecarbothioamide was synthesized. It was characterized by making elemental analysis, assisted by experimental ^{1}H NMR, ^{13}C NMR, FT- Raman (4000-50 cm^{-1}), FT-IR (4000-400 cm^{-1}), and UV–Vis (200–400 nm) spectra and evaluating its anticancer activity, for human carcinoma cell lines HeLa (cervical), IMR-32 (neuroblastoma) and A549 (lung). Crystal and molecular structure of the molecule was determined by means of X-ray diffractometry, which showed that it belongs to triclinic crystal system, with space group P-1, having two molecules per unit cell (Z = 2). The parameters of the unit cell are a = 6.0960 (6) Å, b = 7.4119 (8) Å, c = 11.9959 (13) Å, α = 82.1695 (4)°, β = 81.6407 (4)°, γ = 88.3283 (4)° at 100 K. Quantum chemical computations were made using density functional theory (DFT), B3LYP functional and 6–311++G (d,p) basis set in order to determine optimized structure parameters, general valence force field, harmonic vibrational frequencies, potential energy distribution, infrared and Raman intensities, NLO properties, frontier molecular orbital parameters and NBO characteristics. Its time-dependent variant (TD-DFT) was used to calculate the oscillator strengths and absorption maxima (λ_{max}) in DMSO-d_6 as a solvent, of various electronic transitions. There was a good agreement between the theoretical and experimental parameters such as molecular structure parameters, IR, Raman and UV–Vis spectra. The rms error between measured and estimated vibrational frequencies was 6.9 cm^{-1}. The calculations showed that the molecule under investigation was good for NLO applications, which was supported by NBO analysis.

1. Introduction

Investigation of heterocyclic thiosemicarbazones gained importance because of their biological activity [1]. Numerous derivatives of thiosemicarbazones are known for their antifungal [2], antitumor [3], antibacterial [4,5], anti-inflammatory [6], antituberculosis [7–9], analgesic [10–12], anticonvulsant [13–15] and HIV-TB co-infection [16] activities. Let us touch upon atleast some of these biological activities in brief. It was demonstrated that thiosemicarbazone derivative of 2-formylpyridine exhibited mild antileukemic activity against I-1210 tumor in mice [17], which was first reported in 1956 [18]. The side chain adjacent to the heterocyclic nitrogen and conjugated NNS tridentate ligand system of thiosemicarbazone is responsible for anticancer activity, which was proved by an investigation of formyl thiosemicarbazones containing various heterocyclic systems [19]. It was identified that metal complexes of thiosemicarbazones possess antifungal activity, which depends on the substituent group at N (1) and N (4) positions of the thiosemicarbazones [20]. This stimulated extensive studies on 2-formylpyridine, 2-benzopyridine and 2-acetylpyridine N (4)–substituted thiosemicarbazones [21–23]. Antimicrobial effect of thiosemicarbazones against some plant pathogenic and saprophylic fungi was reported [24]. The first demonstration of antiviral effect of thiosemicarbazones appeared in 1992, by showing that *p*-aminobenzaldehyde-3-thiosemicarbazone,

* Corresponding author.
E-mail address: laxmareddychem12@gmail.com (K. Laxma Reddy).

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