



# DFT simulation of barrier heights, infrared and Raman spectra, and investigation of vibrational characteristics of 2-((2-aminopyridin-3-yl) methylene) hydrazinecarbothioamide and its *N*-methyl variant<sup>1</sup>

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## ABSTRACT

Fourier transform infrared spectra, for 2-((2-aminopyridin-3-yl) methylene) hydrazinecarbothioamide (APHT) and 2-((2-aminopyridin-3-yl) methylene)-*N*-methylhydrazinecarbothioamide (APMHT), were recorded in the spectral range 4000–400 cm<sup>-1</sup>. Their Raman counterparts were measured in the spectral region 4000–50 cm<sup>-1</sup>. Preliminary values of dihedral angles around five rotating bonds C–NH<sub>2</sub> pyridyl C–CN, N–N, N–CS and C–NH<sub>2</sub> aliphatic in APHT, required for initiating geometry optimization, were obtained by pairing successive bonds and evaluating torsional potential energy for various values of dihedral angle around these bonds in the entire conformational space spanning 0° to 360°. Barrier heights, around five rotating bonds in APHT and six rotating bonds in APMHT were computed, making torsional scans in conformational space from 0° to 360°. This indicated existence of two rotational isomers for APMHT. General valence force field, harmonic vibrational fundamentals, potential energy distribution (PED), along with infrared and Raman intensities were determined using DFT/B3LYP/6-311++G(d,p) level of theory for both the molecules. Good agreement was found between measured and simulated spectra, for APHT and APMHT. This was also true for corresponding Raman spectra. The rms error between experimental and theoretical vibrational frequencies was 9.00 and 6.70 cm<sup>-1</sup>, for APHT and APMHT, respectively. All vibrational fundamentals were assigned unambiguously, on the basis of computed PED, eigenvectors, and literature range for the first time. These assignments were further supported by comparing with attribution of corresponding bonds in the parent molecule pyridine and a related molecule 2-((2-aminopyridin-3-yl)methylene)-*N*-ethylhydrazinecarbothioamide, wherever possible.

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## 1. Introduction

It is well known, that heterocyclic thiosemicarbazones, exhibit analgesic [1–3], anti-inflammatory [4], antitumour [5], anti-oncuvulsant [6–8], antituberculosis [9–11], antibacterial [12,13], antifungal [14] and HIV-TB co-infection [15], activities, which indicates that they have biological importance [16]. This motivated us to synthesize and investigate, structural, electronic and vibrational properties of some derivatives of thiosemicarbazones along with their anticancer activity, using both experimental and theoretical considerations [17]. Very recently we reported some such results, for 2-((2-aminopyridin-3-yl) methylene) hydrazinecarbothioamide (APHT) and 2-((2-aminopyridin-3-yl) methylene)-*N*-methylhydrazinecarbothioamide (APMHT) [18]. It is to be mentioned here that the initial values of dihedral angles around five flexible bonds in APHT (C–NH<sub>2</sub> pyridyl, C–CN, N–N, N–CS, C–NH<sub>2</sub> aliphatic) were determined by confining the torsional potential energy scans to the first half of the conformational space from 0° to 180° (see [18]). This amounts to an implicit assumption that the molecule would exhibit identical behaviour in the second half of the conformational space (from

180° to 360°) as in the first half of the same space. This expectation need not be true. This deficiency in our earlier work [18] has to be addressed by extending the torsional scans to the second half of the conformational space. We undertook this exercise now. Further, barrier to internal rotation, around five rotating bonds of APHT and six flexible bonds in APMHT, alongwith their vibrational properties remained unreported. This article contains such results.

## 2. Experimental details

Both APHT and APMHT as synthesized by us, are solids at room temperature [18,19]. Hence, their FT-IR spectra were measured by diluting each of them in KBr pellet, employing Perkin-Elmer 100S spectrophotometer in the spectral range 4000–400cm<sup>-1</sup>. The instrument was equipped with deuterated triglycine sulphate (DTGS) detector, having liquid nitrogen cooling system. Spectrum of each sample was obtained by co-adding 32 scans. FT Raman spectra of the two samples were recorded, in the 4000–50 cm<sup>-1</sup> stokes region on BRUKER RF27 model interferometer accessory, by co-adding 256

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