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Theoretical and experimental comparative study of a derivative from 2-pyridinecarboxaldehyde which exhibits configurational dynamics

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ABSTRACT

The (E)-4-nitro-N′-(pyridine-2-ylmethylene)benzohydrazide, a derivative from 2-pyridinecarboxaldehyde, displays E/Z isomerization induced by ultraviolet radiation in which the process of photoisomerization was evidenced and followed by 1D ^{1}H NMR. The structure of the compound was determined by FT-IR and NMR techniques and confirmed by single-crystal X-ray diffraction. The results in terms of bond angle and length, chemical shift (^{13}C and ^{1}H) and vibrational frequencies obtained experimentally were compared to computed values at two levels of theory (Restricted Hartree–Fock and Density Functional Theory) using different basis set. The understanding of spectroscopy and dynamic properties of these type of compounds is of importance in view of their potential use in molecular machines and electronic devices.

1. Introduction

Acyl-hydrazones exhibit a large number of applications, among them, we can highlight the information storage. This functional group presents a weak double bond that is able to allow constitutional changes, through substituents interchange [1] establishing itself as a long term information storage strategy. Furthermore, acyl-hydrazones presents dynamical responses to diverse types of stimulus, both chemical (pH and conformational changes induced by metallic ions) and physical (pressure, heat and radiation) [2–5].

From a wide variety of possible stimuli, probably the most feasible is the luminous radiation (especially in UV spectral region) since the energy investment is lower compared to heat or pressure application and it has a higher practical applicability, interruption of stimulus once the system has reached the expected response using changes in the pH solution or the addition of metallic ions, is one of them and systems showing this on/off behavior are commonly known as molecular switches. Herein we present the synthesis, photochemistry and spectroscopy comparison to theoretical calculations of an acyl-hydrazone derivative from 2-pyridinecarboxaldehyde capable of responding to UV radiation through a process of reversible E/Z photoisomerization where the product is stabilized by an intramolecular hydrogen bond.

2. Experimental and computational methods

The starting materials were purchased from Sigma–Aldrich and Alfa Aesar, they were used without any further purification. ^{1}H and ^{13}C NMR spectra were taken in a 400 MHz Bruker Ultra Shield spectrometer and the FT-IR spectra were recorded on a Shimadzu FTIR-8400 instrument.

2.1. Synthesis A-1

An equivalent of 2-pyridinecarboxaldehyde was added to an ethanol solution (7 mL) of 4-nitrobenzohydrazide (1eq) and a trace amount of glacial acetic acid. This mixture was heated under reflux for 3 h, the appearance of precipitate was observed after the first 10 min of reaction. The white solid was filtered and recrystallized

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from ethanol (96% yield). M. p.: 227–228 °C. FT-IR (ν/cm-1): 3221 (N–H), 1659 (C=O), 1595(C=N). ^{1}H NMR (400 MHz, DMSO-d_6), δ/ppm: 12.31 (s, 1 H), 8.64 (d, J = 4.29 Hz, 1 H), 8.49 (s, 1 H), 8.39 (d, J = 8.59 Hz, 2 H), 8.17 (d, J = 8.59 Hz, 2 H), 8.01 (d, J = 7.80 Hz, 1 H) 7.94–7.87 (m, 1 H) 7.47–7.42 (m, 1 H). ^{13}C NMR (100.60 MHz, DMSO-d_6), δ/ppm: 161.76, 152.96, 149.59, 149.38, 149.12, 138.80, 136.95, 129.26, 124.65, 123.69, 120.08. Elemental analysis calculated. (%) for $C_{13}H_{10}N_4O_3$: C, 57.78; H, 3.73; N, 20.73; found: C, 57.86; H, 3.72; N, 20.62.

2.2. Photoisomerization of (E)-4-nitro-N'-(pyridine-2-ylmethylene) benzohydrazide

A solution of *A-1* (in DMSO-d_6), in a NMR Quartz tube was placed 20 cm from a mercury-vapor lamp and was irradiated. Spectra were taken every 10 min starting from zero up to 90 min.

2.3. Crystallography

Single crystal X-Ray diffraction data were collected at Bruker

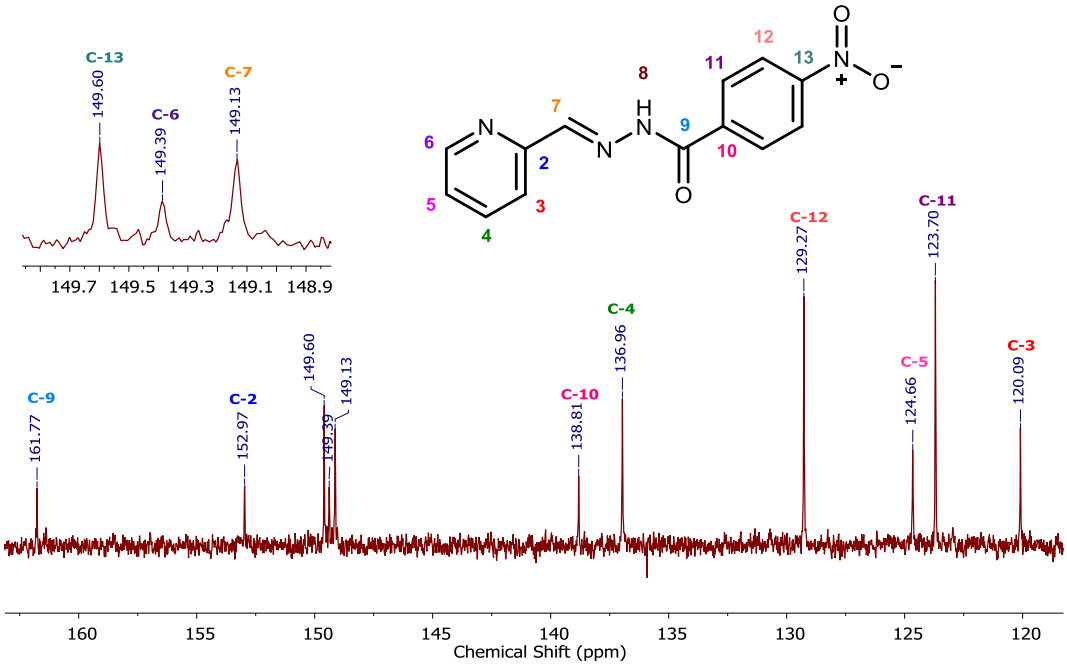

Fig. 1. ^{13}C NMR signals assignments of *A-1*.

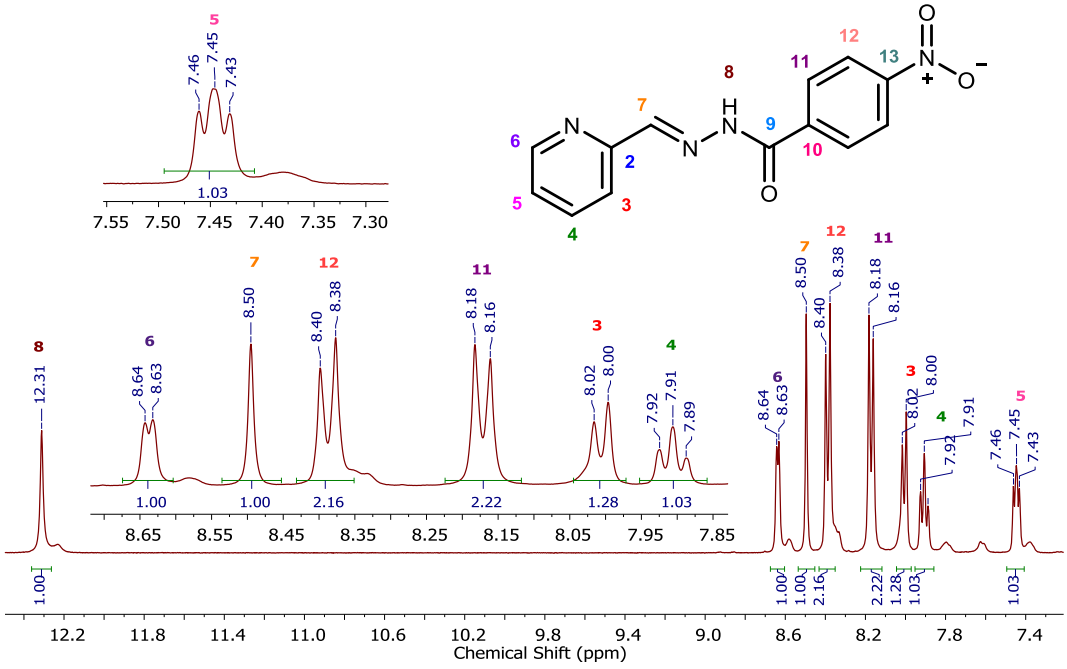

Fig. 2. ^{1}H NMR signals assignments of *A-1*.