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Synthesis and spectral characterization of hydrazone derivative of furfural using experimental and DFT methods

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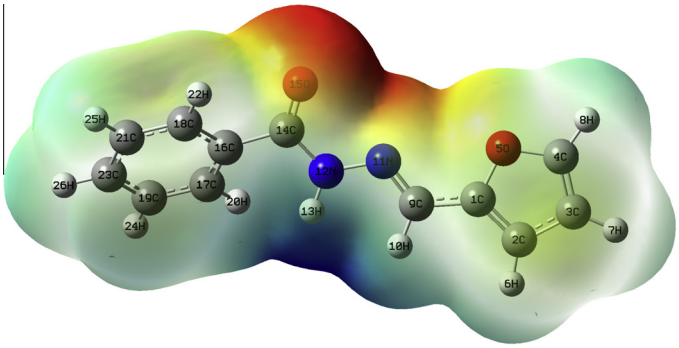
HIGHLIGHTS

- Total energy distribution analysis.
- Natural bond orbital analysis.
- Non-linear optical behavior hydrazone derivatives.
- Band gap energy.
- Molecular electrostatic potential.

GRAPHICAL ABSTRACT



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ABSTRACT

The Spectral Characterization of *(E)-1-(Furan-2-yl) methylene)-2-(1-phenylvinyl) hydrazine* (FMPVH) were carried out by using FT-IR, FT-Raman and UV–Vis., Spectrometry. The B3LYP/6-311++G(d, p) level of optimization has been performed on the title compound. The conformational analysis was performed for this molecule, in which the *cis* and *trans* conformers were studied for spectral characterization. The recorded spectral results were compared with calculated results. The optimized bond parameters of FMPVH molecule was compared with X-ray diffraction data of related molecule. To study the intra-molecular charge transfers within the molecule the Lewis (bonding) and Non-Lewis (anti-bonding) structural calculation was performed. The Non-linear optical behavior of the title compound was measured using first order hyperpolarizability calculation. The atomic charges were calculated and analyzed.

Introduction

The hydrazones in the organic molecule brings several physical and chemical properties. Hydrazones are bearing the >C═N—N< leads the molecule towards nucleophilic and electrophilic nature. In hydrazone moiety the nitrogen atom behaves as nucleophilic and carbon atom behaves as nucleophilic as well as electrophilic nature [1–3]. The ability of hydrazones to react with both electrophilic and nucleophilic reagents widens their application in organic chemistry and designing the new drugs [1,4,5]. Several hydrazone derivatives have been reported as insecticides, nematocides, herbicides, rodenticides and antituburculosis in addition to that some of the hydrazone were found to be active against leukemia, sarcoma and illnesses [5,6]. Two types of photochemical reactions such as

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nitrogen–nitrogen bond cleavage and hydrogen migration from nitrogen to carbon were described for hydrazone [7,8]. The hydrazones were also shown to be involved in bio-molecular reactions such as cycloadditions and condensations [1,4]. In hydrazone containing C=N—N moiety, reveals existence of structural isomerism (E-entgegen 180° and Z-zusammen 0°), in which *E* conformer is most stable than *Z* conformer [9]. In the present investigations our main focus is to study the geometry of the molecule, vibrational behavior, non-linear optical activity and intra-molecular charge transfer analysis. For this we recorded FT-IR, FT-Raman and UV–Vis., spectra and also performed suitable theoretical calculation using B3LYP/6-311++G (d,p) level of basis set.

Experimental details

Synthesis

The 2.1 ml (0.025 mol) ethanolic solution of furan-2-aldehyde was added to (0.025 mol), 3.4 g of aqeous solution benzohydrazide taken in a R.B flask. The reaction mixture was kept over a magnetic stirrer and stirred well in an ice cold condition for an hour. The colorless solid separated out was filtered and dried over vacuum.

FT-IR, FT-Raman and UV–Vis., spectra

The FT-IR spectrum of FMPVH was recorded in the region 400–4000 cm^{-1} on an IFS 66 V spectrophotometer using the KBr pellet technique. The spectrum was recorded at room temperature with a scanning speed of 10 cm^{-1} per minute and at the spectral resolution of 2.0 cm^{-1} in SAIF Laboratory, IIT madras, Tamilnadu, India. The FT-Raman spectrum of title compound was recorded using the 1064 nm line of a Nd:YAG laser as excitation wavelength in the region 50–3500 cm^{-1} on Bruker model IFS 66 V spectrophotometer equipped with an FRA 106 FT-Raman module accessory and at spectral resolution of 4 cm^{-1}. The FT-Raman spectral measurements were carried out from SAIF Laboratory, IIT Madras, Tamilnadu, India. The ultraviolet absorption spectrum of FMPVH was recorded in the range of 200–500 nm using a Perkin Elmer Lambda-35 spectrometer, UV pattern is taken from a 10^{-5} molar solution of FMPVH dissolved in methanol.

Computational details

In order to establish the stable possible conformations, the conformational space of FMPVH compound was scanned with molecular mechanic simulations. For meeting the requirements of both accuracy and computing economy, theoretical methods and basis sets were considered. Density Functional Theory (DFT) has been proved to be extremely useful in treating electronic structure of molecules. The entire calculations were performed at B3LYP/6-311++G(d,p) level of basis set using Gaussian 03 W [10] program package, invoking gradient geometry optimization [10,11]. The optimized structural parameters were used in the vibrational frequency calculations at the DFT level to characterize all stationary points as minima. Then, vibrationaly averaged nuclear positions of FMPVH were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The vibrational modes were assigned on the basis of TED analysis using SQM program [12].

It should be noted that Gaussian 03 W package was able to calculate the Raman activities. The Raman activities were transformed into Raman intensities using Raint program [13] by the expression:

$$I_i = 10^{-12} \times (v_0 - v_i)^4 \times \frac{1}{v_i} \times \mathrm{RA}_i \quad (1)$$

where I_i is the Raman intensity, RA_i is the Raman scattering activities, v_i is the wavenumber of the normal modes and v_0 denotes the wavenumber of the excitation laser [14].

Results and discussion

Molecular geometry

The Optimization of FMPVH molecule was performed with B3LYP/6-311++G(d,p) level of basis set. The molecular geometry of FMPVH was well reproduced with X-ray diffraction data [15]. The optimized structure has shown in Fig. 1. In the present molecule due to the rotation of C_{14}—N_{12}—N_{11}—C_9 dihedral angle there seems a distortion in hydrazone linkage between phenyl and furan rings, rest of the bonds could not been disturbed. In FMPVH molecule the bond length of C_1—C_2, C_1—C_9 and C_2—C_3 are calculated 1.370, 1.445 and 1.425 Å. The experimental bond lengths of above are observed about 1.348, 1.432 and 1.415 Å [15]. The bond C_1—O_5 is appeared as σ bond character, its bond length is calculated about 1.364 Å. Similarly, the σ and π character of C_{14}=O_{15} bond is calculated about 1.212 Å. The experimental value of C_{14}=O_{15} bond is at 1.231 Å [15], which coincides well with calculated value. The σ and π bond characters of N_{12}-C_{14} and C_9—N_{11} are calculated as 1.390 and 1.282 Å are positively deviated with experimental (1.348 Å and 1.273 Å) data [15]. The deviation of bond length C_9—N_{11} is about 0.009 Å, it seems a good linearity with X-ray value [15]. The bond length of N_{11}—N_{12} is observed about 1.384 Å [15] which positively deviated (about 29 Å) from our theoretical value. The other calculated bond lengths in FMPVH were not much distorted in both conformers.

The bond angle of N_{12}—N_{11}—C_9 is calculated about 116.68°. Similarly, the bond angle of N_{11}—N_{12}—C_{14} is calculated as 121.31°, which nearly matches with experimental value of 119.16° [15]. From this investigation it fairly explores that, during the course of rotation of the bond, the entire molecule gets disturbed and the properties of the molecule also changes. From the literature [9] and our theoretical investigation, the optimized structure is more stable. The optimized bond parameters of FMPVH are listed in the Table 1.

Vibrational assignment

The vibrational analysis of FMPVH was studied on the basis of B3LYP/6-311++G (d,p) level of basis set. The vibrational assignments were carried out on the basis of furan, methylene, phenylvinyl and hydrazine group of this molecule. Furthermore, the molecule was predicted at local lowest minima on the potential energy surface and therefore none of the imaginary vibrational frequencies appeared. The title molecule is planar and belongs to C_1 point group. It consists of 26 atoms and hence it can have 72 normal modes of vibrations in which 25 stretching and 47 bending modes. To investigate the exact vibrational behavior of this molecule the total energy distribution (TED) analysis was performed on

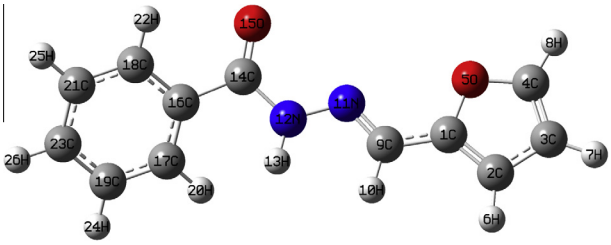

Fig. 1. The optimized molecular structure of FMPVH.