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Identification of structural and spectral properties of synthesized 3-(*p*-isopropylphenyl)-5-(*o*,*m*,*p*-nitrophenyl)-1-phenylformazans: A combined experimental and DFT study

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ABSTRACT

The fomazan compounds 3-(*p*-isopropylphenyl)-5-(*o*,*m*,*p*-nitrophenyl)-5-phenylformazans (**1**–**3**) have been synthesized and characterized by FTIR, UV–Vis and ^{1}H NMR spectroscopic techniques and elemental analysis. Quantum chemical calculations of the molecular structures, vibrational frequencies, gauge including atomic orbital ^{1}H chemical shift values were carried out using the density functional B3LYP method with the 6-311 + G(d,p) basis set. The TD-DFT calculations were carried out using the B3LYP, CAM-B3LYP and PBE1PBE functionals with the 6-311 + G(d,p) basis set to determine the maximum absorbtion wavelength of the UV–Vis spectra for (**1**–**3**). The non-linear optical properties are addressed theoretically. Besides, DFT calculations of the molecular electrostatic potential, the natural bond orbital and thermodynamic properties of (**1**–**3**) were carried out at the B3LYP/6–311 + G(d,p) level of theory.

1. Introduction

Formazans are important class of heterocyclic compounds due to their wide range of applications. They are reported to possess various biological activities, such as anti-viral, anti-fungal, anti-fertility, anti-inflammatory, anti-tubercular, anti-microbial [1–6]. Formazans easily make complexation with metals because of their poly-dentate ligand properties [7]. Formazans and their metal complexes are used as dyes in wool and polyamide fibers and they are also known as ecologically friendly dyes [8]. Formazans form the corresponding tetrazolium salt when oxidized [9], tetrazolium salts are reduced back to formazans. The tetrazolium-formazan system is classified as a marker of vitality and has been used to screen anti-cancer drugs and to determine the activity of tumor cells [9,10]. In addition, formazans are utilized as starting material in the synthesis of various heterocyclic systems [11].

Formazan derivatives have been the subject of some researches focused mainly on their structures and spectra, because of their importance in different sciences. The study of hydrogen bonding in formazan derivatives, characterization of their vibrational frequencies, and the X-ray diffraction data for formazan compounds are some examples which were reported in the literature [12–15]. A large number of experimental and theoretical investigations have been carried out to enrich the information regarding the possible mechanisms of proton transfer and tautomeric equilibria [16–18]. The tautomerism is highly important in the structure and properties of formazans and intramolecular hydrogen bridge in some formazans were studied [18]. The tautomerism of formazans, first described by Penchmann [19], but his results were inconclusive. In 1941 Hunter and Roberts [20] conclusively established for several pairs of formazans that the individuals in each pair were identical, although previously were described as tautomeric. They suggested that formazans were resonance hybrids with a chelated hydrogen-bridge structure. These workers therefore proposed an internally coordinated hydrogen-bond structure, which can exist in two mesomeric forms, **a** and **b**. The formazan molecule thus appears to be a resonance hybrid of these forms (Scheme 1) [21].

In recent years, the study of the synthesis and design of the materials with larger hyperpolarizability (β) has been a hot research topic [22–25]. Because of potential applications in various photonic technologies, the nonlinear optical (NLO) properties of the

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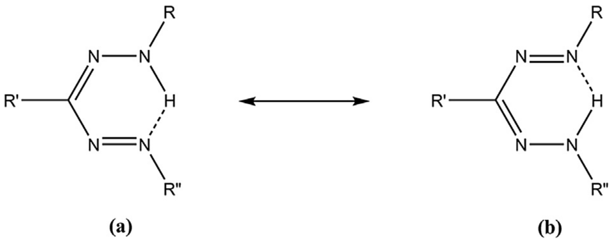

Scheme 1. Tautomeric forms of formazans.

organic molecules have been the object of intense research [26]. Organic molecules showing high optical nonlinearity have potential applications in data storage, optical switching, signal transmission, etc. Using the organic molecules for the nonlinear media has lots of advantages, such as low dielectric constant, low cost and the great diversity of possible organic structures [27]. Devices for applications in optical communications, modulators, optical switches, wavelength filters and optical processors have been created using the NLO response properties of organic molecular systems. During the investigations of organic molecules for NLO, theoretical calculations have made an important contribution to the understanding of the hyperpolarizabilities underlying the molecular NLO processes and the establishment of structure–property relationships [28].

With recent advances in computer hardware and software, it is possible to correctly describe the physicochemical properties of molecules from first principles using various computational techniques [29]. In recent years, density functional theory (DFT) has been a shooting star in molecular modeling. The development of better and better exchange-correlation functionals made it possible to calculate many physicochemical properties with comparable accuracies to traditional correlated *ab*-initio methods, with more favorable computational costs [30]. Literature survey revealed that the DFT has a great accuracy in reproducing the experimental values in molecular geometry, vibrational frequency, NMR, UV–Vis spectra, etc. [31–33].

The aim of this work is to explore the spectral and physicochemical properties of the formazan compounds, 3-(*p*-isopropylphenyl)-5-(*o*,*m*,*p*-nitrophenyl)-1-phenylformazans (Fig. 1), using the DFT calculations. In this study, the geometrical structure, vibrational spectra and assignments, ^{1}H NMR spectra, UV–Vis spectra, nonlinear optical properties, electrostatic potential, frontier molecular orbital energies, natural bond orbitals, natural atomic charges, chemical stability and thermodynamical parameters were investigated on 3-(*p*-isopropylphenyl)-5-(*o*,*m*,*p*-nitrophenyl)-1-phenylformazans. These calculations are valuable for providing insight into molecular properties of formazan compounds.

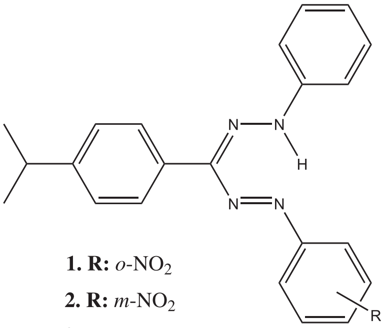

Fig. 1. The structure of the formazan derivatives.

2. Experimental and computational methods

2.1. Physical measurements

The UV–vis spectra of formazans were recorded with UV-1700 Pharma Spectrophotometer using 1 cm quartz cells in 10^{-4} mol L^{-1} CH_2Cl_2. The FTIR spectra were obtained on Nicolet IS10-FTIR spectrometer between 4000 and 400 cm^{-1}. ^{1}H NMR (400 MHz) spectra were performed on Bruker FT-NMR spectrometer. The elemental analysis were carried out using an LECO–CHNS–932 elemental analyzer. Melting points were determined with an electrothermal melting point apparatus and were uncorrected.

2.2. Synthesis of **(1–3)**

The formazans **(1–3)** (Fig. 1) were prepared according to the literature procedures [34]. 1-(4-isopropylbenzylidene)-2-phenylhydrazine (0.01 mol) was dissolved in methanol (35 mL) and sodium hydroxide (1.76 g) was added to this solution. (o,m,p)-nitro anilines were prepared from anilines (0.01 mol) in concentrated HCl (2.5 mL) with sodium nitrite (0.76 g, 0.01 mol) in water (5 mL). This solution was added to hydrazine solution at −5 °C. This mixture was stirred for 2 h at −5 °C and stored 2 days. Compounds **(1–3)** were crystallized from ethanol.

2.2.1. 3-(p-isopropylphenyl)-5-(o-nitrophenyl)-1-phenylformazan **(1)**

Clared red-black crytals; yield 71%; m.p. 172 °C; Anal. calc. for $C_{22}H_{22}N_5O_2$: C; 68.20, H; 5.46, N; 18.07. Found: C; 67.90, H; 5.20, N; 18.25.

2.2.2. 3-(p-isopropylphenyl)-5-(m-nitrophenyl)-1-phenylformazan **(2)**

Clared red-black crytals; yield 78%; m.p. 180 °C; Anal. Calc. for $C_{22}H_{22}N_5O_2$: C; 68.20, H; 5.46, N; 18.07. Found: C; 68.40, H; 5.65, N; 18.45.

2.2.3. 3-(p-isopropylphenyl)-5-(p-nitrophenyl)-1-phenylformazan **(3)**

Clared red-black crytals; yield 65%; m.p. 161 °C; Anal. Calc. for $C_{22}H_{22}N_5O_2$: C; 68.20, H; 5.46, N; 18.07. Found: C; 68.55, H; 5.55, N; 18.32.

2.3. Theoretical methods

The DFT calculations of the compounds **(1–3)** were performed using the Gaussian 09 program package [35]. The Becke's three parameter hybrid functional and Lee-Yang-Parr correlation functionals (B3LYP) were utilized in the calculations with the 6-311 + G(d,p) basic set. The vibrational frequencies were computed at the same level of theory for the optimized structures and the theoretical frequencies were scaled by 0.96 [29]. The vibrational modes were analyzed by means of the atom movements, calculated in Cartesian coordinates and by visual inspection of the vibrational modes animated with GAUSSVIEW molecular visualization program [36]. Vibrational frequencies calculated ascertain the structure was the stable structure (no imaginary frequencies). The thermodynamic parameters of the compounds at different temperatures were also calculated on the basis of vibrational analyses. The geometry of the compounds, together with that of tetramethylsilane (TMS), was fully optimized. The theoretical ^{1}H NMR chemical shift values were calculated using the Gauge-Independent Atomic Orbital (GIAO) method [37]. The ^{1}H NMR chemical shifts are transformed to the TMS scale by subtracting the calculated absolute