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Theoretical and spectroscopic (FT-IR, NMR and UV–Vis.) characterizations of 3-*p*-chlorobenzyl-4-(4-carboxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule

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Fourier transform infrared (FT-IR) spectroscopy in the region 400–4000 cm^{-1}, proton and carbon-13 NMR chemical shifts and UV–Vis. absorption wavelengths of 3-*p*-chlorobenzyl-4-(4-carboxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule have been experimentally investigated. For monomeric and dimeric forms of the title molecule, the optimized molecular structure analyses, vibrational wavenumbers, ^{13}C and ^{1}H NMR chemical shifts and electronic absorption wavelengths of the title molecule have been performed at DFT/B3LYP method with 6-311G(d,p) basis set. The HOMO and LUMO analyses have been theoretically done by using the mentioned calculation level. The obtained experimental values have been compared with calculated data. The computed vibrational frequencies, NMR chemical shifts and UV–Vis. wavelengths have been found to be in a good agreement with experimental values and spectral results of similar structures in the literature.

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1. Introduction

The compounds including 1*H*-1,2,4-triazol and 4,5-dihydro-1*H*-1,2,4-triazol-5-one groups belong to a very broad spectrum of biological activities such as antioxidant [1–3], antibacterial [4–8], antifungal [9], anti-inflammatory [10], anti-HIV [11], antitumor [12], anticonvulsant [13], pharmacological activity [14], antiviral [8], antihypertensive [15], antitubercular [16] and analgesic [17,18] properties. The structural, spectroscopic and electronic (HOMO, LUMO, NBO, MEP, etc.) properties of 4,5-dihydro-1*H*-1,2,4-triazol-5-one derivatives were investigated by using quantum chemical computational methods (HF, DFT, MP2, etc.) by many researchers in the literature [19–24].

In this study, we were presented the synthesis of 3-*p*-chlorobenzyl-4-(4-carboxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**3**) which was obtained from the reaction of compound **(1)** with 4-carboxybenzaldehyde (2) (Scheme 1). The starting compound 3-*p*-chlorobenzyl-4-amino-4,5-dihydro-1*H*-1,2,4-triazol-5-one **(1)** was prepared from the reaction of ethyl acetate ethoxycarbonylhydrazone with an aqueous solution of hydrazine hydrate as described in the literature [25,26].

The researchers have used very extensive quantum chemical computation methods for investigation of structural, spectroscopic, magnetic, electronic and thermodynamic properties of the molecular systems. Density functional theory (DFT) which is one of these methods has been used in many studies in the literature for effective and accuracy evaluation of molecular properties [27–33]. The aim in this study is to investigate molecular structure, vibrational frequencies, ^{1}H and ^{13}C NMR chemical shifts, UV–Vis. absorption spectra and HOMO-LUMO properties of monomeric and dimeric forms of 3-*p*-chlorobenzyl-4-(4-carboxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one molecule, both experimentally and theoretically. The theoretical computations have been made to support experimental data at

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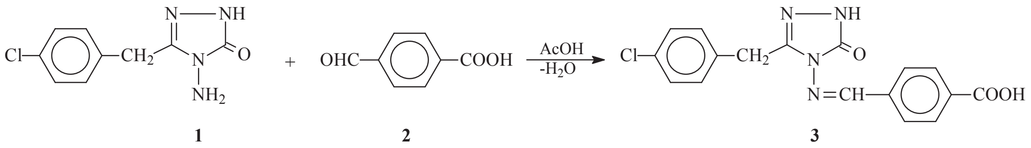

Scheme 1. Syntheses route of compound **3**.

DFT/B3LYP/6-311G(d,p) level.

2. Experimental

Chemical reagents and all solvents were purchased from Merck AG, Aldrich and Fluka. Melting point which is uncorrected was determined in open glass capillaries by using an Electrothermal digital melting point apparatus.

The compound **1** (0.01 mol) was dissolved in acetic acid (20 mL) and treated with 4-carboxybenzaldehyde **(2)** (0.01 mol). The mixture was refluxed for 1 h and then evaporated at 50–55 °C in vacuo. Several recrystallizations of the residue from ethanol gave pure compound 3-*p*-chlorobenzyl-4-(4-carboxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazol-5-one (**3**) as colorless crystals. Yield 3.49 g, (98%). mp 303 °C. *Anal.* Cal. for $C_{17}H_{13}N_4O_3Cl$ (356.77): C, 57.23; H, 3.67; N, 15.70. Found: C, 57.05; H, 3.66; N, 15.64.

The IR spectrum of the title molecule was recorded at the interval 400-4000 cm^{-1} at room temperature on an ALPHA-P Bruker FT-IR spectrometer in solid phase of the sample. The sample were compressed into self-supporting pellet and introduced into an IR cell equipped with KBr window.

The ^1H and ^{13}C NMR chemical shift spectra of the compound solved in deuterated dimethyl sulfoxide (DMSO-d_6) were recorded with TMS as internal standard using a Bruker spectrometer at 400 MHz and 100 MHz, respectively. The chemical shifts were reported at ppm level relative to tetramethylsilane (TMS).

The UV absorption spectrum of the compound solved in ethanol were measured in the region 200–400 nm by using a PG Instruments Ltd. T80 UV/Vis. spectrometer. Extinction coefficients (ε) were expressed in L mol^{-1} cm^{-1}. The UV spectrum was verified with 2 nm spectral bandwidth and 1 cm quartz cell.

3. Computational details

All quantum chemical calculations were carried out with the GaussView5 and Gaussian 09 programs [34,35]. The optimized molecular geometries of monomeric and dimeric forms, vibrational wavenumbers, proton and carbon-13 NMR chemical shifts, UV–Vis spectroscopic properties and HOMOs-LUMOs analyses of the title molecule have been computed by using DFT/B3LYP (Becke's three parameter exact exchange-functional (B3) combined with gradient-corrected correlational functional of Lee, Yang, Parr (LYP)) method with 6-311G(d,p) basis set [36,37]. All computed vibrational wavenumbers were scaled with 0.9619 for B3LYP/6-311G (d,p) level [38]. The vibrational assignments of the calculated frequencies were performed) by using VEDA 4 program in terms of potential energy distribution (PED [39]. The PED assignments of vibrational bands have been used by many researchers in the literature [40–47].

For the proton and carbon-13 NMR chemical shift calculations, the optimized molecular structures in gas phase and DMSO of monomeric and dimeric forms of the title molecule were first obtained at B3LYP/6-311G(d,p) level by using integral equation formalism polarizable continuum model (IEFPCM) method. Then, NMR chemical shifts for the title molecule were calculated at B3LYP/6-311G(d,p) level in DMSO solvent and gas phase by using gauge invariant atomic orbital (GIAO) method [48–50]. The ^1H and ^{13}C NMR chemical shift values have been computed by using equation $\delta^x_{iso.} = \sigma^{TMS}_{iso.} - \sigma^x_{iso.}$ ($\delta^x_{iso.}$ is the isotropic chemical shift, $\sigma^x_{iso.}$ is the isotropic absolute shielding of the compound and $\sigma^{TMS}_{iso.}$ is the isotropic absolute shielding of TMS). The isotropic absolute shielding values were used to calculate the isotropic chemical shifts δ with respect to TMS.

The UV–Vis. spectroscopic parameters of the title molecule were obtained by using TD-DFT method [51] in gas phase and ethanol solvent. Additionally, the HOMO-1, HOMO, LUMO and LUMO+1 energy values and their shapes were simulated at B3LYP/6-311G(d,p) basis set in gas phase and ethanol.

4. Results and discussion

4.1. Molecular structure

The optimized molecular structures of monomeric and dimeric forms of the title molecule were given in Fig. 1. For monomeric and dimeric forms, the calculated molecular geometric parameters with B3LYP/6-311G(d,p) level are listed in Table S1 (Supplementary materials).

For the title molecule, 3-*p*-chlorobenzyl group is not in same plane with 4-(4-carboxybenzylidenamino)-4,5-dihydro-1*H*-1,2,4-triazole-5-one group. Therefore, the title molecule is non-planar. The C8–C18–C19–C20 dihedral angle value is 89.894°, whereas the C12–C11–C10–N4, C11–C10–N4–N1 and C10–N4–N1–C9 dihedral angles are found as 180°, −180° and 0°, respectively. Similarly, the dihedral angle value between two benzene ring planes is calculated as 90°. The N2–N3, N2=C8, C9=O5, N1–C8, N1–C9 and N3–C9 bond lengths in the triazole group are computed as 1.379 Å, 1.294 Å, 1.215 Å, 1.391 Å, 1.422 Å and 1.368 Å. The N1–N4 and C8–C18 bond lengths are found to be 1.367 Å and 1.498 Å. The N4=C10 bond length is exhibited double bond characteristic with 1.286 Å value [52,53]. Pitucha et al. [19] recorded as 1.2323(17) Å by X-Ray analysis C=O bond length for a 1*H*-1,2,4-triazol-5-one derivative compound. Ustabaş et al. [54] obtained as 1.212(4) Å by X-Ray technique C=O bond length in 1*H*-1,2,4-triazol-5-one group of 1-(benzoylmethyl)-4-[(2,4-dichlorobenzylidene)amino]-3-(2-thienylmethyl)-4,5-dihydro-1H-1,2,4-triazol-5-one molecule. Ocak et al. [55] measured 1.280(4) Å and 1.404(4) Å values for C=N and N–N bond lengths in triazole group of 1-acetyl-3-(*p*-chlorobenzyl)-4-(*p*-chlorobenzylidenamino)-4,5-dihydro-1H-1,2,4-triazol-5-one molecule. Similarly, they found as 1.726(4) Å C=N bond length in aliphatic group of the mentioned compound, while they observed as 1.744(4) Å and 1.742(4) Å for C–Cl bond lengths. The C22–Cl38 bond length that is the longest bond of the title molecule is obtained as 1.761 Å with B3LYP/6-311G(d,p) level.

The C17=O6, C17–O7 and O7–H26 bond lengths in the carboxyl group are calculated as 1.208 Å, 1.356 Å and 0.968 Å for monomer form of the title molecule. But, these bond lengths for dimeric form are found as 1.229 Å, 1.320 Å and 1.000 Å, respectively. Similarly, the O6–C17–O7, C17–O7–H26, O6–C17–C14 and O7–C17–C14 bond angles are at 122.231°,106.214°, 124.869° and 112.900° for monomer form of the title molecule. These bond

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