



Keto-enol tautomerism of (E)-2-[(3,4-dimethylphenylimino)methyl]-4-nitrophenol: Synthesis, X-ray, FT-IR, UV–Vis, NMR and quantum chemical characterizations



Arzu Özek Yıldırım ^{a,*}, M. Hakkı Yıldırım ^b, Çiğdem Albayrak Kaştaş ^c

^a Faculty of Arts and Science, Giresun University, Turkey

^b Dereği Vocational School, Giresun University, Turkey

^c Samsun Vocational School, Ondokuz Mayıs University, Turkey

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ABSTRACT

(E)-2-[(3,4-dimethylphenylimino)methyl]-4-nitrophenol, which is a new Schiff base compound, was synthesized and characterized by experimental and computational methods. Molecular geometry, harmonic oscillator model of aromaticity (HOMA) indices, intra- and inter-molecular interactions in the crystal structure were determined by using single crystal X-ray diffraction technique. The optimized structures, which are obtained by Gaussian and Slater type orbitals, were compared to experimental structures to determine how much correlation is found between the experimental and the calculated properties. Intramolecular and hyperconjugative interactions of bonds have been found by Natural Bond Orbital analysis. The experimental infrared spectrum of the compound has been analyzed in detail by the calculated infrared spectra and Potential Energy Distribution analysis. To find out about the correlation between the solvent polarity and the enol-keto equilibrium, experimental UV–Visible spectra of the compound were obtained in benzene, CHCl₃, EtOH and DMSO solvents. In these solvents, the UV–Vis spectra and relaxed potential energy surface scan (PES) calculations have been performed to get more insight into the equilibrium dynamics. Solvent effects in UV–Vis and PES calculations have been taken into account by using Polarizable Continuum Modelling method. ¹H and ¹³C NMR spectra of the compound (in DMSO) were analyzed. The computational study of nonlinear optical properties shows that the compound can be used for the development of nonlinear optical materials.

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1. Introduction

In recent years, synthesis and characterizations of the Schiff base compounds and their metal complexes have attracted the attention of researchers [1–10]. Their potential applications can be found in chemistry [11–14], pharmaceutical and biological fields [15–17]. Schiff bases can display photochromic and thermochromic properties, depending on the prototropic tautomerism, the molecular geometry and the crystal packing [18,19]. The migration of a proton between the two stable form of the molecule has been defined as the prototropic tautomerism by Lapworth and Hann [20]. In spite of the relatively only a small fraction of the molecules has this feature, the prototropic tautomerism has received the

attention of researchers. In Schiff bases, the prototropic tautomerism emerges from the transformation of the enol tautomeric form [21] to keto tautomeric form [22] and vice versa. In addition to the effects of the media, the electron donating and withdrawing substituents affect the tautomeric form of the molecule [23].

In the current study, a new Schiff base, (E)-2-[(3,4-dimethylphenylimino)methyl]-4-nitrophenol, has been firstly synthesized, the structural and electronic properties characterized by using spectroscopic techniques and the computational methods. Molecular structure and intermolecular interactions have been found by using single crystal X-ray diffraction techniques. Its spectral characterizations have been carried out by experimental Fourier transform infrared, proton and carbon NMR, UV–Visible spectroscopy and computational (DFT and TD-DFT) methods. Also, the geometry optimization and infrared spectrum calculations were performed by using Slater type orbitals (STO) in Amsterdam Density Functional (ADF) software. The tautomeric equilibrium of

* Corresponding author.

E-mail address: arzu.ozek.yildirim@giresun.edu.tr (A. Özek Yıldırım).

the compound between the enol, keto and transition state (TS) forms have been investigated in the vacuum and solvent media. In addition, nonlinear optical (NLO) properties and Natural Bond Orbital (NBO) analysis of the compound have been studied by DFT methods.

2. Material and methods

2.1. Synthesis

(E)-2-[(3,4-dimethylphenylimino)methyl]-4-nitrophenol was prepared by refluxing a mixture of 2-hydroxy-5-nitrobenzaldehyde (0.5 g, 3 mmol) in 20 ml ethanol and 3,4-dimethylaniline (0.36 g, 3 mmol) in 20 ml ethanol for 1 h. The pure single crystals of the compound were acquired by slow evaporation of ethanol solution (yield; 86%, m.p. 451–453 K).

2.2. Spectroscopic measurements

Fourier transform infrared spectral data was collected in the 4000–400 cm^{-1} region with a Bruker Vertex 80 V spectrometer using KBr pellet technique. UV–Visible spectra were measured within 200–800 nm range in benzene, chloroform, ethanol and DMSO solvents on a Thermo Scientific Evolution Array spectrometer. The ^1H and ^{13}C NMR spectral data were obtained in DMSO solution on a Bruker AVANCE III 400 MHz spectrometer using TMS as an internal reference.

2.3. Single crystal structure determination

Data collection were performed with a STOE IPDS II diffractometer by using MoK_α radiation at 296 K. The crystal structure solution was found by using SHELXS [24] and structure refined with SHELXL [24] in WinGX software [25]. Position of H1 atom (hydroxyl hydrogen) was found from a difference Fourier map and the other H atoms were located geometrically. Molecular drawing was prepared with ORTEP-3 for Windows [26] and the crystal packing figure was drawn by PLUTON [27] software. The details of crystal structure solution and the refinement were given in Table S1 (Supplementary material). The crystallographic information file of the compound can be obtained from The Cambridge Crystallographic Data Centre (CCDC 1043761) via www.ccdc.cam.ac.uk/structures.

2.4. Computational methods

Gaussian type orbital calculations (GTO) were performed by using Gaussian 09W [28] software at the DFT/B3LYP level of theory [29] with 6–311++G (d,p) basis set. The molecular geometry obtained from X-ray diffraction was selected as an initial geometry of the enol structure and this geometry has been fully optimized with Beryny optimization algorithm [30] in Gaussian 09W. The changes in the molecular structure during the proton transfer process have been acquired by doing relaxed potential energy surface (PES) scan calculations in the vacuum and solvent media along the O–H...N path (moving H atom from O to N). The initial geometries of TS and keto tautomer were obtained from PES calculation in vacuum. The global maximum on PES coordinate corresponds to TS, while the local minimum represents keto tautomer. Beryny transition state optimization technique was used for transition state optimization. Frequency calculation of the optimized TS structure gave one negative value which is correspond to proton transfer coordinate. GTO and STO type infrared spectra calculations of the compound were performed on the optimized enol structure in the vacuum. The frequencies were scaled by 0.9688 [31] for GTO and 0.9648 [32]

for STO. Potential energy distributions and assignments of the scaled GTO frequencies were calculated by using VEDA4 software [33]. Theoretical UV–Vis. spectra of the enol and keto structures were obtained with the TD-DFT/B3LYP method [34–37]. Solvent effects in the potential energy surface scan calculations, enol/keto structure optimizations and theoretical UV–Vis. spectra calculations were modelled by using Polarizable Continuum Model (PCM) [38,39]. All the Slater type orbital (STO) calculations were performed by using ADF 2009.01 [40–42] software package. Geometry optimization and infrared calculation were carried out using DFT/B3LYP methods, with the TZP basis sets.

3. Results and discussion

3.1. Molecular and crystal structure

The titled compound crystallizes in the centrosymmetric *P*-1 space group. Molecular structure of the compound with atom labelling scheme is given in Fig. 1. The all geometric parameters with corresponding calculated values have been presented in Table S2.

X-ray crystallography analysis of the compound reveals that the C2–O1 (1.328 (4) Å) bond length indicates a single-bond character, whereas the C7–N1 (1.290 (4) Å) bond length indicates a double-bond character. Hence, the prototropic hydrogen atom (H1) is located on atom O1, thus showing a preference for the phenol–imine tautomer in the solid state. Bond lengths of the nitro group, which are N2–O2 and N2–O3, are found to be 1.227 (4) and 1.227 (3). The other structural parameters are in harmony with related Schiff base compounds [43,44]. According to Mavridis et al. [45], thermochromic and photochromic properties are associated with the molecular planarity in Schiff bases. The dihedral angle between C1/C6 and C8/C13 rings showing the planarity of the title molecule is 1.205 (2)° and this planarity may lead to a thermochromic feature.

The optimized geometries of the compound obtained by using the GTO and STO were in the harmony with the XRD geometry. The root mean square errors (RMSE) in bond lengths have been calculated as 0.091 Å for XRD/GTO comparison and 0.089 Å for XRD/STO comparison while the RMSE's of bond angles have been calculated as 1.54° and 1.48°, respectively. For the bond lengths, the biggest deviations occur at C7–H7 and C9–H9 bonds with the difference being 0.165 Å, 0.155 Å for GTO and 0.162 Å, 0.151 Å for STO, respectively. C2–O1–H1 bond angle has the greatest differences for the bond angle with 5.6° for GTO and 6.1° for STO. The largest deviations between the experimental and calculated values are observed in the bond length and angle involved in hydrogen bonds. Besides that, to visualize the results of RMS calculations, a superimposition of the experimental and calculated structures is given in

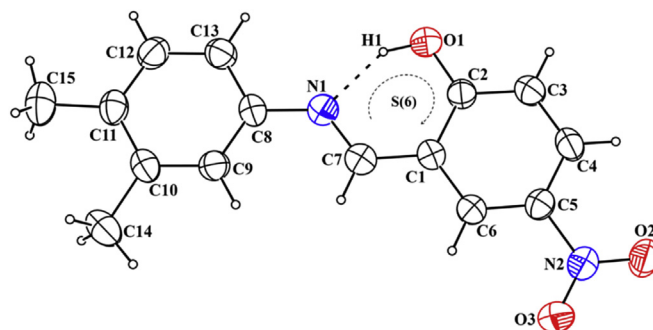


Fig. 1. Ortep-III molecular drawing of the title compound.

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