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Computational and experimental studies of 2-[(E)-hydrazinylidenemethyl]-6-methoxy-4-[(E)-phenyldiazenyl]phenol and its tautomers

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ABSTRACT

A new azo-chromophore group containing a hydrazine-Schiff base compound, 2-[(E)-hydrazinylidenemethyl]-6-methoxy-4-[(E)-phenyldiazenyl]phenol, was synthesized and structurally characterized by single crystal X-ray diffraction study. The compound was found to crystallise in *orthorhombic* crystal system with *Pca2(1)* space group. In the structure, the molecule exhibits a phenol-imine intramolecular hydrogen bond and the $-NH_2$ group also involves in intermolecular hydrogen bonding with one of the nitrogen atom of the azo group ($-N{=}N-$) forming a 1D zigzag chain. Computational studies were performed on the titled compound and its tautomers. As computationally, this compound and its tautomers were optimized by using M062X/6-311G(d,p) level. According to thermodynamic parameters, the most stable tautomer was found to be azo-enol form. This result was then taken into account and spectral studies, which are IR, UV–Vis and NMR spectra, of this compound were performed and examined in detail. All calculations were performed at gas phase ($\varepsilon = 1.000$), 2-propanol ($\varepsilon = 19.264$), 1,2-ethanediol ($\varepsilon = 40.245$), water ($\varepsilon = 78.355$), formamide ($\varepsilon = 108.940$) and N-methylformamide-mixture ($\varepsilon = 181.560$).

1. Introduction

Hydrazine is one of the most important chemical compound and its derivatives are mainly used in pharmaceuticals, fuel cell, heat stabilizers, fuel for aircraft, rockets, missiles, satellites, explosive, pesticide, dyestuffs and corrosion inhibitors [1–8]. Adsorption and reaction of hydrazine and its derivatives are important topic due to their relevance in energy related application [9–14]. Hydrazine derivatives are used as corrosion inhibitor or agent in corrosion processes [15–17].

In our previous works, we have investigated the synthesis, spectral, structural and biological properties of new azo chromophore group containing ligands and their transition metal complexes [18]. Here, in continuation of our interest in this field, a new azo-group containing hydrazine-Schiff base compound 2-[(E)-hydrazinylidenemethyl]-6-methoxy-4-[(E)-phenyldiazenyl]phenol was synthesized and structurally characterized by X-ray diffraction study. Schematic representation of mentioned compound and its tautomers are given in Scheme 1. Computational investigations were carried out on mentioned tautomers. Gas phase and five different solvent were selected for calculation to investigate the solvent effect on electronic and structural properties. The most stable tautomer in six different environments was determined using some thermodynamic parameters which were total energy (E_{TOTAL}), enthalpy (H) and Gibbs free energy (G). Some structural parameters were calculated for the most stable tautomer. Calculated and experimental parameters were then subjected to correlation analysis for each media. Correlation constants (R^2) are calculated and so compatibility between experimental and calculated data were investigated. Additionally, IR, UV–Vis, ^1H and ^{13}C NMR of the most stable tautomer were calculated in different solvent media and the gas phase and investigated in detail. Chemical reactivity of the most stable isomer were investigated using some quantum chemical parameters which were energy of the highest

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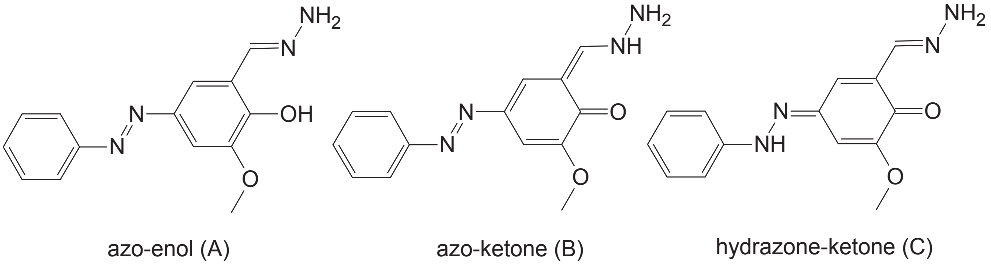

Scheme 1. The possible tautomers (A–C) of the titled azo-Schiff base.

occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap (E_{GAP}) between frontier molecular orbitals (FMOs), global hardness (η), global softness (σ), chemical potentials (CP), electronegativity (χ), electrophilicity index (ω), nucleophilicity index (N), dipole moment (μ), the average linear polarizability (α), the anisotropy of polarizability (Δα), the first hyperpolarizability (β).

2. Experimental

2.1. Chemicals

The azo group containing *o*-vanillin derivative compound, 2-hydroxy-3-methoxy-5-[(E)-phenyldiazenyl]benzaldehyde was prepared according to the reported method [19]. All reagents and solvents for synthesis and analysis were purchased from commercial sources and used as received unless otherwise noted.

2.2. Physical measurements

Data collection for X-ray crystallography was completed using a Bruker APEX2 CCD diffractometer and data reduction was performed using Bruker SAINT. SHELXS97 was used to solve and SHELXL2014/6 to refine the structure [20].

2.3. Preparation of the compound

A typical procedure for the synthesis of the azo-Schiff base was as follows: hydrazinemonohydrate (0.002 mol, 0.10 g) in methanol (20 mL) was slowly added to a methanol solution (50 mL) containing 2-hydroxy-3-methoxy-5-[(E)-phenyldiazenyl]benzaldehyde (0.0015 mol, 0.384 g). The orange coloured mixture was refluxed for 5 h and cooled to the room temperature. Crystals formed in the mother liquor were collected for X-ray analysis.

2.4. X-ray structure solution and refinement

Data for the titled compound was collected at 296(2) K on a Bruker ApexII CCD diffractometer using Mo-*Kα* radiation (λ = 0.71073 Å). Data reduction was performed using Bruker SAINT [21]. The structure was solved by direct methods and refined on F^2 using all the reflections. All the non-hydrogen atoms were refined using anisotropic atomic displacement parameters and hydrogen atoms bonded to carbon atoms were inserted at calculated positions using a riding model. Hydrogen atoms bonded to the nitrogen (N4) and oxygen (O1) atoms were located from difference maps and refined with temperature factors riding on the carrying atoms.

2.5. Computational details

All computational processes of mentioned complexes were carried out on GaussView 5.0.8 [22], Gaussian 09 AML64-G09 Revision-C.01 programs [23] and ChemBioDraw Ultra Version (13.0.0.3015) [24]. Geometries of mentioned tautomers were fully optimized at M062X/6-311G(d,p) level in six different media, gas phase (a), 2-propanol (b), 1,2-ethanediol (c), water (d), formamide (e) and N-methylformamide-mixture (f). Calculations in the solvent media, conductor-like polarizable continuum model (CPCM) method was taken into account [25]. The vibration frequency analyses indicate that optimized structures of relevant molecules are at stationary points corresponding to local minima without imaginary frequencies. To calculate the UV–Vis spectra in media, TD-M062X method was used for the most stable tautomer and gauge-including-atomic-orbital (GIAO) method with M062X/6-311G(d,p) level was used to calculate NMR spectra for the most stable tautomer [26,27]. Some quantum chemical parameters which are energy of the highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap (E_{GAP}) between frontier molecular orbitals (FMOs), global hardness (η), global softness (σ), chemical potentials (CP), electronegativity (χ), electrophilicity index (ω), nucleophilicity index (N), total static dipole moment (μ), the average linear polarizability (α), the anisotropy of polarizability (Δα), the first hyperpolarizability (β) are calculated using following equations:

$$E_{GAP} = E_{LUMO} - E_{HOMO} \tag{1}$$

$$I = -E_{HOMO} \tag{2}$$

$$A = -E_{LUMO} \tag{3}$$

$$\eta = \frac{I - A}{2} \tag{4}$$

$$\sigma = \frac{1}{\eta} \tag{5}$$

$$\chi = \frac{|E_{HOMO} + E_{LUMO}|}{2} \tag{6}$$

$$CP = -\chi \tag{7}$$

$$\omega = \frac{CP^2}{2\eta} \tag{8}$$

$$N = \frac{1}{\omega} \tag{9}$$