



Synthesis, Spectral, Theoretical and Thermal Analysis of (Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine isomer

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Abstract

(Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine Schiff base was prepared by condensing equivalent amount of (2,4-dinitrophenyl)hydrazine with 5-bromothiophene-2-carbaldehyde in ethanol under reflux condition. EA, EI-MS spectral, IR, TG/DTG, UV-visible and theoretical calculation were used to assign the Z- isomer formed over E one.

Keywords: FT-IR; condensation; TG/DTG; Schiff bases.

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1. Introduction

Schiff bases are the condensation products of ketones or aldehydes with primary amines. They contain –HC=N– azomethine group which were first synthesized by H. Schiff [1]. The extensive applications of Schiff bases including the biological activities are as antibacterial, antifungal, antioxidant, anti-inflammatory and antitumor agents [2]. They have been used as organic

intermediates for production of chemicals used in pharmaceuticals [3], rubber additives [4], liquid crystals [5], polymer and analytical chemistry [6] and corrosion inhibitors [7]. The presence of $>C=N-$ group in Schiff bases was reported to enhance their adsorption ability and corrosion inhibition efficiency [8]. Schiff bases with nitrogen and oxygen donors show photochromism and thermochromism in the solid state [9].

In coordination chemistry, Schiff base have been extensively used as ligands mainly due to their facile syntheses, electronic properties, easily tunable steric, good solubility and forming stable complexes with the transition metals [10-15].

In connection with our current research on the characterization of Schiff base ligands [16], here in this work, (Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine Schiff was prepared and characterized. The condensation reaction was monitored by IR.

Experimental section

The UV-visible spectrum was measured by using a TU-1901 double-beam UV-visible spectrophotometer. The IR spectra for samples were recorded using Perkin Elmer Spectrum 1000 FT-IR Spectrometer. EI-MS data was obtained on a Finnigan 711A (8 kV) (PerkinElmer Inc., Waltham, MA, USA). TG/DTA spectrum was measured by using a TGA-7 PerkinElmer thermogravimetric analyzer (PerkinElmer Inc., Waltham, MA, USA).

A solution of 2,4-dinitrophenyl)hydrazine 1 mmol in EtOH (30 mL) was mixed with 5-bromothiophene-2-carbaldehyde 1.1 mmol and allowed to reflux under stirring for 4h. The resulting mixture was concentrated under reduced pressure and the title compound was precipitated by the addition of 100 mL of *n*-hexane. The precipitates were filtered off, washed three times with 80 mL of distilled water. EI-MS spectral, IR, elemental analysis, TG/DTG, UV-visible and theoretical calculation were used to assign the Z- isomer formation over E one as seen in Scheme 1.

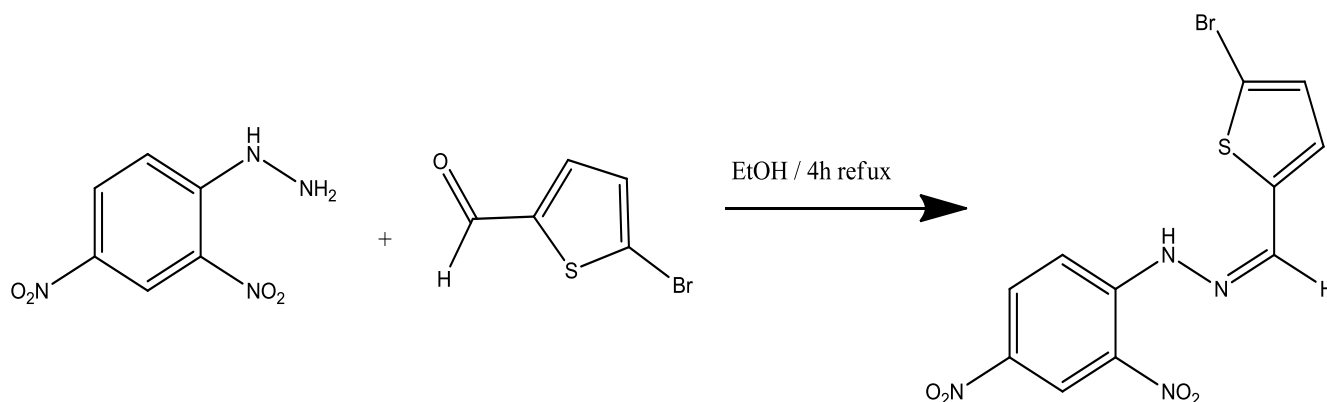
Full geometry HOMO and LUMO optimization of (Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine was carried out using density functional theory (DFT) at the B3LYP level [17]. All calculations were carried out using the GAUSSIAN 09 program package with the aid of the GaussView visualization program [18]. Gauss Sum was used to calculate the fractional contributions of various groups to each molecular orbital [19].

Result and Discussion:

Synthesis of (Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine

(Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine was synthesized by condensing equimolar amounts of (2,4-dinitrophenyl)hydrazine and 5-bromothiophene-2-

carbaldehyde in absolute ethanol at reflux condition for 4h, as shown in **Scheme 1**. The product is red solid product, complete soluble in dichloromethane and THF and soluble partially in ROH, insoluble in water and non-polar solvents like *n*-hexane.



Scheme 1. Synthesis of the (Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine.

The elemental analysis and mass spectroscopy

The elemental analysis of the compound is consistent with the proposed molecular formula (Calcd. for $C_{11}H_7BrN_4O_4S$: C, 35.60; H, 1.90; N, 15.09. Found: C, 35.45; H, 1.71; N, 14.65). EI-MS of the compound is in good agreement with the assigned structure, the experimental molecular ion $[M^+]$ $m/z = 368.2$ (369.9 theoretical).

FT-IR investigation

In order to monitor the condensation reaction, the starting materials were subjected to IR before/and after it react to produce the desired compound. The formation of the product was confirmed by the C=O (at 1650 cm^{-1}) shifted down to C=N (at 1588 cm^{-1}) as seen in **Figure 1b and 1c**. The volume, shape and chemical shift of NH_2 and NH stretching vibration of hydrazine at 3320 cm^{-1} was reduced in volume and chemical shift to 3310 cm^{-1} which supported the formation of the (Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine, see in Fig/ 1a and 1c.

Frontier molecular orbital analysis

The ability of the molecule to donate an electron is associated with the HOMO and the characteristic of the LUMO is associated with the molecule's electron affinity. The HOMO and LUMO energies are very useful to gauge the chemical reactivity of the molecule and are very important terms in quantum chemistry [20, 21]. The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to the

LUMO. The pictorial representation of the HOMO and the LUMO in the gaseous phase is shown in Figure 2.

The HOMO lies at -0.19336 eV and whereas the LUMO is located at -0.18320 eV with 0.011 eV the frontier orbital energy gap. It is more easily are the electrons excited from the ground to the excited state with this low energy gap. The energy gap explains the eventual charge transfer interaction within the molecule and is useful in determining molecular electrical transport properties [21].

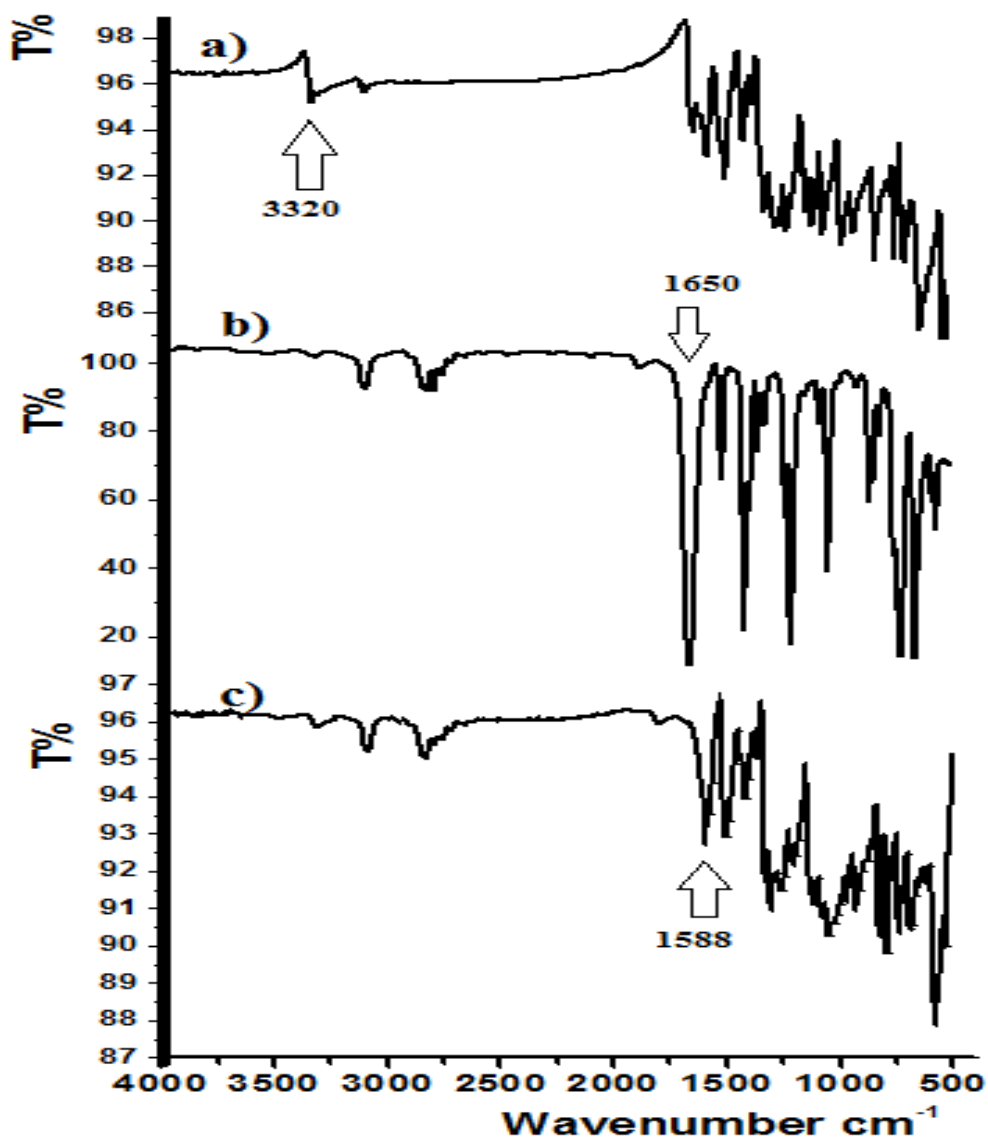


Fig.1. IR spectra of: a) 2,4-dinitrophenylhydrazine (starting material), b) 5-bromothiophene-2-carbaldehyde (starting material) and c) *N*-[(1*E*)-(3-bromophenyl)methylene]-*N*-(2-piperidin-1-ylethyl)amine (product).

Electronic absorption

The electronic absorption spectrum of the prepared compound was acquired in THF, Figure 3 showed the electronic absorption as expected (on the UV region only) at $\lambda_{\text{max}} = 260$ and 390 nm which assigned mainly to intra-ligand π -n and π - π^* transitions.

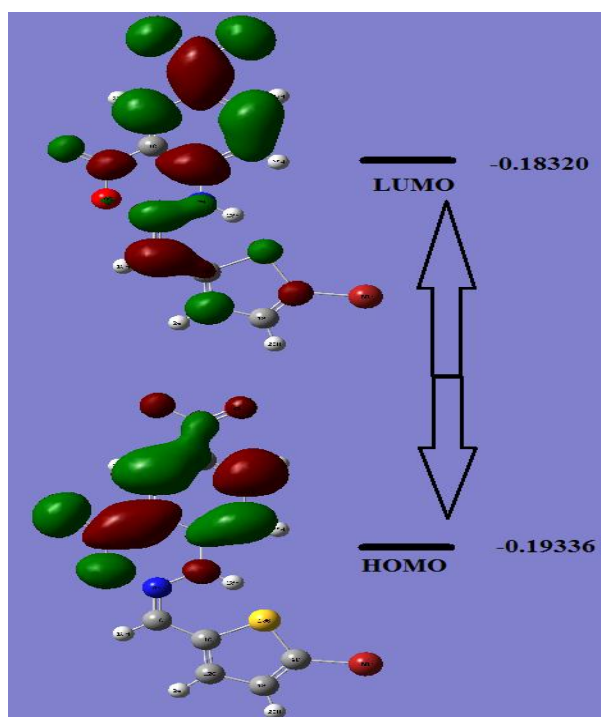


Fig. 2. HOMO and LUMO plots of (Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine.

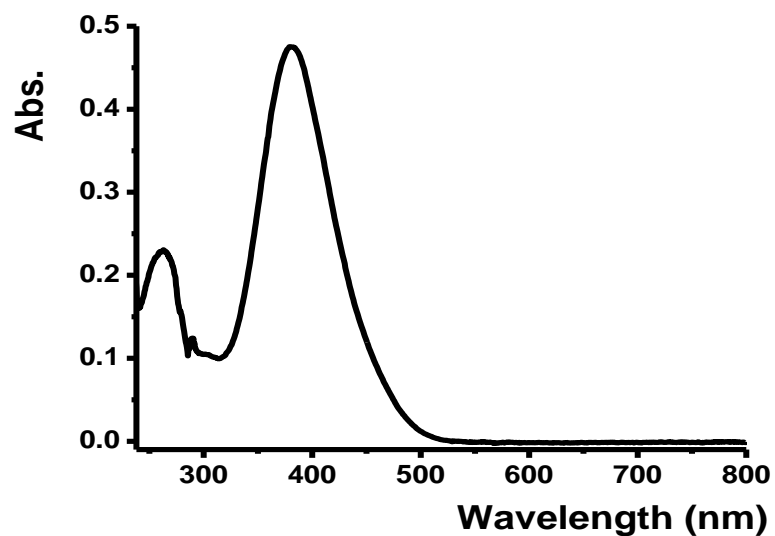


Fig. 3. UV-Vis spectrum of 1×10^{-5} M product dissolved in THF at RT.

TG/DTG analysis

The thermal properties TG/DTG of the title compound was investigated under an open atmosphere in the range of 0–250 °C and heating rate of 10 °C/min. Figure 4 showed simple decomposition process with one broad step typical decomposition, started from 110 °C and end at 160 °C, one DTG = 135 °C signal with weight loss ~96% and without intermediate decomposition step.

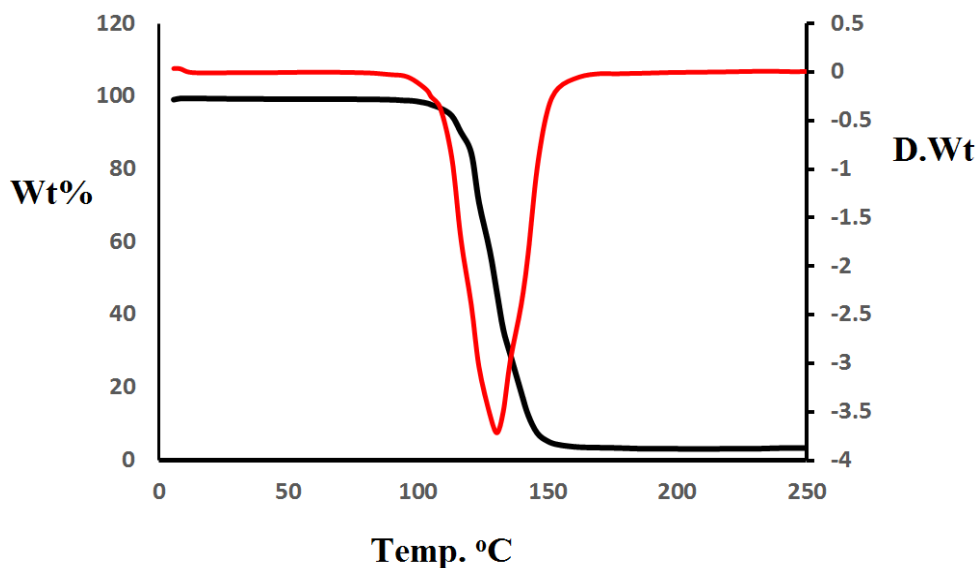


Fig. 4. TG/DTG thermal curve of the desired compound.

Conclusions

(Z)-1-((5-bromothiophen-2-yl)methylene)-2-(2,4-dinitrophenyl)hydrazine was made available through condensing of (2,4-dinitrophenyl)hydrazine with 5-bromothiophene-2-carbaldehyde in good yield and fast technique. Based on the theoretical calculation and experimental physical measurements Z- isomer is favored over E- isomer.

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