Journal of Molecular Structure 1156 (2018) 91–104

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Synthesis, spectroscopic characterization and DFT calculations of novel Schiff base containing thiophene ring

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ARTICLE INFO

Article history:
Received 16 October 2017
Received in revised form
19 November 2017
Accepted 21 November 2017
Available online 22 November 2017

Keywords:
2-Hydroxy-5-(thiophen-2-yl)benzaldehyde
2-Amino-6-methylbenzoic acid
Schiff base
Vibrational spectroscopy
NMR chemical shifts
Density Functional Theory (DFT)

ABSTRACT

In this study, a new Schiff base derivative, 2-[(2-hydroxy-5-thiophen-2-yl-benzylidene)-amino]-6-methyl-benzoic acid **(5)**, which has a thiophene ring and N, O donor groups, was successfully prepared by the condensation reaction of 2-hydroxy-5-(thiophen-2-yl)benzaldehyde **(3)** and 2-amino-6-methylbenzoic acid **(4)**. The characterization of a Schiff base derivative **(5)** was performed by experimentally the UV–Vis., FTIR, ^{1}H and ^{13}C NMR spectroscopic methods and elemental analysis. Density Functional Theory (DFT/B3LYP/6-311+G(d, p)) calculations were used to examine the optimized molecular geometry, vibrational frequencies, ^{1}H and ^{13}C NMR chemical shifts, UV–Vis. spectroscopic parameters, HOMO-LUMO energies and molecular electrostatic potential (MEP) map of the compound **(5)** and the theoretical results were compared to the experimental data. In addition, the energetic behaviors such as the sum of electronic and thermal free energy (SETFE), atomic charges, dipole moment of the compound **(5)** in solvent media were investigated using the B3LYP method with the 6-311+G(d, p) basis set. The obtained experimental and theoretical results were found to be compatible with each other and they were supported the proposed molecular structure for the synthesized Schiff base derivative **(5)**.

1. Introduction

Schiff base derivatives are the compounds containing azomethine group (–HC=N), which also known as imine functional group and they have considerably taken attention because of their biological activities such as anticancer [1,2], antibacterial [3], antifungal and antimicrobial [3,4]. These compounds constitute the most important class of photochromic materials, which are potential in optoelectronic applications [5–7]. In recent years, nonlinear optical (NLO) behaviors and the electrochemical properties of Schiff base ligands including a variety of substituents with different electron-donating and electron-withdrawing groups have been investigated for the potential applications [8,9]. In addition, Schiff base ligands perform an important role in inorganic chemistry due to their synthetic flexibility, selectivity and sensitivity towards the transition metal ions [10,11]. The metal complexes of Schiff bases derived from heterocyclic compounds containing nitrogen, oxygen and sulfur as ligand atoms are used for biological applications in clinical and pharmacological areas [10–14].

Thiophene and its derivatives are important heterocyclic compounds. They are used in technologies as a charge transporting molecules in transistors, super capacitors, organic solar cells, electrochromic materials, organic light-emitting diodes and nonlinear optic materials [15–20]. Recently, Schiff base compounds containing thiophene ring have been extensively investigated, because these compounds exhibit a variety of medicinal and biological activities such as anti-inflammatory, antibacterial, analgesic, anticancer, antidepressant and antimicrobial [21–27]. In addition, it is also known that some thiophene-based Schiff base derivatives have influence as corrosion inhibitors [28]. Therefore, the design and synthesis of novel molecules incorporating the thiophene ring have drawn a great interest.

In recent years, theoretical calculation methods have been widely used in theoretical modeling and design of functional materials such as drug molecules. The development of computational chemistry has led to the prediction of physical and chemical properties in the biological and chemical systems. In addition, the theoretical calculations are largely contributed to the spectroscopic studies performing by experimentally [9,11,21,29–31]. The Density Functional Theory (DFT) has been intensively employed for the calculation of various properties of some thiophene derivatives such as molecular structure, UV–Vis, FT-IR and NMR spectra, HOMO-LUMO energies, charge distributions and nonlinear optical

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https://doi.org/10.1016/j.molstruc.2017.11.089
0022-2860/

(NLO) behaviors. The reliable results consistent with experimental data have been attained for these types of compounds [9,11,21,22,27,32–34].

In this present study, the synthesis of a novel Schiff base derivative **(5)** which was derived from the condensation reaction of 2-hydroxy-5-(thiophen-2-yl)benzaldehyde **(3)** and 2-amino-6-methylbenzoic acid **(4)** (Scheme 1) was reported. The structural characterization of the compound **(5)** was experimentally accomplished by UV–Vis, FTIR, ^{1}H NMR and ^{13}C NMR spectroscopic methods and elemental analysis. The optimized molecular geometry, IR frequencies, ^{1}H and ^{13}C NMR chemical shifts, UV–Vis spectra, HOMO-LUMO energies, molecular electrostatic potential (MEP) map, dipole moment and atomic charges of the compound **(5)** were investigated using the DFT method at the B3LYP level with the 6-311+G(d, p) basis set. The experimental data of the compound **(5)** obtained from UV–Vis, FTIR, ^{1}H and ^{13}C NMR spectra were compared to the calculated results from the DFT method.

2. Experimental

2.1. Materials and methods

5-Bromosalicylaldehyde, bis(triphenylphosphine)palladium (II) dichloride [$Cl_2Pd(PPh_3)_2$], 2-tributylstannylthiophene and 2-amino-6-methylbenzoic acid were commercially obtained from Sigma-Aldrich and Across. All reagents and organic solvents were used without further purification. A Sanyo Gallenkamp melting point apparatus was used for determination of the melting points (m.p.) of the synthesized compounds. Electronic absorption spectra of the compound **(5)** in various solvents such as ethyl acetate (EtOAc), tetrahydrofuran (THF), methanol (MeOH), dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were attained by using SHIMADZU UV-3150 UV-VIS-NIR spectrophotometer. Fourier Transformed Infrared (FTIR) spectroscopic analysis was performed with KBr pellet by a Perkin Elmer Spectrum 100 FT-IR spectrometer. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) nuclear magnetic resonance spectra were recorded on an Agilent DD2 NMR (400 MHz) Spectrometer. ^{1}H and ^{13}C chemical shifts were measured relative to tetramethylsilane in DMSO-d_6, spectral splitting; s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; m, multiplied; and br, broad. The elemental analysis of the synthesized compounds was determined by an ELEMENTAR VARIO ELIII elemental analyzer (CHNS).

2.2. Synthesis

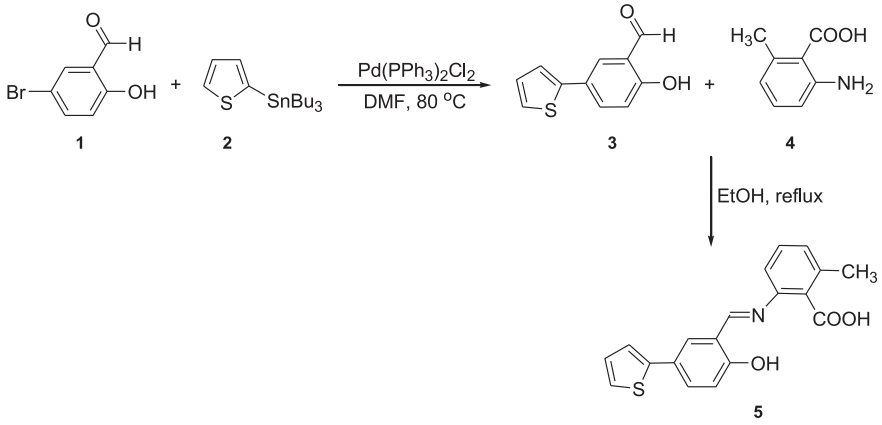
2.2.1. Synthesis of 2-[(2-hydroxy-5-thiophen-2-yl-benzylidene)-amino]-6-methyl-benzoic acid **(5)**

In this study, 2-hydroxy-5-(thiophen-2-yl)benzaldehyde **(3)** was synthesized according to the procedure described in the literature [20]. To a solution of the compound **(3)** (0.2 g, 1.0 mmol) in ethanol (30 mL) was added a solution of 2-amino-6-methylbenzoic acid **(4)** (0.15 g, 1.0 mmol) in ethanol (15 mL) with continuous stirring, and the mixture was refluxed for 24 h. The completion of the reaction, monitored through TLC. The reaction mixture was then cooled to room temperature and ethanol was removed. The obtained residue was washed with ethanol and dried in the room temperature. The product was recrystallized in the mixture of ethanol:dichloromethane (1:3). The yield of the red product **(5)** was 60% (0.20 g), (m.p. 209–213 °C). FTIR (KBr, cm^{-1}) 3785.70 (ν_{O-H} for −COOH), 3434.59 ($\nu_{O-H\ phenolic}$), 3070.60 ($\nu_{Ar\ C-H}$), 2918.70–2851.00 ($\nu_{AliphaticC-H}$), 1696.27 ($\nu_{C=O}$ for −COOH), 1626.84 ($\nu_{C=N,\ strong}$), 1597.30–1465.20 ($\nu_{Ar\ C=C}$), 774.52 (ν_{C-S-C}). ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) 13.32 (s, 1H, −COO**H**, broad), 12.83 (s, 1H, ArO−**H**), 9.01 (s, 1H, −C**H**=N), 7.92 (d, 1H, J = 2.4 Hz, Ar−**H**), 7.70 (dd, 1H, J = 8.8, J = 2.4 Hz, Ar−**H**), 7.45 (d, 1H, J = 5.2 Hz, Th−**H**), 7.41–7.33 (m, 3H, Ar−**H**), 7.18 (d, 1H, J = 7,6, Ar−**H**), 7.09 (dd, 1H, J = 8.8, J = 3.6 Hz, Ar−**H**), 6.97 (d, 1H, J = 8.4 Hz, Th−**H**), 2.29 (s, 3H, −C**H$_3$**). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) 169.95, 164.09, 160.12, 144.80, 143.08, 135.08, 132.07, 131.09, 130.25, 129.88, 129.01, 128.88, 125.72, 125.22, 123.14, 119.84, 117.89, 115.78, 19.35. Elemental anal. calcd. for $C_{19}H_{15}NO_3S$: C, 67.64; H,4.48; N, 4.15; O, 14.23; S, 9.50%. Found C, 67.15; H, 4.49; N, 4.16; S, 9.29%.

3. Theoretical details

The entire set of calculations was performed by DFT level on a personal computer using the ChemDraw Professional 16 Individual ASL SN Win [35], Gaussian 09 program [36] and GaussView 5.0.8 [37]. The theoretical calculations for the compound **(5)** were carried out using DFT (Density Functional Theory)/B3LYP (Becke's three parameter exact exchange-functional (B3) combined with gradient-corrected correlational functional of Lee, Yang, Parr (LYP)) method with the 6-311+G(d, p) basis set [38,39].

In these study firstly, the geometry of the most stable conformation was optimized for compound **(5)** with the Gaussian09 program DFT/B3LYP method at 6-311+G(d, p) level. The optimized geometry was employed to calculate the frequencies in gas phase and solvent media at functional B3LYP method. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) chemical shifts of the title compound



Scheme 1. Synthesis of 2-[(2-hydroxy-5-thiophen-2-yl-benzylidene)-amino]-6-methyl-benzoic acid **(5)**.