Journal of Molecular Structure 1127 (2017) 626–635

Contents lists available at ScienceDirect

Journal of Molecular Structure

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

Synthesis of a new heterocyclic Schiff base ligand "(E)-5-benzoyl-4-phenyl-1-((pyridin-2-ylmethylene) amino) pyrimidin-2(1H)-one": An experimental and computational modeling study

Mecit Ozdemir [a, *], Mehmet Sonmez [b], Fatih Sen [c], Muharrem Dincer [d], Namık Ozdemir [e]

[a] Department of Food Processing, Vocational High School, Kilis 7 Aralik University, Kilis, Turkey
[b] Department of Chemistry, Faculty of Arts & Sciences, Gaziantep University, Gaziantep, Turkey
[c] Department of Opticianry, Vocational High School of Health Services, Kilis 7 Aralik University, Kilis, Turkey
[d] Department of Physics, Faculty of Arts & Sciences, Ondokuz Mayıs University, Samsun, Turkey
[e] Department of Secondary School Science and Mathematics Education, Faculty of Education, Ondokuz Mayıs University, Samsun, Turkey

ARTICLE INFO

Article history:
Received 11 May 2016
Received in revised form
10 August 2016
Accepted 11 August 2016
Available online 12 August 2016

Keywords:
X-ray structure
Schiff base
DFT
Frontier molecular orbitals (FMOs)
NLO

ABSTRACT

In this study, a new heterocyclic Schiff base has been synthesized and characterized using FT-IR, NMR (^{1}H NMR, ^{13}C NMR), UV–Vis, Mass spectroscopies and single-crystal X-ray diffraction method. The molecular geometry obtained from the X-ray structure determination was optimized using Density Functional Theory (DFT/B3LYP) method with the 6-31G+(d, p) basis set in ground state. From the optimized geometry of the title molecule, the geometric parameters (bond lengths, bond angles and torsion angles), vibrational wavenumbers and chemical shifts were computed. In addition, the molecular electrostatic potential (MEP), frontier molecular orbitals (FMOs) and nonlinear optical (NLO) property of this molecule were determined using a DFT protocol at the B3LYP/6-31+G (d, p) level. For the purpose of the structural conformity of the title molecule, the theoretical results were compared with the experimental values. This comparison indicated that the theoretically calculated results are in agreement with the experimental data on the whole.

1. Introduction

For the last past years, the comparison studies of experimental results with theoretically calculated data for the structural conformity of new compounds have increasingly become more popular in the computional and theoretical chemistry. The molecular geometry and spectroscopic property of the novel compounds can be accurately determined by employing instrumental analyses and also theoretical calculation methods. Likewise, the accuracy of the theoretical data can be controlled by superposition of spectrums which are obtained from experimental analyses and theoretically calculated data. Furthermore, the success of theoretical methods may become compatible with experimental measurements [1–3]. From these points of view, Hartree Fock (HF) and Density Functional Theory (DFT) methods have been widely used by physicists to study the electronic structure of molecules. HF and DFT methods calculate a great variety of chemical structures and properties: molecular geometries, nonlinear optical property (NLO), vibrational frequencies, chemical shifts, UV–Vis. absorption frequencies [4–6]. Besides, a quantum mechanical calculation can be carried out using HF and DFT methods. These two theoretical methods provide very good results without running any experimental parameters [7]. However, anyone is prompted to make a comparison between these two approaches, it can be said that DFT gives more accurate outcomes.

Schiff base ligands are generally prepared from primary amines and aldehydes or ketones by the condensation reactions resulting an imine (azomethine) group ((R)–CH=N–) [8]. As is well known, they are the most widely used ligands due to their facile synthesis, remarkable versatility and good solubility in common organic solvents such as ethanol, chloroform, ethyl acetate, acetone etc. [9]. Moreover, Schiff base ligands are an important class of compounds in organic chemistry exhibiting biological and pharmacological activities in many cases [10–14]. Most of Schiff base ligands show biological activities such as antibacterial [15], anticancer [16,17], anti-inflammatory [18], antifungal [19], antitumor [20],

* Corresponding author.
E-mail address: mecitozdemir@kilis.edu.tr (M. Ozdemir).

http://dx.doi.org/10.1016/j.molstruc.2016.08.031
0022-2860/

antiparasitic [21], antiviral [22] and *anti*-HIV [23]. Besides, they have been also used for some applications; sensor [24,25], electrodes [26], conducting polymer [27,28], energy storage [29], enzymatic application [30], solar cell etc [31]. Briefly, Schiff base ligands have still attracted a considerable attention of researchers over the past years due to their wide range of applications.

Herein, we have described the synthesis, characterization, and computional studies of a new heterocyclic Schiff base bearing pyridine and pyrimidine cycles. The title compound was successfully investigated using experimental results and theoretically calculated data. For the experimental studies of the title compound, FT-IR, ^{1}H NMR, ^{13}C NMR, UV–Vis., Mass spectroscopy and Single-crystal X-ray diffraction methods were successfully carried out. Theoretical molecular geometry, vibrational frequencies, NMR chemical shifts were calculated using DFT at the B3LYP/6-31+G (d, p) level. The calculated geometric parameters, vibrational frequencies and NMR chemical shifts were also matched with experimental results.

2. Experimental and theoretical methods

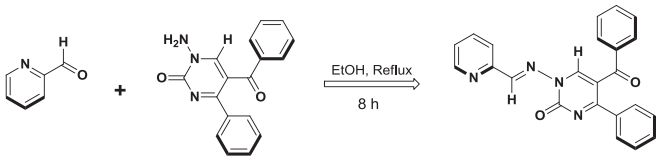
2.1. Materials and instruments

Unless otherwise specified, chemicals were purchased from commercial suppliers and used without further purification. They were 2-formylpyridine, silica gel G, methanol (MeOH), ethanol (EtOH), dichloromethane (DCM), n-hexane (Hex) and ethyl acetate (EtOAc) used as organic solvents. 1-Amino-5-benzoyl-4-phenyl-(1*H*)-pyrimidine-2-on *(N*-Aminopyrimidine) was synthesized as given in the previous report [32].

Structural characterization of the title compound was carried out using NMR (^{1}H, ^{13}C) ESI-MS, FT-IR, UV–Vis. spectroscopies, Elemental analysis and Melting point determination. The ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD 400 NMR spectrometer using deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as an internal standard. FT-IR spectra were recorded on PerkinElmer Spectrum 100 spectrometer. Elemental analysis was performed on a Perkin-Elmer 240 B micro analyzer. Absorption spectra were measured using a Perkin Elmer LAMBDA 850 UV/Vis. Melting points were measured on a RY-1 micro melting point apparatus. The electron impact (ESI) mass spectra (70 eV) were conducted using a Perkin-Elmer detection system.

2.2. Synthesis of Schiff base ligand

Schiff base ligand was synthesized according to the previous reports with a little change [33]. To a stirred solution of 2-formylpyridine (1.08 g, 10 mmol) in anhydrous ethanol (50 ml) in a 250-mL two-necked flask fitted with a condenser was slowly added a solution of *N*-aminopyrimidine (2.91 g, 10 mmol) in anhydrous ethanol (25 ml). The reaction mixture was allowed to heat to reflux temperature and stirred for 8 h under an inert atmosphere. The solvent was then removed via a rotary evaporator at 50 °C, the residue was washed with anhydrous diethyl ether and cold methanol, and this product was purified by silica gel column chromatography using EtOAc/EtOH (1:3, v/v) as an eluent to afford a 3.04 g pure product, an 80% yield of yellow compound. The purity of the compound was checked by thin layer chromatography (TLC) using silica gel G. It was observed that the title compound shows good solubility in polor organic solvents such as methanol, ethanol, acetone, chloroform and ethyl acetate. In addition, the single crystal of title compound suitable for X-ray diffraction was obtained by slow evaporation from ethyl acetate. M.p.: 193 °C. Anal. calcd. (%) For $C_{23}H_{16}N_4O_2$: C, 72.62; H, 4.24; N, 14.73. Found: C, 72.1; H, 4.18; N, 15.01 (see Scheme 1).



Scheme 1. Synthesis of the title compound.

2.3. X-ray crystal structure determination

In order to demonstrate the molecular structure of the title compound, a suitable sample of size 0.030 × 0.320 × 0.450 mm was selected for the crystallographic study. All diffraction measurements were carried out at room temperature (296 K) using graphite monochromated Mo Kα (λ = 0.71073 A) radiation and an STOE IPDS 2 diffractometer. A total of 12797 data were collected in the range $2.6° < \theta < 25°$ by the rotation mode. And then, cell parameters were determined using X-AREA software. In addition, absorption correction ($\mu = 0.22$ mm^{-1}) was achieved conducting the integration method (X-RED software) [34]. The structure of molecule was solved using direct methods (SHELXS-97) implemented in the WinGX [35,36]. All non-hydrogen atoms were anisotropically refined using the full-matrix least squares procedure based on F^2 (SHELXL-97) [37]. And then, hydrogen atoms (H) were geometrically positioned and treated using a riding model. The bond lengths of atoms were fixed at 0.86, 0.93, 0.97 and 0.96 Å for NH, CH, CH_2 and CH_3 atoms, respectively. The crystallographic tool PLATON was also used to analyze the molecular structure of the title compound and to show the results of the theoretical calculations [38]. The details of data collection conditions and the parameters of refinement process are shown in Table 1.

2.4. Theoretical calculations

All calculated results were performed using Gaussian 03

Table 1
Crystallographic data for the title compound.

CCDC deposition no.	983000
Chemical formula	$2(C_{23}H_{16}N_4O_2)$, CH_2Cl_2
Formula weight	845.72
Temperature (K)	296
Wavelength (Å)	0.71073 Mo Kα
Crystal system	Monoclinic
Space group	C 2/c
Unit cell parameters	
$a \neq b \neq c$ (Å)	13.6857 (14), 9.8689 (7), 30.392 (3)
$\alpha = \gamma \neq \beta$ (°)	90.00, 92.291 (8)
Volume (Å^3)	4101.6 (7)
Z	4
Calculated density (Mg/m^3)	1.370
μ (mm^{-1})	0.215
F_{000}	1752
Crystal size (mm)	0.030 × 0.320 × 0.450
h_{min}, h_{max}	−16, 16
k_{min}, k_{max}	−11, 11
l_{min}, l_{max}	−33, 36
Theta range for data collection (°)	$2.6 \leq \theta \leq 25$
Measured reflections	12797
Independent/observed reflections	3598
Refinement method	Full-matrix least-squares on F^2
wR (F^2)	0.115
R_{int}	0.076
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.26, −0.32