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A comparative study on 4-(4-(3-mesityl-3-methylcyclobutyl)thiazole-2-yl)-1-thia-4-azaspiro[4.5]decan-3-one: Experimental and density functional methods

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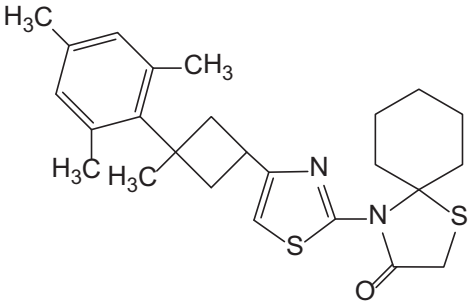
HIGHLIGHTS

- A novel cyclobutane compound was synthesized.
- It was brought to light the molecular structure by X-ray diffraction.
- The compound was characterized by FT-IR and NMR spectroscopies.
- Geometric parameters, vibrational frequencies and chemical shifts were calculated by DFT methods.
- Experimental data was supported by theoretical and literature values.

GRAPHICAL ABSTRACT



X-Ray Structure – DFT Studies – IR and NMR Spectroscopies

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ABSTRACT

In the present study, combined experimental and computational study on molecular structure and spectroscopic assignments of title compound has been reported. The crystal was synthesized and its molecular structure brought to light by X-ray single crystal structure determination method. The spectroscopic properties of the compound were examined by FT-IR and NMR (^{1}H and ^{13}C) techniques. FT-IR spectrum in solid state was observed in the region 4000–400 cm^{-1}. The ^{1}H and ^{13}C NMR spectra were recorded in Acetone-d_6 and $CDCl_3$ solvents. The molecular geometry were those obtained from the X-ray structure determination was optimized using Density Functional Theory (DFT/B3LYP) method with the 6-31G(d, p) and 6-31+G(d, p) basis sets in ground state. From the optimized geometry of the molecule, geometric parameters (bond lengths, bond angles and torsion angles), vibrational assignments and chemical shifts of the title compound have been calculated theoretically and compared with the experimental data.

Introduction

Researchers in areas of crystallography bring to light the molecular structure of a compound by X-ray, neutron and electron diffractions. Although there are different advantages one from the others, today, the most commonly used method is X-ray diffraction. It used to determine their molecular geometry from organic compounds to metal complexes with high accuracy. In order to support the experimental data, it draws on quantum chemical computational methods. It is a well-known fact that the Density Functional Theory (DFT) is the most popular method in computational chemistry for the past 10 years. The electronic structure and spectroscopic assignments of a molecule which given

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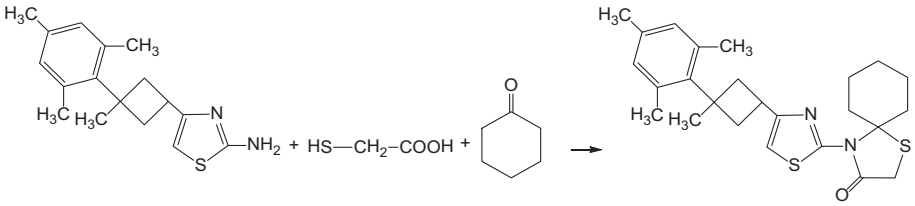

Scheme 1. Synthetic pathway for the synthesis of the target compound.

Table 1
Crystal data and structure refinement parameters for the title compound.

CCDC deposition no.	1031981
Chemical formula	$C_{25}H_{32}N_2OS_2$
Formula weight	440.65
Temperature (K)	296
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	Pbca
Unit cell parameters	
$a \neq b \neq c$ (Å)	12.2181 (10), 21.6835 (17), 17.9853 (16)
$\alpha = \gamma = \beta$ (°)	90
Volume (Å^3)	4764.9 (7)
Z	8
Calculated density (Mg/m^3)	1.229
μ (mm^{-1})	0.24
F_{000}	1888
Crystal size (mm)	0.350 × 0.153 × 0.030
h_{min}, h_{max}	−13, 13
k_{min}, k_{max}	−24, 24
l_{min}, l_{max}	−19, 20
θ_{max} θ_{min} (°)	23.7, 1.9
Measured reflections	23,707
Independent reflections	3605
Refinement method	Full-matrix least-squares on F^2
Goof = S	0.93
$R[F^2 > 2\sigma(F^2)]$	0.079
$wR(F^2)$	0.093
R_{int}	0.243
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.16, −0.16

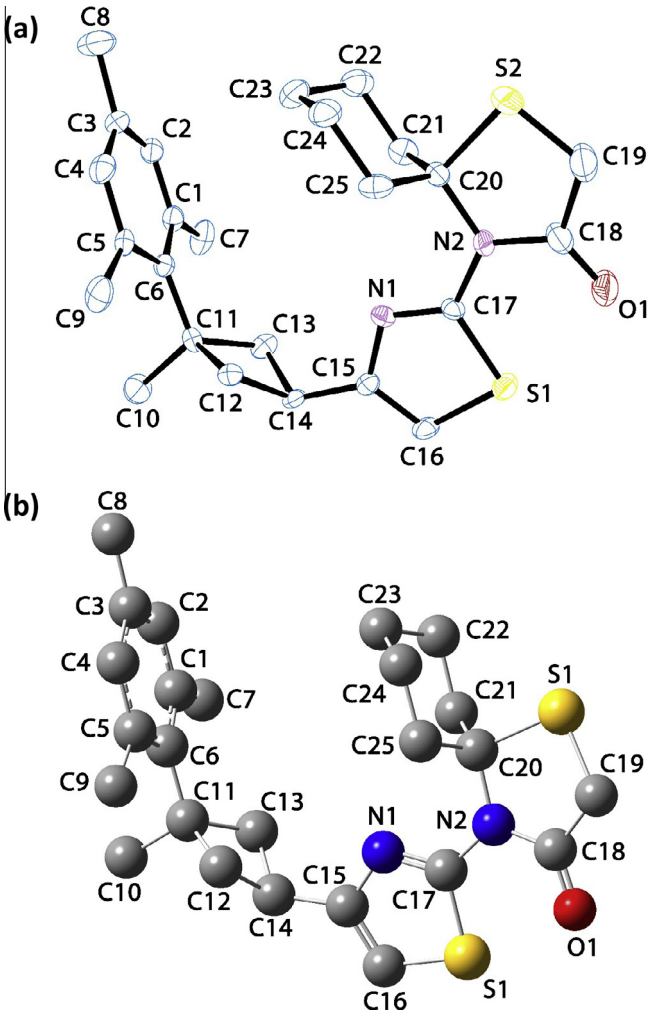

Fig. 1. (a) A view of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. (b) The theoretical geometric structure of the title compound (B3LYP/6-31+G(d, p) level). Hydrogen atoms omitted for clarity.

molecular geometry, have calculated with this method. DFT provides a variety of methods such as: LSDA, BPV86, and B3LYP. B3LYP stands for Becke 3-Parameter (Exchange), Lee, Yang and Parr (correlation; density functional theory) [1,2]. B3LYP has attracted considerable attention due to their compatible results with the experimental data in the fields such as physics, chemistry and materials science.

Thiazole and its derivatives have biological significance, e.g., they are found in the vitamin B1 molecule and in coenzyme cocarboxylase [3]. The penicillin molecule also contains a thiazolidine ring. 2-Aminothiazoles are known mainly as biologically active compounds with a broad range of activity and as intermediates in the synthesis of antibiotics and dyes [4]. Not only most popular anticancer drugs carboplatin and lobaplatin; but enloplatin, mibaplatin, sebriplatin, and zenitplatin are also cyclobutane derivatives and are used as effective anticancer drugs [5]. In the light of the effects given above, the compounds containing cyclobutane and thiazole functionalities in one molecule have seen to be important.

To the best of our knowledge, the title compound is a novel compound firstly synthesized in our laboratories by us and there is no any information present in literature about its molecular and vibrational spectroscopic properties.

Our work makes up of the synthesis, molecular structure and spectroscopic characterization of the title compound. In the paper, a combination of experimental and theoretical studies has been given. The molecular structure of a compound brought to light by X-ray diffraction method. The Fourier Transform Infrared (FT-IR) and Nuclear Magnetic Resonance (NMR) (^{1}H and ^{13}C) spectra were recorded. Following, the initial guess of the compound was first obtained from the X-ray coordinates was optimized by Density Functional Theory (DFT) with the Becke 3-Parameter-Lee–Yang–Parr (B3LYP) functional, where the 6-31G(d, p) and 6-31G+(d, p) basis sets were employed. Theoretical calculations were also carried out for spectral assignments of the optimized geometry of the synthesized compound. The calculated molecular structures (geometric parameters), theoretical scaled vibrational