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Tridentate SNS pincer type ligand: Synthesis, structural and spectroscopic analysis of a novel pyridine and *m*-xylene compound with thioether-bridge

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ABSTRACT

Taking into account the broad spectrum of catalytic and bioactivity, it has been importance the compounds containing pyridine in the molecular structure. Here we report the synthesis, structural and spectroscopic analysis of a novel compound (the title compound) containing pyridine and *m*-xylene with thioether-bridge. The molecular structure of compound brought to light by X-ray single crystal structure determination. The spectroscopic properties of the compound were examined by FT-IR and NMR (^{1}H and ^{13}C) techniques. FT-IR spectra of the target compound in solid state was observed in the region 4000–400 cm^{-1}. The ^{1}H and ^{13}C NMR spectra were recorded in DMSO-d$_6$ solution. 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) basis set 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 theoretically calculated and compared with the experimental data.

1. Introduction

Over the last century, nitrogen heterocycles are an important class of compounds that have been extensively studied due to their numerous applications and biological activities. Among the heterocyclic compounds containing nitrogen atom, pyridine, that is, a six-membered heterocyclic ring, and it is structurally similar to the benzene, with one methine group (=CH−) replaced by a nitrogen atom. Pyridine derivatives have been shown to exhibit a broad range of activities including anti-HlV [1], antiviral [2], anticancer [3,4], anticonvulsant [4,5], antimicrobial [6–8], antifungal and antimycobacterial activities [9]. In addition to that pyridine cores appear in many naturally occurring bioactive compounds, they also produced synthetically using various methods. Most known of these methods are Chichibabin synthesis [10], Dealkylation of alkyl pyridines [11], Hantzsch pyridine synthesis [12], and Bönnemann cyclization [13].

It is known that the thioether is a functional group in organosulfur chemistry and symbolize with the connectivity R^1-S-R^2. Thioethers were also called sulfides and structurally similar to the ethers, which have a sulfur instead of an oxygen atom between the two R. Most of the thioether derivatives are known to be associated with a broad spectrum of bioactivity, such as antiviral [14] and insecticidal [15]. Also, the oxidation products of thioethers, namely sulfoxides and sulfones, are widely used as drug, agrochemical, and synthetic intermediates [16–18]. Moreover, Thioether ligands containing a pyridine group and theirs tridentate SNS pincer type complexes have attracted much interest because of their good activities in a wide range of catalytic processes [19].

The increasing studies on thioether ligand and the various properties examined in studies done on this subject (catalytic processes [20,21], biological activities [22] etc.) encouraged us to study in this area.

According to above passages, pyridine derivatives and thioether-

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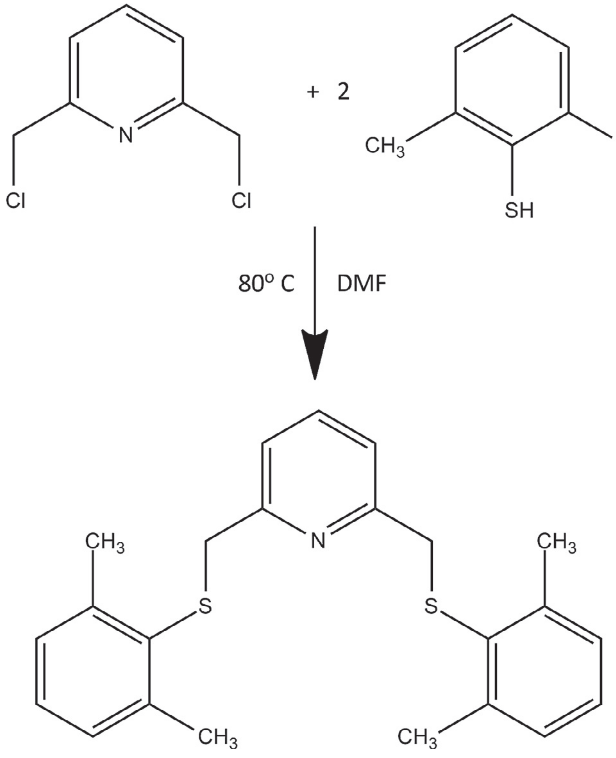
bridge/sulfides compounds have attracted considerable attention over many years, due to their important catalytic and biological activities. The title compound is a novel compound firstly synthesized in our laboratories by us.

Determination of the structural and spectroscopic properties of compounds using both experimental techniques and theoretical methods has been attracted interest for many years. There are many studies on this subject in the literature [23–40], etc. DFT method was used in these studies due to the fact that it has great accuracy in reproducing the experimental values for the geometries, vibrational frequencies, chemical shifts, etc. Literature survey reveals that to the best of our knowledge, no experimental and computational study on the title compound has been published in the literature yet. The aim of the present work was to describe and characterize both experimentally and theoretically the molecular structure, vibrational frequencies and chemical shifts of the compound. In experimental study, the molecule was prepared and characterized by single-crystal X-ray diffraction, FT-IR and NMR techniques. In theoretical study, the molecular structure of the title compound in the ground state have been calculated using the density functional method (DFT) (B3LYP) with 6-31 + G(d, p) basis set. The calculated geometric parameters (bond lengths, bond angles, torsion angles), vibrational assignments and chemical shifts compared with their experimental data.

2. Experimental and theoretical methods

2.1. Synthesis of the title compound

A mixture of 2,6-dimethylbenzenethiol (0.276 g, 2 mmol) and 2,6-bis(chloromethyl)pyridine (0.176 g, 1 mmol) was stirred at 80 °C for further 48 h in DMF (20 ml) in the presence potassium carbonate (0.542 g, 4 mmol) and potassium iodide (0.166 g, 1 mmol). (Scheme 1). After cooling to room temperature, the mixture was poured into ice water and was extracted three times with chloroform. The organic phase was evaporated and recrystallized in diethylether-methanol (4:1). It was obtained as a yellow crystalline (76%); mp.82–83 °C. Anal. Calc. For $C_{23}H_{25}NS_2$ (379.14): C, 72.78: H, 6.64: N, 3.69: S, 16.89%. Found: C, 72.71: H, 6.65: N, 3.94: S, 16.51%.



Scheme 1. Synthesis of title compound.

2.2. General remarks

All reactions involving thiols were carried out under nitrogen atmosphere. All the reactants and solvents (95–99% purity) were purchased from Aldrich and Merck and used without further purification. Elemental analyses were measured on a CHNS analyzer Thermo Scientific Flash EA 2000. FT-IR spectra were measured on a Perkin-Elmer Spectrum 100 FTIR (ATR sampling accessory) spectrophotometer. The NMR analysis was performed at room temperature on sample dissolved in DMSO-d_6 with TMS as an internal standard. ^{1}H and ^{13}C NMR spectra were acquired using a Bruker High Performance Digital FT-NMR (400 MHz) spectrometer.

2.3. Crystal structures determination and refinement

A suitable sample of size 0.660 × 0.360 × 0.160 mm was selected for the crystallographic study. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated Mo Kα (λ = 0.71073 Å) radiation and an STOE IPDS 2 diffractometer. A total of 20944 reflections with [1.8° < θ < 28.7°] were collected in the rotation mode and cell parameters were determined by using X-AREA software [41]. Absorption correction (μ = 0.26 mm^{-1}) was achieved by the integration method via X-RED software [41]. The structure was solved by direct methods using SHELXS-97 [42]. All non-hydrogen atoms were refined anisotropically by the full-matrix least squares procedure based on F^2 using SHELXL-97 [43]. All H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.93, 0.97 and 0.96 Å for CH, CH_2 and CH_3 atoms, respectively. The general purpose crystallographic tool PLATON [44] was used for the

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

CCDC deposition no.	1440538
Chemical formula	$C_{23}H_{25}NS_2$
Formula weight	379.56
Temperature (K)	296
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell parameters	
$a \neq b \neq c$ (Å)	8.4469 (8), 22.7961 (12), 11.1856 (8)
$\alpha = \gamma \neq \beta$ (°)	90, 101.807 (6)
Volume (Å^3)	2108.3 (3)
Z	4
Calculated density (Mg/m^3)	1.196
μ (mm^{-1})	0.26
F_{000}	808
Crystal size (mm)	0.160 × 0.260 × 0.660
h_{min}, h_{max}	−8, 10
k_{min}, k_{max}	−27, 27
l_{min}, l_{max}	−13, 13
θ_{max} θ_{min} (°)	25.0, 1.8
Measured reflections	9903
Independent reflections	3672
Refinement method	Full-matrix least-squares on F^2
Goof = S	0.80
$R[F^2 > 2\sigma(F^2)]$	0.040
$wR(F^2)$	0.077
R_{int}	0.042
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e/Å^3)	0.16, −0.15