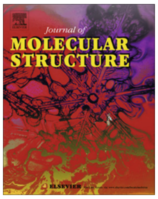
Journal of Molecular Structure 1048 (2013) 382–391

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Structure

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



Quantum chemical, spectroscopic and X-ray diffraction studies of 5-methoxy-2-({4-[3-methyl-3-mesityl-cyclobutyl]-thiazol-2-yl}-hydrazonomethyl)-phenol

Hanife Saraçoğlu [a,*], Alaaddin Cukurovali [b]

[a] Department of Middle Education, Educational Faculty, Ondokuz Mayis University, 55139 Kurupelit, Samsun, Turkey
[b] Department of Chemistry, Faculty of Sciences, Firat University, 23119 Elazig, Turkey

HIGHLIGHTS

- We investigate molecular and crystal structure of the new hydrazone derivative.
- Crystal structure is stabilized by N—H···O and C—H···π intermolecular hydrogen bonds.
- The title compound is a good candidate as a nonlinear optical material.

ARTICLE INFO

Article history:
Received 30 April 2013
Received in revised form 4 June 2013
Accepted 4 June 2013
Available online 10 June 2013

Keywords:
Computational chemistry
X-ray structure determination
NMR spectroscopy
Frontier molecular orbitals
Molecular electrostatic potential

ABSTRACT

The title molecule, 5-methoxy-2-({4-[3-methyl-3-mesityl-cyclobutyl]-thiazol-2-yl}-hydrazonomethyl)-phenol (C_{25} H_{29} N_3 O_2 S), was prepared and characterized by elemental analysis, ^{1}H NMR, ^{13}C NMR, IR and X-ray single-crystal determination. The compound crystallizes in the monoclinic space group $P2_1/c$ with $a = 18.9647(4)$ Å, $b = 11.0203(3)$ Å, $c = 10.8562(2)$ Å and $\beta = 91.546(2)°$. In addition to the molecular geometry from X-ray determination, vibrational frequencies and gauge, including atomic orbital (GIAO) ^{1}H and ^{13}C NMR chemical shift values of the title compound in the ground state, were calculated using the Hartree–Fock and density functional methods with the 6-31G(d, p) basis set. The calculated results show that the optimized geometries can well reproduce the crystal structure. Besides, the theoretical vibrational frequencies and chemical shift values show good agreement with experimental values. The calculated first hyperpolarizability of the title compound are greater than those of urea. DFT calculations of the molecular electrostatic potentials, frontier molecular orbitals and thermodynamic properties of the title compound were carried out at the B3LYP/6-31G(d, p) level of theory.

1. Introduction

Schiff bases constitute an interesting class of chelating agents, capable of coordination with one or more metal ions to form mononuclear as well as polynuclear metal complexes [1,2]. Some of these applications could be found in analytical chemistry and serve as biochemical models [3,4]. Most Schiff bases have antibacterial, anticancer, anti-inflammatory and antitoxic activities and the sulfur-containing Schiff bases are particularly effective [5]. Various thiazole derivatives show herbicidal, anti-inflammatory, antimicrobial and antiparasite activity [6,7] and also liquid crystal properties [8]. The thiazole ring is known to be a part of vitamin B1, cocarboxylase, and the cyclic system of penicillin [9]. Thiazole itself and its derivatives are of importance in biological systems as anti-inflammatory, analgesic agents and inhibitors on lipoxygenase activities [10,11]. Various hydrazone ligands possess strong bactericidal, herbicidal, insecticidal and fungicidal properties [12]. In addition, hydrazones have analytical applications [13–15]. Hydrazones have interesting ligational properties due to the presence of several potential coordination sites [16], and both transition and non-transition metal complexes of these ligands have been synthesized earlier. Structures of the most recognized of the starting substances and the title compound are given in Scheme 1.

These ligands containing cyclobutane, thiazole and Schiff base functions in their molecules seem to be suitable candidates for further chemical modifications and may be pharmacologically active and useful as ligands in coordination chemistry. Taking into account the above observations this compound has been synthesized in a similar manner of our ongoing biological active compounds research program [17].

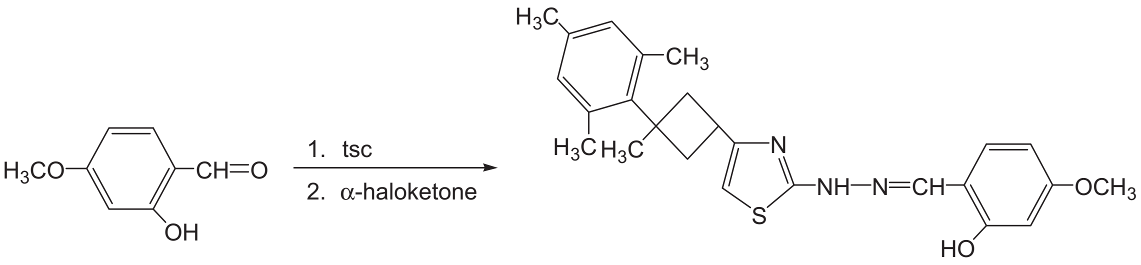
In this study, we present results of a detailed investigation of the synthesis and structural characterization of 5-methoxy-2-({4-

---

* Corresponding author. Address: Department of Middle Education, Educational Faculty, Ondokuz Mayis University, TR-55139 Kurupelit, Samsun, Turkey. Fax: +90 362 4576081.

E-mail addresses: hanifesa@omu.edu.tr, hanifesaracoglu@yahoo.com (H. Saraçoğlu).

0022-2860/$ - see front matter © 2013 Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.molstruc.2013.06.009



Scheme 1. Reaction sequence for synthesis of the title compound.

[3-methyl-3-mesityl-cyclobutyl]-thiazol-2-yl}-hydrazonomethyl)-phenol by using single crystal X-ray, ^{1}H NMR, ^{13}C NMR and quantum chemical methods. The vibrational assignments of the title compound in the ground state have been calculated by using the Hartree–Fock (HF) and DFT(B3LYP) methods with 6-31G(d, p) basis set. The structural geometry, molecular electrostatic potential (MEP) and frontier molecular orbitals (FMO) properties of the title compound were studied at the B3LYP/6-31G(d, p) level. A comparison of the experimental and theoretical spectra can be very useful in making correct assignments and understanding the basic chemical shift molecular structure relationship. And so, these calculations are valuable for providing insight into molecular analysis.

2. Experimental

2.1. Synthesis of the title compound

To a solution of 2-hydroxy-4-methoxy-benzaldehyde (1.5215 g, 10 mmol) in 50 mL of ethanol, thiosemicarbazide (tsc) (0.9113 g, 10 mmol) in 20 mL of absolute ethanol was added and the mixture was refluxed. End of the reaction was determined by monitoring the course of the reaction with IR spectroscopy. Subsequently, a solution of 1-methyl-1-mesityl-3-(2-chloro-1-oxoethyl) cyclobutane (α-haloketone) (2.6479 g, 10 mmol) in 20 mL of absolute ethanol was added dropwise. After addition of α-haloketone, the temperature was raised to 323–328 K and stirred at this temperature for 2 h. The solution was cooled to room temperature and then made alkaline with an aqueous solution of NH_3 (5%), and white precipitate separated by suction. washed with aqueous NH_3 solution several times and dried in air. Suitable single crystals for crystal structure determination were obtained by slow evaporation of its ethanol solution: Brilliant brownish red crystals. Overall yield: 67%. M.p.: 486 K (EtOH).

2.2. Crystallography

The data collection was performed at 296 K on a Stoe-IPDS-2 diffractometer equipped with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The structure was solved by direct methods using SHELXS-97 and refined by a full-matrix least-squares procedure using the program SHELXL-97 [18]. All non-hydrogen atoms were easily found from the different Fourier maps and refined anisotropically. All hydrogen atoms were included using a riding model and refined isotropically with CH = 0.93 (for phenyl groups), CH_2 = 0.97, CH_3 = 0.96, CH = 0.98, NH = 0.86 and OH = 0.82 Å. U_{iso}(H) = 1.2U_{eq} (1.5 U_{eq} for methyl group). Details of the data collection conditions and the parameters of the refinement process are given in Supplementary material.

2.3. Computational methods

The molecular structure of the title compound in the ground state (*in vacuo*) was optimized by HF and B3LYP methods with 6-31G(d, p) basis set. For the modeling, the initial guess of the title compound was first obtained from the X-ray coordinates. Then vibrational frequencies for optimized molecular structure were calculated and scaled by 0.8929 [19] and 0.9885 [20], respectively. The geometry of the title compound, together with that of tetramethylsilane (TMS), was fully optimized. ^{1}H and ^{13}C NMR chemical shifts were calculated within GIAO approach [21,22] applying B3LYP and HF methods [23] with 6-31G(d, p) basis set. All the calculations were performed by using Gauss-View molecular visualization program [24] and Gaussian 03 program package [25] on personal computer without specifying any symmetry for the title molecule.

The molecular electrostatic potential (MEP) was evaluated to research the reactive sites of the title compound using B3LYP/6-31G(d, p) method. On the basis of vibrational analysis, the thermodynamic properties of the molecule at different temperatures were calculated. In addition, frontier molecular orbital (FMO) analysis was carried out with the same level.

3. Results and discussion

3.1. Description of the crystal structure

The title compound, an ORTEP [26] view of which is shown in Fig. 1, crystallizes in the monoclinic space group *P2₁/c* with four molecules in the unit cell. The asymmetric unit in the crystal structure contains only one molecule.

The title compound contains thiazole, hydrazone, mesityl, 5-methoxy phenol and cylobutane moieties. The thiazole and 5-methxy phenol rings are planar with maximum deviations of −0.0039(15) and −0.0053(18) Å, respectively. The dihedral angles between the mesityl plane A (C1—C6), the cyclobutane plane B (C10—C14), the thiazole plane C (S1/N1/C15—C17) and the phenol plane D (C19—C24) are 43.00 (9)° (A/B), 77.86 (6)° (A/C), 83.02 (6)° (A/D), 36.75 (12)° (B/C), 46.29 (11)° (B/D) and 14.16 (13)° (C/D).

In the thiazole ring, the S1—C16 and S1—C17 bond lengths (Table 2) are shorter than the accepted value for an S-Csp^2 single bond with 1.76 Å, resulting from the conjugation of the electrons of the

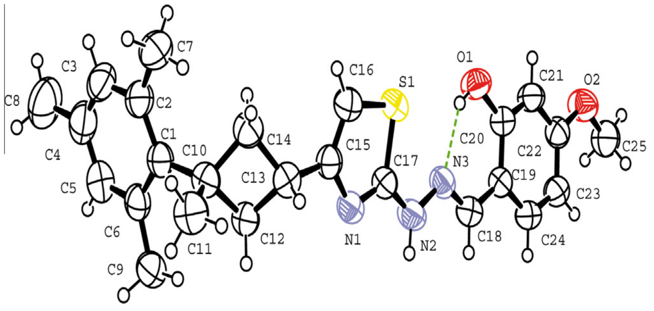


Fig. 1. Ortep III diagram of the title compound. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.