



Contents lists available at SciVerse ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

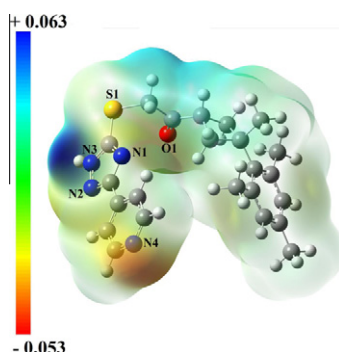
1-(3-Methyl-3-mesityl)-cyclobutyl-2-(5-pyridin-4-yl-2H-[1,2,4]triazol-3-ylsulfanyl)-ethanone: X-ray structure, spectroscopic characterization and DFT studies

Ersin İnkaya^{a,*}, Muharrem Dinçer^a, Öner Ekici^b, Alaaddin Cukurovali^b^a Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Kurupelit, Samsun, Turkey^b Department of Chemistry, Faculty of Sciences, Firat University, 23200 Elazığ, Turkey

HIGHLIGHTS

- ▶ 1,2,4 Triazole; X-ray single crystal diffraction.
- ▶ Density functional theory (DFT).
- ▶ Molecular electrostatic potential (MEP) distribution, frontier molecular orbitals (FMOs).
- ▶ Non-linear optical properties of the title compound have been calculated.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 8 March 2012

Received in revised form 8 September 2012

Accepted 14 September 2012

Available online 6 October 2012

Keywords:

X-ray structure determination

IR and NMR spectroscopy

DFT calculations

[1,2,4] Triazole

Cyclobutane

Non-linear optical properties

ABSTRACT

The triazole compound 1-(3-Methyl-3-mesityl)-cyclobutyl-2-(5-pyridin-4-yl-2H-[1,2,4]triazol-3-ylsulfanyl)-ethanone, (C₂₃H₂₆N₄O₅), was characterized by X-ray single crystal diffraction technique, IR NMR spectroscopy and quantum chemical computational methods as both experimental and theoretically. The compound crystallizes in the monoclinic space group *P*2₁/*c* with *Z* = 4. The molecular geometry was also optimized using density functional theory (DFT/B3LYP) method with the 6-311G(d,p) basis set in ground state and compared with the experimental data. The computed vibrational frequencies are used to determine the types of molecular motions associated with each of the experimental bands observed. The results of the calculations were applied to simulate spectra of the title compound, which show excellent agreement with observed spectra. Data of the title compound display significant structure correlation and provide the basis for future design of efficient materials having the derivatives of 1,2,4-triazole. From the optimized geometry of the molecule, vibrational frequencies, gauge-independent atomic orbital (GIAO) ¹H and ¹³C NMR chemical shift values, molecular electrostatic potential (MEP) distribution, non-linear optical properties and frontier molecular orbitals (FMOs) of the title compound were performed at B3LYP/6-311G(d,p). On the basis of theoretical vibrational analyses, the thermodynamic properties (standard heat capacities, standard entropies, and standard enthalpy changes) of the title compound at different temperatures have been calculated, revealing the correlations between $C_{p,m}^0$, S_m^0 , ΔH_m^0 and temperatures. The predicted non-linear optical properties of the title compound are much greater than those of urea. Data of the title compound display significant structure-correlation and provide the basis for future design of efficient materials having the derivatives of 1,2,4-triazole.

© 2012 Elsevier B.V. All rights reserved.

* Corresponding author. Tel.: +90 362 3121919x5256; fax: +90 362 4576081.

E-mail address: ersin.inkaya@oposta.omu.edu.tr (E. İnkaya).

Introduction

The chemistry and structure of heterocyclic compounds has been an active field of study for a long time. The synthesis of 1,2,4-triazoles and investigation of their chemical and biological behavior have gained more importance in recent decades for biological, medicinal and agricultural reasons. 1,2,4-triazole and 1,2,4-triazol-3-one are reported to exhibit a broad spectrum of biological activities such as antifungal, antimicrobial, hypoglycemic, antihypertensive, analgesic, antiparasitic, antiviral, anti-inflammatory, antitumor and anti-HIV properties [1–7]. Substituted 1,2,4-triazoles have also been applied as ligands to obtain metal complexes with specific properties [8–10]. The title triazol compound is a novel compound firstly synthesized in our laboratories by us.

It is well known that derivatives of triazole may exist in several tautomeric forms. Even in the case of unsubstituted triazole molecule it is possible to find two tautomers namely 1,3,4- and 1,2,4-triazole differing in location of hydrogen atom and double bonds within ring [11–13]. Presence of substituents and formation of intermolecular hydrogen bonds can influence tautomeric equilibrium [14,15]. In particular, it was found that disubstituted derivatives of 1,2,4-triazole exist in 1H tautomeric form if electron-accepting substituents occupy the third position, and electron-donating substituents reside in the fifth position of 1,2,4-triazole ring [16]. In the case of symmetric disubstituted derivatives, triazole ring exists as a mixture of 1H and 2H tautomers. Therefore determination of the most stable tautomers is also very important for this type of biologically active compounds.

Due to the developments in computational chemistry over the past decade, research into the theoretical modeling of drug design, functional material design, etc., has become much more mature. Many important chemical and physical properties of biological and chemical systems can be predicted from first principles using various computational techniques [17]. In recent years, density functional theory (DFT) has been a shooting star in theoretical modeling. The development of better and better exchange–correlation functional has made it possible to calculate many molecular properties with accuracy comparable to traditional correlated *ab initio* methods, at more favorable computational cost [18]. A survey of the literature revealed that DFT has great accuracy in reproducing the experimental values for the geometry, dipole moment, vibrational frequency, etc. [19–25].

In this paper, we report the synthesis, characterization and crystal structure of 1-(3-Methyl-3-mesityl)-cyclobutyl-2-(5-pyridin-4-yl-2H-[1,2,4]triazol-3-ylsulfanyl)-ethanone, (C₂₃H₂₆N₄OS), as well as theoretical studies using the DFT/B3LYP/6-311G(d,p) method. The aim of the present work was to describe and characterize the molecular structure, vibrational properties and chemical shifts of the title compound, both experimentally and theoretically. 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. Molecular electrostatic potential (MEP), frontier molecular orbitals (FMOs), thermodynamic parameters and non-linear optical properties of the title compound were studied at the B3LYP/6-311G(d,p) level. We also make comparisons between experimental and calculated values.

Experimental and theoretical methods

General remarks

The melting points were determined in open capillary tubes on a digital Gallenkamp melting point apparatus and are uncorrected. The IR spectrum of the title compound was recorded in the range 4000–400 cm⁻¹ using a Mattson 1000 FT-IR spectrometer with

KBr pellets. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were recorded on a Varian-Mercury-Plus 400 MHz spectrometer using TMS as internal standard and CDCl₃ (Chloroform) as solvent.

Synthesis

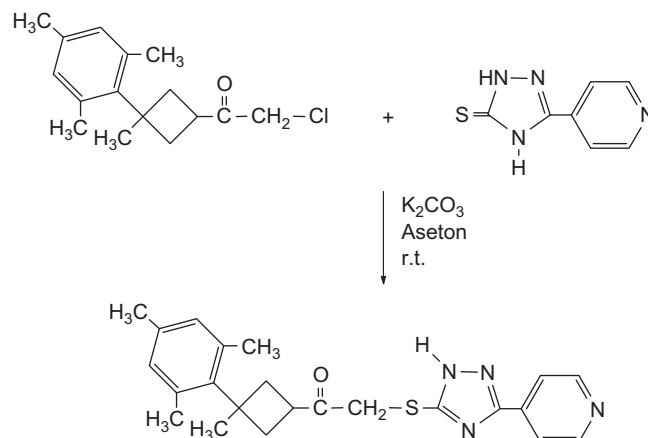
The synthesis of the title compound was simply carried out in the following reaction Scheme 1. A solution of 0.2227 g (1 mmol) of 2-Chloro-1-(3-Methyl-3-mesityl-cyclobutyl)-ethanone was dissolved in 50 mL of dry acetone containing 1 mmol K₂CO₃. To this solution, 0.1782 g (1 mmol) of 5-pyridin-4-yl-2,4-dihydro-[1,2,4]triazole-3-thione solution in 20 mL dry acetone was added dropwise in 2 h period at room temperature with stirring. The compound thus obtained was filtered, washed with copious water and crystallized from ethanol. Light yellow crystals. Yield: 88%. M.p.: 486 K (EtOH).

Crystallography

The single-crystal X-ray data was collected on a STOE diffractometer with an IPDS(II) image plate detector. All diffraction measurements were performed at room temperature (296 K) using graphite monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Reflection data was recorded in the rotation mode using the ω scan technique by using X-AREA software [26]. Unit cell parameters were determined from least-squares refinement of setting angles with θ in the range $2.6 \leq \theta \leq 26$. The structure was solved by direct methods using SHELXS-97 [27] implemented in WinGX program suit. The refinement was carried out by full-matrix least-squares method on the positional and anisotropic temperature parameters of the non-hydrogen atoms, or equivalently corresponding to 263 crystallographic parameters, using SHELXL-97 [28]. All H atoms were positioned geometrically and treated using a riding model, fixing the bond lengths at 0.86, 0.93, 0.97 and 0.96 Å for NH, CH, CH₂ and CH₃ atoms, respectively. Data collection: X-AREA, cell refinement: X-AREA, data reduction: X-RED32 [29]. Details of the data collection conditions and the parameters of refinement process are given in Table 1. The general-purpose crystallographic tool PLATON [30] was used for the structure analysis and presentation of the results. The molecular graphic were done using ORTEP-3 for Windows [31]. Details of the data collection conditions and the parameters of the refinement process are given in Table 1.

Theoretical

The molecular structure of the compound in the ground state (*in vacuo*) was optimized using density functional theory (DFT/B3LYP) [32,33] method with the 6-311G(d,p) [34] basis set. All



Scheme 1. The synthetic route for the title compound.

Download English Version:

<https://daneshyari.com/en/article/1235055>

Download Persian Version:

<https://daneshyari.com/article/1235055>

[Daneshyari.com](https://daneshyari.com)