



Structural and spectral speciation on methyl 2-(3-(furan-2-carbonyl)thioureido)benzoate: A comparative experimental and theoretical study



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HIGHLIGHTS

- A one-pot synthesis of methyl 2-(3-(furan-2-carbonyl)thioureido)benzoate is reported.
- X-ray structure analysis confirmed a trans-cis geometry in the thiourea moiety.
- DFT-B3LYP/6-311G(d,p) method showed good correlation with the experimental X-ray and vibrational, NMR and electronic spectral data.
- MEP map confirmed the solid-state interactions.

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ABSTRACT

A new thiourea derivative, methyl 2-(3-(furan-2-carbonyl)thioureido)benzoate (MFCTB) is synthesized and characterized by elemental analysis, FT-IR, FT-Raman, electronic, NMR and single crystal X-ray diffraction study. The compound crystallizes in the orthorhombic space group *Pbca* with *Z* = 8. The molecular geometry was also optimized using density functional theory (DFT) employing B3LYP exchange correlation with the 6-311G(d,p) basis set. The theoretically calculated bond parameters are in good agreement with the experimentally obtained results as reflected by C=S 1.673 (1.668), C=O 1.221 (1.228) Å, bond distances. The infrared spectra of the compound showed four significant vibrations $\delta(\text{N-H})$ (I), $\nu(\text{C-N})$ (II and III) and $\nu(\text{C=S})$ (IV) around 1500, 1300, 1100 and 750 cm^{-1} and matched well with DFT calculated values. The ¹H NMR spectrum of the compound shows mainly three peaks S=C–NH, O=C–NH and O=C–OCH₃ at 13.25 (12.94); 9.25 (8.99) and 3.94 (3.81) ppm, respectively and displayed good correlation while its ¹³C NMR spectrum showed some differences with its theoretical counterpart. Also electronic spectrum of the compound which comprises mainly two bands around 289 and 325 was compared with the theoretical spectrum obtained from time-dependent (TD) DFT and a good agreement is observed. The molecular electrostatic potential (MEP) map shows the negative potential sites are on oxygen, sulphur and nitrogen atoms and the positive potential sites are around the hydrogen atoms.

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1. Introduction

There is considerable interest in the detailed structural studies of substituted thioureas because of their diverse application in different fields. The pharmaceutical importance of substituted thioureas is proved by their wide variety of biological activities such as antibacterial, antifungal, anticancer, anti-tubercular and antiviral [1–5]. A number of N,N'-disubstituted carbonyl thioureas have

been used extensively as commercial fungicides, herbicides and insecticides [6,7]. The inhibitory activity of some pyridazine derivatives carrying thiourea moiety against *Staphylococcus aureus*, *Escherichia coli*, *Candida albicans* and *Candida parapsilosis* has been reported [8]. Thiourea and its derivatives have also been used as effective corrosion inhibitors because sulphur atom is easily protonated in acidic solution [9–11]. These compounds are also used in the separation of platinum group metals [12] and as catalysts in the palladium-catalyzed Suzuki and Heck reactions [13–15]. Nonlinear optical properties displayed by substituted thioureas and their complexes are of great importance as these compounds have found applications in the areas of laser technology, optical

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communication and data storage technology [16–19]. The intramolecular hydrogen interactions between carbonyl oxygen and hydrogen atom of nitrogen is common in N-aryyl-N'-aryyl thioureas [20–23]. Moreover, the hydrogen-bonding ability of the thiourea moiety has extensively been used in construction of anion receptors [24–26]. The structural and conformational properties of many aroyl thioureas have been investigated in recent past [27–34]. Currently, DFT is commonly being used to examine the electronic structure of compounds owing to its accuracy, user friendliness and relative fastness in studying relatively large molecules [35–39]. DFT coupled with TD-DFT calculations are being performed in recent times to establish the nature of orbitals involved in transition processes and to correlate the structural parameters with the spectroscopic properties of the molecule [40–42]. As part of our continuing work on thiourea derivatives [20–22,43], we present here the synthesis, structure and DFT calculations on methyl 2-(3-(furan-2-carbonyl)thioureido)benzoate (MFCTB). The aim of the present work was to describe and characterize the molecular structure, vibrational studies, chemical shifts and electronic transitions of MFCTB, both experimentally and theoretically. A comparative experimental and theoretical study can be very useful in understanding structure–property relationships. Molecular electrostatic potential (MEP) distribution of MFCTB was also studied in order to examine the probable sites for an interaction with electrophilic and nucleophilic species.

2. Experimental

2.1. Synthesis of methyl 2-(3-(furan-2-carbonyl)thioureido)benzoate (MFCTB)

The MFCTB was prepared by reacting furoyl chloride with ammonium thiocyanate to give first furoyl isothiocyanate, which further reacts with methyl anthranilate in acetone in a 1:1 ratio resulting in colourless crystalline solid in 85% yield (Scheme 1).

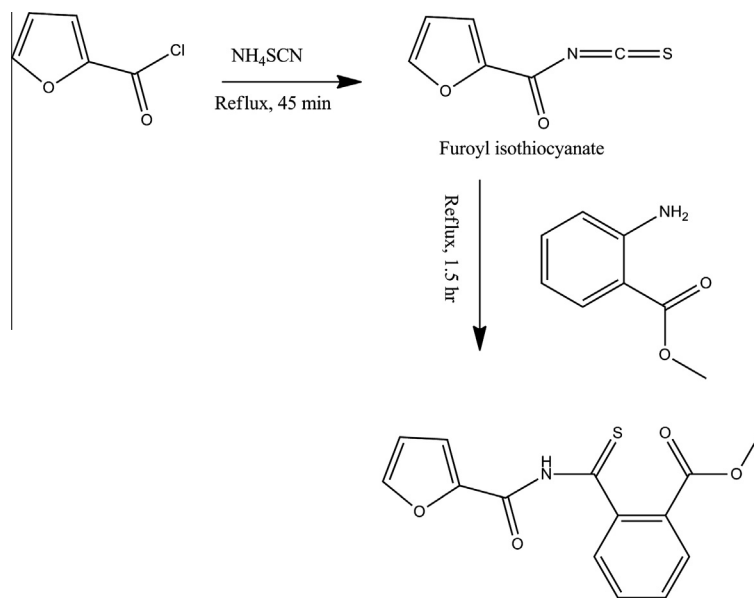
2.1.1. Detailed procedure

A solution of furoyl chloride (0.01 mol, 0.984 mL) in acetone (50 mL) was added drop wise to a suspension of ammonium thiocyanate (0.01 mol, 0.76 g) in acetone (30 mL) and the reaction

mixture was heated to reflux for 30 min. After cooling to room temperature, a solution of methyl anthranilate (0.01 mol, 1.30 mL) in acetone (20 mL) was added to it gradually with constant stirring and the resulting mixture was further refluxed for 1 h. The reaction mixture was poured into five times of its volume of cold water. The solid product obtained on filtration was washed with water and re-crystallized from an ethanol solution. Colourless crystals suitable for X-ray diffraction were obtained in few days on slow evaporation of solvent. Yield 85%, m.p.: 222–223 °C. Anal. Calc. for $C_{14}H_{12}N_2O_4S$: C, 55.25; H, 3.97; N, 9.21%. Found: C, 55.05; H, 3.82; N, 9.11%. FT-IR (KBr, cm^{-1}): 3412, 3129 (N–H), 3034 (aromatic C–H), 2948 (aliphatic C–H), 1709 (ester, C=O), 1684 (C=O), 1605, 1583 (aromatic, C=C), 1541 (thioamide-I), 1345 (thioamide-II), 1131 (thioamide-III), 782 (thioamide-IV). FT-Raman (cm^{-1}): 3409, 3148 (N–H), 3087 (aromatic C–H), 2948 (aliphatic C–H), 1711 (ester, C=O), 1683 (C=O), 1606, 1585 (aromatic, C=C), 1541 (thioamide-I), 1344 (thioamide-II), 1131 (thioamide-III), 781 (thioamide-IV). UV-Visible (λ_{max}/nm) ($\epsilon/M^{-1} - cm^{-1}$) ($CHCl_3$): 325 (59,900), 289.5 (152,000). 1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 13.25 (s, 1H, CSNH), 9.25 (s, 1H, CONH), 8.52–6.62 (m, 3H, C_4H_3O), 8.02–7.30 (m, 4H, C_6H_4), 3.94 (s, 3H, CH_3O). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 178.1 (C=S), 166.4 ($COOCH_3$), 155.5 (C=O), 145.1, 138.6, 132.7, 132.2, 131.0, 126.0, 122.3, 119.2, 118.7, 113.6 (aromatic-C), 52.3 (OCH_3).

2.2. Physical measurements

Elemental analyzes were performed on a CE-440 Exeter Analytical CHN analyzer. The FT-IR spectrum of the MFCTB was recorded as KBr pellets (4000 – 400 cm^{-1}) on a Varian 3100 FT-IR Excalibur series spectrophotometer. The FT-Raman spectrum was recorded at a 1 cm^{-1} resolution with a micro-Raman spectrometer equipped with a grating of 2400 lines/mm and a Peltier cooled CCD detector. The excitation source used was the 514.5 nm line from an Argon plus laser. The laser power at the sample position was typically 5–10 mW. 1H and ^{13}C NMR spectra were obtained on a JEOL FT-NMR AL 300 spectrometer in $CDCl_3$ with chemical shifts relative to $SiMe_4$. Electronic spectrum was recorded on a Shimadzu UV-1700 Pharma Spec. UV-Visible spectrophotometer.



1-Methyl-2-(3-(furan-2-carbonyl)thioureido)benzoate (MFCTB)

Scheme 1. Synthesis of methyl-2-(3-(furan-2-carbonyl)thioureido)benzoate.

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