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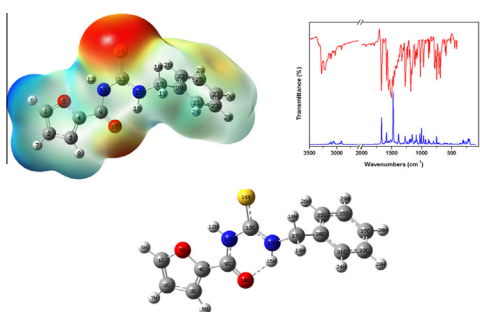
## Quantum chemical studies on molecular structure, spectroscopic (IR, Raman, UV–Vis), NBO and Homo–Lumo analysis of 1-benzyl-3-(2-furoyl) thiourea

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### HIGHLIGHTS

- The molecular structure of 1-benzyl-3-(2-furoyl) thiourea was determined by DFT calculations.
- The vibrational frequencies and UV–visible spectrum have been calculated and correlated.
- NBO analysis was performed to evaluate the stability of the molecule.
- Weak intramolecular interactions and ellipticity were analyzed by AIM approach.
- HOMO and LUMO analysis were used to evaluate some molecular properties.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Vibrational and electronic spectra for 1-benzyl-3-(2-furoyl) thiourea were calculated by using density functional method (B3LYP) with different basis sets. The complete assignment of all vibrational modes was performed on basis of the calculated frequencies and comparing with the reported IR and Raman spectra for that thiourea derivative. UV–visible absorption spectra of the compound dissolved in methanol were recorded and analyzed using time dependent density functional theory (TD-DFT). The calculated values for the geometrical parameters of the title compound are consistent with the ones reported from XRD studies. The stability of the molecule, related to hyper-conjugative interactions, and electron delocalization were evaluated using natural bond orbital (NBO) analysis. Intra-molecular interactions were studied by AIM approach. The HOMO and LUMO analysis are used to determine the charge transfer within the molecule. Molecular electrostatic potential map was performed by the DFT method.

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### Introduction

Thiourea ( $\text{NH}_2\text{CSNH}_2$ ) derivatives are very useful building blocks for the synthesis of a wide range of aliphatic macromolecular and

heterocyclic compounds [1–3]. These compounds could be used as ligand to form complexes with different transition metals [4–10]. Thiourea derivatives usually behave as planar ligands where both, S and N atoms are donor sites able to participate in the coordination with the metal center. Substituted thioureas, however, show more diverse coordination chemistry related to their conformational isomerism, steric effects, presence of donor sites on substituent groups and intra-molecular interactions [2]. Thiourea

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derivates display a wide range of biological activity including antibacterial, antifungal, antitubercular, antithyroid, antihelminthic, insecticidal, herbicidal and plant growth regulator properties [11–14]. In particular, aroylthioureas have been successful used in environmental control, as ionophores in ion selective electrodes [8].

From vibrational (IR and Raman) and electronic spectra valuable structural information is obtained. For thiourea derivatives, the active sites for complex formation with metals can be identified from such spectroscopic information [2]. However, the spectral regions where such vibrations appear are rich in signals from combination of vibration modes, overlapping of bands and complex vibration within the molecules. A comparison of IR and Raman spectra facilitates the identification of active sites [15]. A best option is found from comparative experimental and computational studies. This contribution illustrates that possibility for 1-benzyl-3-(2-furoyl) thiourea, a ligand of known crystal structure [16], whose complexes with heavy metals (Hg, Cd) have also been studied [15]. The calculated vibrational and electronic spectra were compared with the experimental ones. The computational study includes the natural bond orbital (NBO) and atoms in molecules (AIM) analysis. The HOMO and LUMO analysis have been used to elucidate information regarding ionization potential (IP), electron affinity (EA), electronegativity ( $\chi$ ), electrophilicity index ( $\omega$ ), hardness ( $\eta$ ), softness ( $s$ ) and chemical potential ( $\mu$ ) and all correlated. To the best of our knowledge, no analogue study has been reported for the considered thiourea derivate. The preparation and structural study of the ligand under study have been reported elsewhere [2]. UV–Vis spectra, not previously reported were collected in the course of this study using methanol solution and a Cary spectrophotometer.

## Experimental details

### Synthesis

The 1-benzyl-3-(2-furoyl) thiourea compound was synthesized according to a procedure reported by Otazo et al. [8]. In the synthesis the furoyl chloride was converted into furoyl isothiocyanate and then condensing with the benzylamine. Elemental analysis for  $C_{13}H_{12}N_2O_2S$ ; found: C (67.73%), H (4.75), N (8.23%), S (9.34%); calculated: C (67.86%), H (4.46), N (8.33%), S (9.52%).

### Characterization

Infrared spectrum of the solid was recorded on a FT-IR spectrophotometer (Atti Mattson, Genesis Series) using the KBr pressed disk technique in the range of 4000–400  $cm^{-1}$  in transmission mode with 10 scans at a resolution of 2  $cm^{-1}$ . Raman spectrum was collected by a capillary sample technique on a Perkin Elmer system 2000 NIR-FT-RAMAN and a Lexel model 98 krypton ion laser ( $\lambda = 647.1$  nm). The laser power at the sample surface was restricted to 40 mW. The spectral band pass of the Raman spectrometer was 4  $cm^{-1}$  and the 90° configuration used with an incidence angle of 60° on the metal surface when taking surface-enhanced Raman scattering (SERS). The UV–Vis spectrum in methanol was recorded at room temperature in the 250–700 nm wavelength range using a Cary 50 spectrophotometer. Sample was placed in quartz cuvette (1 cm path length).

## Computational details

Theoretical calculations were performed using the program package Gaussian 03 [17]. Geometry optimizations were performed at DFT levels using the 6-31G(d,p), 6-311++G(d,p) and 6-311++G(3df,3pd) basis sets. DFT calculations were performed

using Becke's three-parameter hybrid exchange functional [18] (B3) combined with both the Lee–Yang–Parr gradient-corrected correlation functional [19] (LYP). All calculations were performed using standard gradient techniques and default convergence criteria. The stability of the optimized geometries was confirmed by wavenumber calculations, which gave positive values for all the obtained wavenumbers. The vibrational modes were assigned by means of visual inspection using the Gaussview 05 program [20]. A comparison was performed between the theoretically calculated frequencies and the experimentally measured frequencies.

The prediction of Raman intensities was carried out by following the procedure outlined below. The Raman activities ( $S_i$ ) were calculated by Gaussian 03 and converted to relative Raman intensity ( $I_i$ ) using the following relation from the basic theory of Raman scattering [21]:

$$I_i = \frac{f(v_o - v_i)^4 S_i}{v_i [1 - \exp(-hc v_i / kT)]} \quad (1)$$

where  $v_o$  is the laser exciting wavenumber in  $cm^{-1}$  (in this work, we have used the excitation wavenumber  $v_o = 15453.5$   $cm^{-1}$ , which corresponds to the wavelength of 647.1 nm of the laser),  $v_i$  the vibrational wavenumber of the  $i$ th normal mode (in  $cm^{-1}$ ),  $h$ ,  $c$  and  $k$  are universal constants, and  $f$  is the suitably chosen common scaling factor for all the peaks intensities ( $10^{-12}$ ).

A natural bond orbital (NBO) calculation was performed at the B3LYP/6-311++G(d,p) level using the program NBO 3.1 [22] as implemented in Gaussian 03 package. This analysis were performed in order to understand various second order interactions between the filled orbitals of one subsystem and vacant orbitals of another subsystem, in order to have a measure of the intramolecular delocalization of hyper-conjugation. The topological properties of the electron density at the bond critical points (BCP) have been characterized using the atoms in molecules (AIM) at the B3LYP/6-311++G(d,p) level by using the AIM2000 code [23,24]. The molecular electrostatic potential (MEP) of the title compound is illustrated and evaluated.

The molecular properties such as ionization potential, electronegativity, chemical potential, chemical hardness, softness and global electrophilicity index have been deduced from HOMO–LUMO analysis employing B3LYP/6-311++G(d,p) method. In order to understand the electronic properties, the theoretical UV–visible spectra have been computed by TD-DFT method with 6-311++G(d,p) basis sets for gas phase and solvent (methanol) effect also has been taken into consideration by implementing IEFPCM model on same level of theory.

## Results and discussion

### Quantum chemical calculations

#### Molecular structure

Fig. 1 shows the optimized molecular structure of the title compound calculated at B3LYP/6-311++G(d,p) level of theory. The dihedral angles C(4)–C(9)–N(11)–C(13) and N(11)–C(13)–N(15)–C(17) are 179.5° and –179.3°, respectively indicating that in the molecule, the thiourea group is essentially planar. The torsion angles C(13)–N(11)–C(9)–O(10), C(9)–N(11)–C(13)–N(15) and S(14)–C(13)–N(11)–C(9) are –0.52°, 0.881° and –179.1°, respectively showing that the conformation of the molecule with respect to the thiocarbonyl and carbonyl moieties is twisted. The optimized geometrical parameters calculated at B3LYP method with 6-31G(d,p), 6-311++G(d,p) and 6-311++G(3df,3pd) basis sets are shown in Table 1. These results are compared with the values reported by X-ray diffraction methods for the title compound [16]. The difference in experimental and calculated geometrical

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