



# Synthesis, growth, molecular structure and spectral studies of 1,3 diglycynyl thiourea by density functional method



M. Kumar<sup>a</sup>, R. Kanagadurai<sup>b</sup>, G. Mani<sup>a</sup>, S. Gunasekaran<sup>c</sup>, S. Kumaresan<sup>a,\*</sup>

<sup>a</sup> PG and Research Department of Physics, Arignar Anna Government Arts College, Cheyyar 604 407, India

<sup>b</sup> PG and Research Department of Physics, Presidency College, Chennai 600 005, India

<sup>c</sup> St. Peter's University, Avadi, Chennai 600 109, India

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## ABSTRACT

Glycine is an important amino acid for building up protein synthesis and thiourea – a matrix metal multiplier combines to form a hybrid single crystal. Crystals of 1,3 diglycynyl thiourea were grown from aqueous solution by slow evaporation method. Powder X-ray diffraction analysis confirms that 1,3 diglycynyl thiourea crystallizes to monoclinic system. It is predicted that the molecular structure of 1,3 diglycynyl thiourea having well-defined bonding between C—O...H and N—H...O bond with a distance of 1.946 Å through hydrogen bonding. The structure and spectroscopic data of the molecule in the ground state have been calculated using ab initio Hartree Fock (HF) and density functional theory (DFT) (B3LYP) methods by employing 6-31 G(d,p) basis sets. Optical absorption study reveals that the transparency of the crystal in the entire visible region and the cutoff wavelength was found to be 236 nm. Mullikan population analyses on atomic charges analysis and molecular electrostatic potential and total density distribution are constructed to understand the electronic properties. The detailed interpretation of the vibrational spectra has been made on the basis of normal coordinate analysis. It is reported that there is a good agreement between theoretical and observed values.

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## 1. Introduction

The need for materials which combine large non linear optical characteristics with resistance to physical and chemical attack and good growth properties has led to the investigation of the semi organic materials. Semi organics are formed by combining organic molecules of high polarizability with mechanically strong and thermally stable inorganic molecules. The search for novel materials gaining increased attention in recent years and a wide variety of both organic and inorganic materials has been developed. Problems with both classes of materials have resulted in the investigation of semi organics [1–6]. The semi organic materials have the potentials for combining the high optical non linearity and chemical flexibility of organics with thermal stabilities and excellent transmittance of inorganic [7,8]. In search of these semi organic materials, urea and urea analogs have been explored [9]. 1,3 Diglycynyl thiourea single crystals were grown and characterized by XRD, optical and thermal properties were reported [10]. However, the detailed ab initio HF and B3LYP comparative studies on the complete FTIR spectrum and UV–vis spectrum of 1,3 diglycynyl thiourea have not

been reported so far. Therefore, in the present study, molecular geometry, optimized parameters and vibrational frequencies are computed and the performances of the computational methods for HF and DFT (B3LYP) levels at 6-31 G(d,p) basis sets is compared. In this study, density functional theory (DFT/B3LYP) and by using hybrid functional, ab initio Hartree–Fock (HF) computations of the vibrational spectrum, the molecular geometry, and atomic charges calculations were carried out for 1,3 diglycynyl thiourea molecule. The experimental geometric data of the molecule were taken from the Cambridge crystallographic database [11]. The entire calculations were performed using ab initio HF and density functional theory (DFT) to support our wave number assignment. Density functional calculations are reported to provide excellent vibrational wave number of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation for basis set deficiencies and for the anharmonicity.

## 2. Experimental

### 2.1. Synthesis

Glycine (AR) grade and thiourea (AR) were taken in the ratio 2:1 in distilled water and stirred in a magnetic stirrer for 6 h at room temperature. The solution was heated in steps of 5 °C and

\* Corresponding author. Tel.: +91 4182 22 5313.

E-mail address: [yeskay72@gmail.com](mailto:yeskay72@gmail.com) (S. Kumaresan).

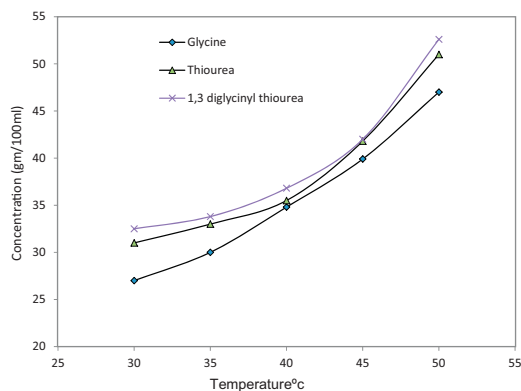


Fig. 1. Solubility curves for glycine, thiourea and 1,3 diglycyl thiourea.

the precipitates if any to get dissolved. The solution is filtered and refluxed for homogeneity and purity. The obtained product is 1,3 diglycyl thiourea.



## 2.2. Solubility test

Solubility of 1,3 diglycyl thiourea has been determined for five different temperatures at 30 °C, 35 °C, 40 °C, 45 °C and 50 °C. Re-crystallized salt is used for this purpose. A 250 ml glass beaker containing 100 ml of deionized water was placed in the temperature bath. The initial temperature of the bath was set at 30 °C. The beaker was closed with a sheet and placed in the magnetic stirrer. The synthesized salt was added in small amount and the stirring of the solution was continued till the formation of precipitate, which confirmed the saturation of the solution. The stirring further confirmed to have uniform temperature and concentration throughout the entire volume of the solution. On reaching the saturation, the equilibrium concentration of the solution was analyzed gravimetrically. The same procedure was followed for glycine and thiourea. Fig. 1 shows the solubility curves of glycine, thiourea and 1,3 diglycyl thiourea.

## 2.3. Growth of 1,3 diglycyl thiourea single crystals

Single crystals of 1,3 diglycyl thiourea were grown by slow evaporation technique at room temperature. Saturated solutions were prepared using re-crystallized salt at room temperature. The solutions were filtered using filter paper and kept undisturbed at room temperature and allow evaporating the solvent by covering a perforated thin mica sheet over the beaker. Transparent and optically good quality seeds were selected for the growth experiments. The period of growth ranged between 3 and 4 weeks and the harvested crystals are characterized. The photograph of optically transparent 1,3 diglycyl thiourea single crystals are shown in Fig. 2.

## 3. Theoretical methods

### 3.1. Molecular geometry

The entire calculations were performed at ab initio HF and DFT (B3LYP) levels at 6-31 G(d,p) basis sets on a Pentium V/1.6 GHz personal computer using Gaussian 03W program package [12] and applying geometry optimization [13]. Initial geometry generated was minimized at the Hartree–Fock levels using 6-31 G(d,p) basis set and again re-optimized at DFT (B3LYP) levels at 6-31 G(d,p) basis sets. The optimized structural parameters were used in the

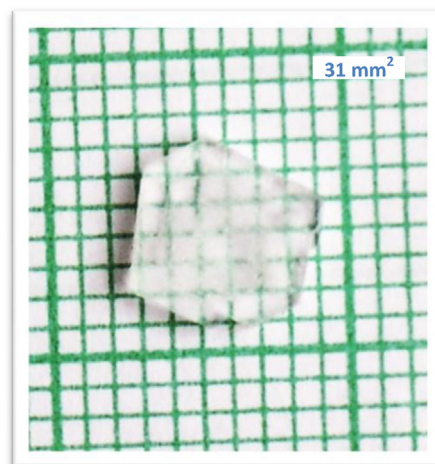


Fig. 2. Photograph of a grown 1,3 diglycyl thiourea single crystal.

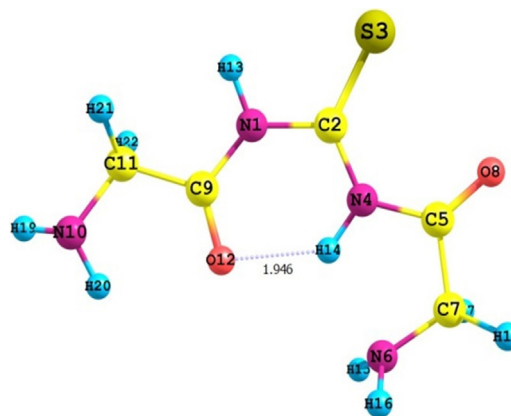


Fig. 3. The optimized structure of 1,3 diglycyl thiourea at DFT/6-31 G(d,p).

vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. The ground state optimized structural parameters such as bond length, bond angle and dihedral angle in various basis sets are presented in Table 1. From the theoretical values, it is found that some of the calculated parameters are slightly deviated from the experimental values, due to the fact that theoretical calculations belong to molecule in the gaseous phase and the experimental results belong to molecule in solid state. In this work, we performed full geometry optimization of the title compound. The optimized structure of title compound at DFT is shown in Fig. 3. The B3LYP method leads to geometry parameters, which are close to experimental data. A statistical treatment of these data shows that for the bond lengths B3LYP/6-31 G(d,p) are slightly better than the HF/6-31 G(d,p) geometry. The slight variation with the experimental value is due to the fact that the optimization performed in an isolated condition, whereas the experimental environment affected the X-ray structure.

### 3.2. Vibrational spectra

The present molecule has  $C_1$  symmetry and has 60 normal modes of vibrations; all the fundamental modes are active in infrared. None of the predicted vibrational spectra have any imaginary frequency, implying that the optimized geometry is located at the local lowest point on the potential energy surface. We know that, ab initio Hartree–Fock and DFT potentials systematically overestimate the vibrational wave numbers. These discrepancies corrected wither by computing harmonic corrections explicitly or

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