# Effects of alkyl groups on hydrogen-bonded supramolecular network of thiosemicarbazones derivatives

**Iasmin Alves Ribeiro[1] (IC), Renan L. de Farias[1]* (PG), Adriano B. de Oliveira[1] (PQ), Christian Näther[2] (PQ), Inke Jess[2] (PQ)**

* renan.lira@ufs.br

[1] *Departamento de Química, Universidade Federal de Sergipe, Av. Marechal Rondon s/n, Campus, 49100-000 São Cristóvão-SE, Brazil*

[2] *Institut für Anorganische Chemie, Christian-Albrechts-Universität zu Kiel, Max-Eyth Strasse 2, D-24118 Kiel, Germany*

Palavras Chave: *Thiosemicarbazones*, *Supramolecularity, Single Crystal X-Ray Diffraction*

## Introduction

The recognition motifs by non-covalent bonds allow specific supramolecular frameworks[1]. The hydrogen bond has both strength and directionality for the supramolecular chemistry[1]. Thiosemicarbazone derivatives (TSC's) have capacity to form multiple hydrogen bonds [the terminal and azometine N-atoms can act as H-donors and the S-atom and iminic N-atom as H-acceptors][2]. Our interest and on-going research concerning the structural chemistry of TSC's covers a wide range of properties, from three dimensional arrangements of molecules to their pharmacological properties. Thus, the study of supramolecular networks of these chemical species is important due to the chemical structure-biological properties relationship. Herein we would like to report the comparative study among the crystal structures of a new 1-(2*H*-1, 3-benzodioxol-5-yl)ethanone 4-ethylthiosemicarbazide (MAETSC) and two already related molecules that belong the same class of compounds[2,3]. The carbonylated precursor of them, (3', 4'-methylenedioxy)acetophenone (MA), is a secondary metabolite from Amazonian Magnoliid trees that belong to the *Lauraceae* family[2].

## Results and Discussion

The compounds were obtained *via* the Shiff base synthesis using, equimolar amounts of MA and 4-*X*-thiosemicarbazide derivatives (X = –*H*, –$CH_3$ and –$C_2H_5$). The reagents were stirred and refluxed in ethanol for 6h with hydrochloridric acid catalysis. After cooling and filtering, the TSC derivatives MATSC, MAMTSC and MAETSC were obtained. Suitable crystals for single crystal X-ray diffraction grow in DMSO after slow evaporation of the solvent.

The MAETSC crystallizes in triclinic space group $P\bar{1}$ (nº 2), $Z$ = 2 with $a$ = 5.7207 (3) Å, $b$ = 10.6225 (6) Å, $c$ = 10.8103 (6) Å and $\alpha$ = 83.908 (5)$^0$, $\beta$ = 79.913 (5)$^0$, $\gamma$ = 87.029 (5)$^0$, $wR(F^2)$ = 0.039. The **Figure 1** shows the crystal structure of the MAETSC with the molecules connected by pairs of N–H•••S hydrogen bonds building dimers. Additionally, the dimers are stacked along the *a*-axis. Finally, an intramolecular N–H•••N interaction is also observed. When compared with other crystal structures, such as MATSC and MAETSC, was observed that these substituents at the terminal N-atom of the TSC's play a determinant role concerning the connections and consequently on the supramolecularity, for example 3D-network, 2D-polymers and discrete units. We suggest that, since one final H-atom was changed for a methyl group the chance to obtain a 3-D H-bonded network decreases and the dimensionality falls to a two dimensional arrangement, as well as, the change for an ethyl substituent decreases the structure dimensionality to discrete units.

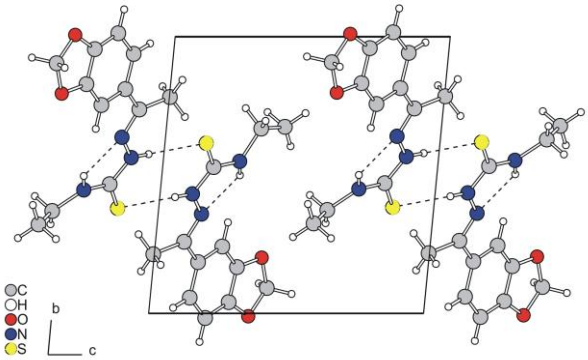


**Figure 1.** Crystal structure of the MAETSC viewed along the *a*-axis, with inter- and intramolecular hydrogen bonding shown as dashed lines.

## Conclusion

This work shows the synthesis and characterization by single crystal X-ray diffraction of a TSC derivative and the investigation over H-bonded supramolecular networks. We suggest that the presence of –*H*, –$CH_3$ and –$C_2H_5$ groups at the terminal N-atom have a strong influence on the supramolecularity of the structure of the TSC compounds on solid state, namely reducing their dimensionality with the increasing alkyl-chain size of the substituent.

## Acknowledgements

I. A. R. thanks CINTTEC/FAPITEC/UFS for the award of a PIBITI scholarship.

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