



3-Methylthio-4-phenyl-5-phenylamino-1,2,4-triazole hexabromotellurate: X-ray and computational study

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ABSTRACT

The structure of a newly synthesized 3-methylthio-4-phenyl-5-phenylamino-1,2,4-triazole **1** and its hexabromotellurate salt **2** was investigated. The X-ray diffraction study of **2** gives the insight on the different interaction types in the crystal. The DFT calculations were used for the comprehensive study of the intramolecular and intermolecular forces that are present in the title 3-methylthio-4-phenyl-5-phenylamino-1,2,4-triazole hexabromotellurate. The presence of three different aromatic moieties in the investigated compounds cause π - π stacking interactions which were studied through the Hirshfeld surface analysis and with the discrimination of weak interaction types by filling color to a reduced density gradient (RDG) function isosurface. The RDG in the crystalline state was calculated upon experimental molecular geometry by partitions of the crystal to QM part that was calculated at M06-L/6-311G(d,p) level, and the semi-empirical QM part that was modeled with the PM7 method in QM/MM-like manner. The reactivity of 3-methylthio-4-phenyl-5-phenylamino-1,2,4-triazole and its protonated form was also discussed in terms of conceptual DFT theory and it shows the tendency of sulfur to be the most active center in an electrophilic and radical attack, whereas the site for nucleophilic substitution is medium dependent and not an unequivocal. NICS(1) index was used for the analysis of aromaticity of three different cyclic moieties. The present study insights the changes in the structure of a polyfunctional substituted triazole upon its protonation and explains these changes with the analysis of weak interactions.

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1. Introduction

The synthetic chemistry of 1,2,4-triazole experiences a significant development due to semiconducting properties of some materials from this family [1] and due to the continued expansion of biological activity [2–5] and pharmaceutical application [6–8]. Non-covalent interactions of aromatic rings (e.g.: C–H ... π , π - π , cation- π interactions) are key forces in different areas of chemistry and biochemistry [9,10]. Despite being relatively weak, these interactions can show great influence, especially when they occur in abundance. An understanding of the effect of structure and the substituent's nature on these interactions can explain many chemical and biochemical processes [11]. The missing data in this

area can be obtained by studying model non-covalent dimers, either through experiment or computation. In literature there are plenty of works where investigators use simple electrostatic models for the explanation of the nature of these interactions [12,13]. Also, relatively newer results were obtained with advanced computational calculations concerning new aspects on the effects of substituents on π - π interactions [14,15].

On the basis of this, we reasoned that a computational study of 3-thio-5-phenylamino-1,2,4-triazole system can provide important information about the state of knowledge in triazole chemistry. In the present study, we have synthesized a 3-methylthio-4-phenyl-5-phenylamino-1,2,4-triazole and its hexabromotellurate salt (Scheme 1) that were characterized by an X-ray diffraction study (XRD) and different theoretical approaches.

The main aim of our study was to investigate the weak interactions and reactivity indexes of the newly synthesized polyfunctional triazole and its hexabromotellurate salt because hexabromotellurates

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