3,3-Dimethylacylthioureas: "S", "-S", "U" or "W" Conformation?

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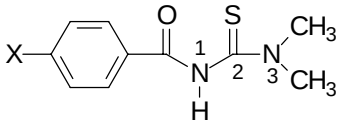
Abstract: We report a study of 3,3-dimethyl substituted acylthioureas. X ray data and quantum mechanical calculations demonstrated that the "S" conformation is the most stable both for the acylthioureas and the corresponding anions. The high regioselectivity towards S-alkylation is explained on the basis of the localization of the HOMO mainly over the sulfur atom.

Introduction

The acylthioureid group present in acylthioureas [1], contains three heteroatoms of different hardness. Thus it is expected that depending on the reaction conditions different series of N, O, or S alkylated derivatives may result [2]. The goal of this work was to study the reasons that favor the experimentally observed isothiourea formation (S-alkylation product) [3].

Experimental

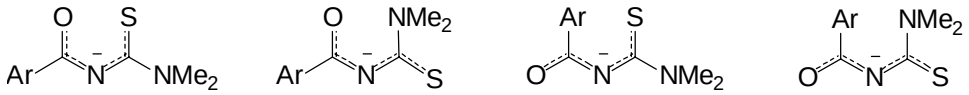
Acylthioureas studied: 1-(4'-X-benzoyl)-3,3-dimethylthiourea, with X = H, Me, Br, Cl were obtained by a 3 step synthetic sequence as described previously [2]. X-ray difraction studies were carried out on single crystals of the latter 3 compounds.



Geometry optimization: Were carried out with the programs Hyperchem 5.02, MOPAC 6.0 and Gaussian 94.

Results and Discussion

The main 4 conformers (S, -S, U and W) of the compounds mentioned in Experimental and their corresponding anions were optimized using semiempirical (AM1 and PM3) and *ab initio* methods. The calculated structures were compared with single crystal X-ray difraction data when available. Experimental and calculated geometries, predict the S conformation as the most stable for the four thioureas. HF calculations also predict the S conformation as the most stable for the corresponding anions, independently of the electronegativity of the substituent X.



U **S** **-S** **W**

Frontier orbital calculations, show that the HOMO in the anions is localized mainly over the sulfur atom. Larger substituents on N-3 (*e.g.* 3,3-diethyl substituted analogs), do not show differences regarding the preferred conformation.

References and Notes

1. Rodriguez, Y.; Macias, A. *Chem. Het.* **1987**, 508.
2. Plutin, A. Master Thesis, Universidad de la Habana, 1997.
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