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

M. Sosa¹, M. Piris² and G. Burton³

¹Facultad de Química, Universidad de La Habana, Cuba
²Instituto Superior de Ciencias y Tecnologías Nucleares, Cuba
³Depto. de Química Orgánica, Facultad de Ciencias Exactas y Naturales Universidad de Buenos Aires, Argentina
E-mail: mairim@fq.oc.uh.cu

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 diffraction 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 \textit{ab initio} methods. The calculated structures were compared with single crystal X-ray diffraction 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.

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

References and Notes