Conformational analysis of 2-chloro-1-(furan-2-yl)ethanone

Jéssica Valença[1] (PG)*, Paulo Roberto Olivato[1] (PQ)*, Daniel Nopper Silva Rodrigues[1] (PQ)

[1] *Instituto de Química, Universidade de São Paulo, São Paulo, Brasil, *e-mail: jvalenca@iq.usp.br, prolivat@iq.usp.*

Key words: *Conformational Analysis, infrared Spectroscopy, Theoretical Calculations*

Introduction

In the present work, the conformational analysis of 2-chloro-1-(furan-2-yl)ethanone **A** (Scheme 1) was performed through IR spectroscopy in solvents of increasing polarity supported by theoretical calculations.

$$\alpha = O\,(1) - C\,(2) - C\,(3) - C\ell\,(4)$$
$$\delta = O\,(1) - C\,(2) - C\,(5) - O\,(6)$$
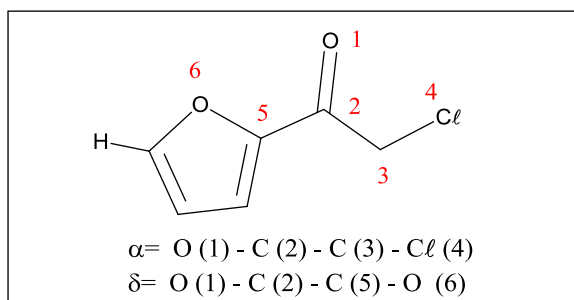
Scheme 1. Compound **A**

Results and Discussion

The compound **A** is commercial (Ablock Pharmatech).

The IR carbonyl stretching bands (ν_{CO}) were obtained, for **A** in solvents of increasing polarity, both in the fundamental (n-C_6H_{14}, $CC\ell_4$, $CHC\ell_3$, $CH_2C\ell_2$, CH_3CN) and in the first overtone ($CC\ell_4$) regions to verify the existence of the conformational isomerism.

The analysis of the ν_{CO} band of **A** by *curve fit* program revealed the existence of a doublet in n-C_6H_{14}, $CC\ell_4$, $CHC\ell_3$, $CH_2C\ell_2$, and $CH3CN$. The lower frequency component is the most intense one in n-C_6H_{14} and $CC\ell_4$. The increase of the solvent polarity intensifies the doublet higher frequency component as observed in $CHC\ell_3$, $CH_2C\ell_2$, and $CH3CN$.

M052X[1]/aug-cc-pVTZ calculations indicate the existence of four conformers in gas phase for **A** based on the dihedral angles *α-δ* (Scheme 1): *gauche-anti* (*g-a*)(ν_{CO} 1807 cm^{-1}), *gauche-syn* (*g-s*) (ν_{CO} 1808 cm^{-1}), *cis-anti* (*c-a*) (ν_{CO} 1827 cm^{-1}) and *cis-syn* (*c-s*) (ν_{CO} 1830 cm^{-1}) with relative populations about *ca.* 52%, 9% 37%, and 2%, respectively.

The results of the solvation calculations by Polarizable Continuum Model (PCM) in the solvents n-C_7H_{16}, $CC\ell_4$, $CHC\ell_3$, $CH_2C\ell_2$, CH_3CN, indicate that the relative population of the higher polarity conformer *c-s* increases as the solvent polarity increases and the population of the conformer *g-a* decreases.

The computed NBO (*Natural Bond Orbital*) for compound **A** suggests that the *gauche* conformers relative to the *α* dihedral angle (*g-a* and *g-s*) are stabilized by $\sigma_{C(3)-C\ell\,(4)}/\pi^*_{C(2)=O(1)}$ $\pi^*_{C(2)=O(1)}/\sigma^*_{C(3)-C\ell\,(4)}$, $\sigma_{C(3)-C\ell(4)}/\sigma^*_{C(2)=O(1)}$, and $\pi_{C(2)=O(1)}/\sigma^*_{C(3)-C\ell(4)}$ interactions.

Additionally the *cis* conformers (*c-s* and *c-a*), are slightly stabilized by $\sigma_{C(3)-C\ell\,(4)}/\sigma^*_{C(2)-C(5)}$ and $\sigma_{C(2)-C(5)}/\sigma^*_{C(3)-C\ell\,(4)}$ interactions.

The lower stability of the *syn* conformers (*g-s* and *c-s*) relative to *anti* conformers (*g-a* and *c-a*), occur due to the repulsive electrostatic interaction between negatively charged oxygen atoms O(1)...O(6) which are at a distance of *ca.* 0,34 Å smaller than the sum of Van der Waals radii.

The comparison between the experimental IR spectra and the computed PCM data for **A** in n-C_6H_{14} $CC\ell_4$, $CHC\ell_3$, $CH_2C\ell_2$, and CH_3CN, allows us to assign the higher frequency ν_{CO} doublet component to the *c-a* and *c-s* conformers, and the lower frequency component to the *g-a* and *g-s* ones.

All theoretical calculations were performed in Gaussian 09.

Conclusions

The matching between the theoretical results and the analytically resolved IR ν_{CO} band in solvents (n-C_6H_{14} $CC\ell_4$, $CH_2C\ell_2$ and CH_3CN) allow us to ascribe the *c-a* and *c-s* conformers to the higher ν_{CO} frequency component and the *g-a* and *g-s* conformers to the lower ν_{CO} frequency component.

Acknowledgements

[1] Zhao, Y.; Schultz, N. E.; Truhlar, D. G. *J. Chem. Theory and Comput.*, 2 (**2006**), 364-82.