

Conformational study of 2-bromo-1-(furan-2-yl)ethanone and 2-bromo-1-(5-nitrofuran-2-yl)ethanone

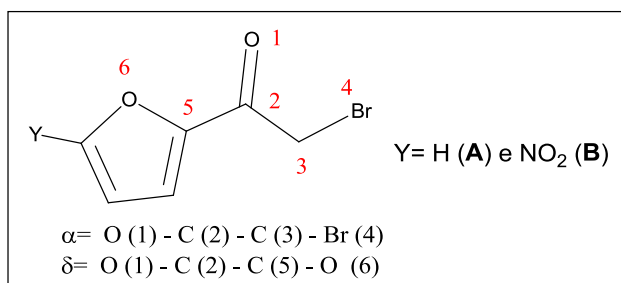
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Introduction

In the present work, the conformational analysis of 2-bromo-1-(furan-2-yl)ethanone **A** and 2-bromo-1-(5-nitrofuran-2-yl)ethanone **B** (Scheme 1) was performed through IR spectroscopy in solvents of increasing polarity supported by theoretical calculations.



Scheme 1. Compounds **A** and **B**

Results and Discussion

The compounds **A** and **B** are commercial (Ablock Pharmatech).

The IR carbonyl stretching bands (ν_{CO}) were obtained, for compounds **A** and **B** in solvents of increasing polarity, both in the fundamental (*n*-C₆H₁₄, CCl₄, CHCl₃, CH₂Cl₂, CH₃CN) and in the first overtone (CCl₄) regions to verify the existence of the conformational isomerism.

The analysis of the ν_{CO} band of **A** and **B** by *curve fit* program revealed the existence of a doublet in *n*-C₆H₁₄, CCl₄, CH₂Cl₂, and CH₃CN, being the lower frequency component the most intense one. The increase of the solvent polarity intensifies the doublet higher frequency component, except in CHCl₃ for which a triplet is found.

M052X¹/aug-cc-pVTZ calculations indicate the existence of four conformers in gas phase for **A** and **B**, based on the dihedral angles α - δ (Scheme 1): *gauche-anti* (*g-a*) (ν_{CO} ca. 1814 cm⁻¹), *gauche-syn* (*g-s*) (ν_{CO} ca. 1817 cm⁻¹), *cis-anti* (*c-a*) (ν_{CO} ca. 1829 cm⁻¹) and *cis-syn* (*c-s*) (ca. ν_{CO} 1841 cm⁻¹) with relative populations about ca. 80%, 7% 13%, and 1% respectively.

The results of the solvation calculations by Polarizable Continuum Model (PCM) in the solvents *n*-C₇H₁₆, CCl₄, CHCl₃, CH₂Cl₂, CH₃CN, indicate that the relative population of the conformer with the higher polarity *c-s* increases as the solvent polarity

increase and the population of the conformer *g-s* decrease.

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

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

The lower stability of the *sin* 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** and **B** in *n*-C₆H₁₄, CCl₄, CH₂Cl₂, CH₃CN, 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.

The abnormal carbonyl triplet observed in the IR spectrum in CHCl₃ may be justified to specific solvent interactions that continuum models of solvation cannot describe.

All theoretical calculations were performed in Gaussian 09.

Conclusion

The matching between the theoretical results and the analytically resolved IR ν_{CO} band in solvents (*n*-C₆H₁₄, CCl₄, CH₂Cl₂ and CH₃CN) 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.

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