

Effect of Intramolecular Hydrogen Bond OH...O in 1,3-butanediol and 3-methoxybutanol

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INTRODUCTION

Intramolecular hydrogen bonds (IAHB) are responsible for stabilizing interactions of important structures to life, as carbohydrates and DNA. Good prototypes for systems containing strong IAHB are compounds that have two hydroxyl groups.^{1,2}

Oliveira and Rittner³ showed that the increase in the volume group OR [R = CH₃, CH₂CH₂CH₃ and CH(CH₃)₂] increases the strength of IAHB for *cis*-3-alkoxycyclohexanols. Therefore the aim of this study was to analyze the influence of IAHB in conformational stability of 1,3-butanediol and 3-methoxybutanol through theoretical calculations and IR.

METHODS

1,3-butanediol (1,3-BDIOL) and 3-methoxybutanol (3-MBOH) compounds were studied. The optimization and frequency calculations for possible conformers were made with Gaussian09 software using the M06/DEF-2QZP. For the most stable structures were performed NBO study and topological analysis with AIMALL software. IR analyses were made in 0.01; 0.03 and 0.1 mol L⁻¹ using CCl₄ as solvent.

RESULTS AND DISCUSSION

Theoretical calculations shown an energy difference of 0.61 kcal.mol⁻¹ between the most stable conformer containing IAHB (g'gg't) and the most stable without IAHB (tgg'g) for the 1,3-BDIOL. For the 3-MBOH the difference between the more stable conformer with IAHB (g'gg't) and more stable without IAHB (tg'g't) was 0.28 kcal.mol⁻¹.

NBO, QTAIM and frequency calculations shown that there is an increase in the strength of IAHB of 1,3-BDIOL for 3-MBOH. There is an

increase in the transfer of electron (LP_O→σ*_{O-H}) of 4.58 kcal mol⁻¹ for 1,3-BDIOL and of 4.76 kcal for 3-MBOH. The topological analysis with QTAIM showed that there is an increased of E_{IAHB} of 1,3-BDIOL (0.0114 a.u.) for 3-MBOH (0.0115 a.u.). Frequency calculations showed a large increase in Δν (O-H_{free} to O-H_{bonded}) of 75 to 113 cm⁻¹, respectively.

The IR experimental results (Figure 1) agree with the theoretical results showing an increase of 82 cm⁻¹ for 1,3-BDIOL to 103 cm⁻¹ to 3-MBOH. The IR analysis also showed the influence of concentration. OH stretching of IAHB decrease in larger concentrations and the OH stretching of intermolecular hydrogen bond increase.

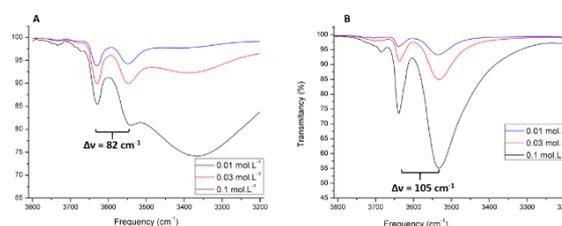


Figure 1. IR spectra of 1,3-BDIOL (A) and 3-MBOH (B) in 0.01; 0.03 and 0.1 mol.L⁻¹.

CONCLUSIONS

The study showed that the structure containing IAHB are more stable for 1,3-BDIOL and 3-MBOH. Furthermore, the increase in the substituent group increases the strength of the IAHB OH...O.

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