Conformational Analysis of 3-amino-1-propanol and 3-N,N-dimethylamino-1-propanol using QTAIM and NBO

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INTRODUCTION

The intramolecular hydrogen bonding (IAHB) is a type of interaction that has great influence on conformational preference in molecular systems, sometimes more than steric effects. Oliveira and Rittner[1,2] showed that the increase in the volume group NRR' [RR = H , RR = CH_3 and R = H, R' = CH_3] increases the strength of the intramolecular hydrogen bond (IAHB) on *cis*-3-aminocyclohexanols. The objective of this study was to analyze the influence of substituent bulk on the strength of IAHB OH···N by theoretical calculations.

METHODS

The conformational analysis of the compounds 3-amino-1-propanol (APOL) and 3-N,N-dimethylamino-1-propanol (DMAPOL) was performed by theoretical calculations . The initial structures were obtained using a conformational search with Tinker program. Optimization and frequency calculations were performed using the theoretical level M062X/aug-cc-pVDZ with Gaussian09 program. Then a statistical thermodynamic analysis was performed to obtain more stable populations and their thermal structures. These structures were subjected to topological analysis QTAIM and NBO.

RESULTS AND DISCUSSION

The results showed that the two compounds showed the IAHB. More stable conformers for APOL and MAPOL showed thermal population of 85.5 and 90.0%, respectively. Gibbs energy (ΔG) of conformers with and without IAHB was of 2.18 and 2.13 kcal.mol^{-1} for APOL and DMAPOL. The QTAIM identified an IAHB OH···N for the two conformers more stables (Figure 1) with the presence of Bond Path (BP), Bond Critical Point (BCP) and Ring Critical Point (RCP). The results of dissociation energy of IAHB OH···N showed that the APOL (0.00934 a.u.) makes an IAHB stronger than the DMAPOL (0.00897 a.u.).[3] Total electronics Energy Density on BCP of IAHB was of 0.000453 and 0.000834 u.a. for APOL and DMAPOL. These results showed that IAHB for APOL has more covalent character. Hyperconjugative interaction (LP(N)→σ*O-H) also showed that the IAHB OH···N for APOL (9.85 kcal.mol^{-1}) is stronger than DMAPOL (8.01 kcal mol^{-1}).

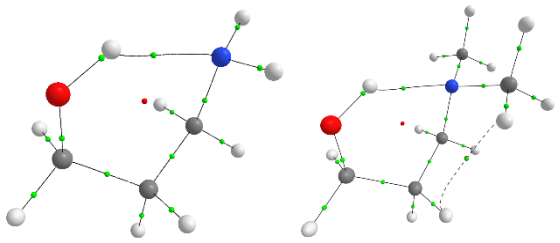

Figure 1. Molecular graphics for APOL and DMAPOL obtained by QTAIM.

CONCLUSIONS

The calculations showed that the 1.3-amipropanols have conformers with a higher thermal population stabilized by IAHB. The higher alkyls substituent favors the increase of 1.3- diaxial steric effect reducing the strength of the IHAB.

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