Conformational Analysis of 1,2-Ethanediol through NBO, QTAIM and NCI Methods

Weslley G. D. P. Silva (G), Josué M. Silla (PG), Matheus P. Freitas (PQ)

[a] *Federal University of Lavras, Department of Chemistry, P.O. Box 3037, 37200-000, Lavras, MG.*
wsilva@quimica.ufla.br

Keywords: Conformational analysis, 1,2-Ethanediol, NBO, QTAIM, NCI.

INTRODUCTION

The presence of intramolecular hydrogen bond (IHB) in vicinal diols has been studied by several groups and it is still under discussion.[1] Since 1,2-ethanediol (1,2-ED) is the simplest molecule containing vicinal hydroxyl groups, it can be an useful model for understanding the influence of hydrogen bond in the conformational equilibrium of this sort of molecules (Figure 1). Earlier studies showed that there is a *gauche* preference in 1,2-ED, which was assigned as due to IHB between the two hydroxyl groups, but this is not consensual.[1,2] Based on the divergences among different investigations, the present work proposes the conformational analysis of 1,2-ED through NBO, QTAIM and NCI methods to investigate the presence of IHB.

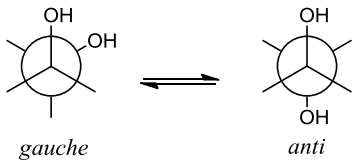

Figure 1. Conformational equilibrium of 1,2-ED.

METHODS

All 27 possible geometries of 1,2-ED were optimized at the B3LYP/6-311G++(d,p) level and frequency calculations were carried out to guarantee that imaginary frequencies were absent. NBO analysis were performed at the same level of theory in the gas phase and implicit DMSO, including deletion of all antibonding and Rydberg-type orbitals using the Gaussian 09 program. QTAIM analysis was carried out to search for possible hydrogen bonds using QTAIMALL program. Non-covalent interactions (NCI) method was performed using the NCIPLOT program.

RESULTS AND DISCUSSION

The optimization calculations confirmed the *gauche* preference for 1,2-ED both in the gas phase and implicit DMSO. According to NBO calculations, the *gauche* conformation is favored by hyperconjugation relative to the *anti* one by 9.3 (gas) and 14.9 kcal mol^{-1} (implicit DMSO). However, such a stabilization was not found to be due to the $n_O \rightarrow \sigma^*_{O\text{-}H}$ interaction (IHB), but rather to antiperiplanar interactions usually invoked to explain the *gauche* effect ($\sigma_{C\text{-}H} \rightarrow \sigma^*_{C\text{-}O}$). QTAIM analysis did not show any bond-path between O···H(O), indicating the absence of IHB in 1,2-ED. On the basis of some controversial cases in the literature,[2] in which a BCP cannot be found in compounds where IHB is expected, the NCI method was applied. Figure 2 shows the NCI isosurface and the respective plot of RDG vs sign(λ2)ρ. The isosurface shows a single circular volume between the two OH moieties due to the collapse of both regions of interaction in the intramolecular bonding and the plot illustrates the presence of two peaks. The peak on the negative sign represents attractive interactions (IHB), while the other belongs to repulsive interactions (ring formation). These interactions are nearly equivalent and, therefore, the overall result of the OH···OH approximation is an interaction neither attractive nor repulsive.

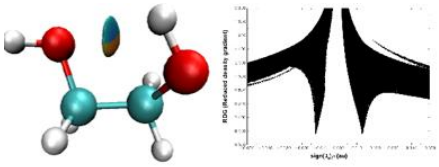

Figure 2: NCI isosurface and plot of RDG vs sign(λ2)ρ for 1,2-ED.

CONCLUSIONS

All three methods (NBO, QTAIM and NCI) converged to the same result with respect to the role of IHB as stabilizing force of the *gauche* conformation in 1,2-ED: it is absent or, at least, not strong enough to rule the conformational equilibrium of 1,2-ED.

ACKNOWLEDGMENTS

Authors are thankful to CNPq and FAPEMIG.

[1] Das, P. et al. *J. Phys. Chem. A.* **2015**, 119, 3710-3720.
[2] Lane, J. R. et al. *J. Chem. Theor. Comput.* **2013**, 9, 3263−3266.