Effects of different substituents on the stability of compounds derived from triphenylimidazol

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INTRODUCTION

The proton coupled electron transfer reaction (PCET) is a formal class of hydrogen atom transfer reactions (HAT), which has shown a broad interest because it is applied to a wide range of chemical and biochemical processes, such as in enzymatic reactions, in photosynthesis and respiration processes[1]. This study aimed at examining the tautomeric balance and stability of the intramolecular hydrogen bond occurring in this class of compounds towards different substituents as in some types of solvents.
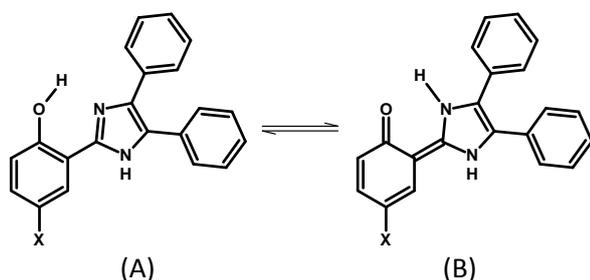

Figure 1. Scheme showing the proton transfer in compound derived from triphenylimidazol.

METHODS

A variety of theoretical approaches have been tested to study the PCET reactions[2], wherein the DFT has emerged as an appropriate tool[3]. In this work, we studied three triphenylimidazolic compounds. The geometry optimization and frequency calculations were performed with the functional M06-2X and the basis set 6-31G(2d,2p) as implemented in Orca software.

RESULTS AND DISCUSSIONS

Free energy values were used to analyze the stability of intramolecular hydrogen bonds that occur in some derivatives of triphenylimidazol, Fig 1. In principle, the free energies in gas-phase and in ethyl acetate (COSMO) were analyzed to three substituents: X = CH_3, H and NO_2. The keto form (B) is less stable than the phenolic form (A), ie, this keto-enol equilibrium that occurs in thiphenylimidazol is shifted to the enol form. However, note that for the $–NO_2$, that is an electron withdrawing group, the difference is significantly lower, probably due the more intense hydrogen bonding (Table 2).

Table 1. Free energy differences between the structures A and B for the three substituents obtained in ethyl acetate

X	ΔG_A° (Eh)	ΔG_B° (Eh)	$\Delta G_B^\circ - \Delta G_A^\circ$ (kJ.mol^{-1})
CH_3	-1033,278	-1033,272	17,02
H	-994,006	-993,999	16,54
NO_2	-1198,448	-1198,445	7,50

Table 2. Distance between the atoms involved in intramolecular hydrogen bond to the structures A and B to three substituents

X	O - H_A (Å)	N - H_A (Å)	O - H_B (Å)	N - H_B (Å)
CH_3	0,970	2,335	1,657	1,030
H	0,970	2,319	1,645	1,030
NO_2	0,976	2,098	1,654	1,038

CONCLUSION

The free energy analysis of the data shows that for all substituents analyzed, the A structures are the most stable. Comparing the free energy amounts, it can see that the stability increases in the following order: $CH_3 > H > NO_2$. Particularly, for $–NO_2$ as substituent, more effective hydrogen bonding approximate the free energy of both structures.

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