Conformational analysis of 2-(((1-phenylethyl)imino)methyl)phenol and its halogen substitutions, as a Schiff base with chiral carbon, A DFT study

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Abstract:
The molecular structure and conformational analysis of 2-(((1-phenylethyl)imino)methyl)phenol, as a Schiff base with a chiral atom, has been done by calculation methods. According to our calculations at B3LYP and MP2 levels of theory, three stable conformers (C1-C3) can be drawn for target molecule. The C1 conformer is the most stable, and relative stability of C2 and C3 are in the range of 1.20-2.67 kcal/mol, in the gas phase and solutions. Also we considered the halogen substitution effects, X=F, Cl, and Br, on the conformation stability at both gas phase and solution. According to our results, the para halogen substitutions have no significant effect on the relative stability of three stable conformers.

Keywords: DFT; Chiral carbon; substitution effect; Conformers stability, Schiff base.

Introduction

Schiff bases have a wide variety of applications in various field such as biology, pharmacy, industry, and etc. [1-4]. 2-(((1-phenylethyl)imino)methyl)phenol (PIMP), as a Schiff base, with one chiral carbon are particularly eye-catch. This molecule shows a fairly strong intramolecular H-bonding (IHB) between the H-atom of the hydroxyl group and the N-atom of the imine moiety. The IHB is caused to an intramolecular proton transfer, associated with a change in π-electron configuration, from the hydroxyl's O atom to the imine's N atom. The mentioned transfer occur under the influence of light, for photochromic, and temperature for thermochromic, Schiff bases, [5]. The aim of present work is to investigate the structure and conformational stability of target molecule and its para halogen substitutions, in gas phase and solution with different solvents by theoretical methods.

Materials and method

All quantum calculations have been done by the Gaussian 09 [6]. The conformation and structure of target molecules have been optimized at the B3LYP, and MP2 levels with using the 6-311++G**, 6-311G**, and 6-31G** basis sets. The SCRF–PCM method were selected for conformation study in acetonitrile and carbon tetrachloride solutions, as a nonpolar and polar solvents, at selected levels and basis sets. Dipole moments of mentioned structures in both phase calculated at B3LYP/6-311++G** level of theory.

Results and Discussion

Three stable conformers of our molecules, PIMP and X-PIMP, with X=F, Cl, and Br are shown in Fig. 1.

Their relative stabilities of three forms of X-PIMP with respect to the most stable form, calculated at different level and basis set, in the gas phase and solution are tabulated in Table1. According to this table, the C1 conformer is the stable form in all target molecules in gas phase and solution.

Fig. 1: Three stable conformers of PIMP and its halogen substitutions. * is shown chiral atom.
According to this Table, in different computational levels and basis sets the following trend is obtained for the stable forms of PIMP and X-PIMP in both gas phase and solution:

\[ C_2 < C_3 < C_1. \]

The energy differences between three stable enol conformers of the p-substituted PIMP in the gas phase and solutions are negligible, in the range of 1.20-2.67, 1.28-2.60, and 1.55-2.45 kcal/mol in the gas phase, CCl₄, and CH₃CN solvents.

**Conclusion**

From the theoretical point of view, three stable conformers can be considered for PIMP, a molecule with a chiral carbon, and its para halogen substitutions. Our calculations, for target molecules, at different levels of theory are shown, that the energy differences between three stable forms are in the range of 1.20-2.67 kcal/mol, in the gas phase and solutions. By the way, the CI, F, and Br substitutions in the para position decreases the absolute energies and increase the stability, but do not significantly effect on the relative energies.

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**References**


