Title: Structural and energetic studies of boronic-acid-functionalized polyaniline (B@Pani) monomers and dimers using Density Functional Theory approach (15 min)

Authors: Michele A. Salvador, Rita Maji, Alice Ruini, Elena Degoli, Rita Magri

Polymers functionalized with boronic acid moieties (R-$B(OH)_2$) have been considered for biological and technological applications, including, for example, drug delivery systems, sensors and self-healing polymers, among others. They are formed by trivalent boron atoms bonded to one alkyl/aryl substituent and two hydroxyl groups (R–$B(OH)_2$). Due to their chemical characteristics, they can behave as hydroxide-attractive molecules, and react with organic compounds containing hydroxyl groups. Also, special attention has been paid to polymers functionalized with boronic acids bonded to phenyl moieties (-Ph-$B(OH)_2$). In this work, we started from a model molecule consisting of two phenyl rings bonded by an amino group where each ring had one hydrogen atom replaced by - $B(OH)_2$. The molecule was submitted to structural optimization using DFT calculations, followed by vibrational frequency calculations to assure that the final structure corresponded to a minimum in the potential energy surface. Finally, we performed two conformation studies: the first one, considering the rotation of one ring with respect to the N atom, and the second one considering the rotation of each hydrogen atom bonded to the oxygen ones. Our results showed that the most stable configuration has the $B(OH)_2$ group on opposite sides of the rings, with one OH group pointing towards the ring and the other pointing to the opposite side. In parallel, we aimed to understand the role of the proximity between the OH group and the NH group, and the formation energy of the boronated structures. To achieve this goal, we considered a structure of one aniline (phenylamine) with one boronated acid group in non-equivalent positions. We observed that the structure with the boronic acid closer to the amino group was more favorable than the one with the boronic acid farther from it.. The formation energy of the structure, calculated as the product minus reagents free energies, is -12.5 kcal/mol. Our following steps include to build larger chains with more aromatic rings and more boronic acid groups, and to understand how properties, such as frontier orbitals and partial charges vary with the increment in size. This research was developed under the framework of the BAT4EVER project (www.bat4ever.eu) that has received funding from the

European Union’s Horizon 2020 research and innovation program under grant agreement No. 957225.

Keywords: conformational study, free energy, oligomers.