Unraveling the Nature of Hydrogen Bonds of “Proton Sponges” Based on Car-Parrinello and Metadynamics Approaches

Autorzy

Beata Kizior

Mariusz Michalczyk

Jarosław J. Panek

Wiktor Zierkiewicz

Aneta Jezierska

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Streszczenie

The nature of intra- and intermolecular non-covalent interactions was studied in four naphthalene derivatives commonly referred to as “proton sponges”. Special attention was paid to an intramolecular hydrogen bond present in the protonated form of the compounds. The unsubstituted “proton sponge” served as a reference structure to study the substituent influence on the hydrogen bond (HB) properties. We selected three compounds substituted by methoxy, amino, and nitro groups. The presence of the substituents either retained the parent symmetry or rendered the compounds asymmetric. In order to reveal the non-covalent interaction properties, the Hirshfeld surface (HS) was computed for the crystal structures of the studied compounds. Next, quantum-chemical simulations were performed in vacuo and in the crystalline phase. Car–Parrinello molecular dynamics (CPMD), Path Integral Molecular Dynamics (PIMD), and metadynamics were employed to investigate the time-evolution changes of metric parameters and free energy profile in both phases. Additionally, for selected snapshots obtained from the CPMD trajectories, non-covalent interactions and electronic structure were studied. Quantum theory of atoms in molecules (QTAIM) and the Density Overlap Regions Indicator (DORI) were applied for this purpose. It was found based on Hirshfeld surfaces that, besides intramolecular hydrogen bonds, other non-covalent interactions are present and have a strong impact on the crystal structure organization. The CPMD results obtained in both phases showed frequent proton transfer phenomena. The proton was strongly delocalized in the applied time-scale and temperature, especially in the PIMD framework. The use of metadynamics allowed for tracing the free energy profiles and confirming that the hydrogen bonds present in “proton sponges” are Low-Barrier Hydrogen Bonds (LBHBs). The electronic and topological analysis quantitatively described the temperature dependence and time-evolution changes of the electronic structure. The covalency of the hydrogen bonds was estimated based on QTAIM analysis. It was found that strong hydrogen bonds show greater covalency, which is additionally determined by the proton position in the hydrogen bridge.

Słowa kluczowe

“proton sponge”, gas phase, crystalline phase, Hirshfeld surface, CPMD, PIMD, metadynamics, QTAIM, DORI

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