

Benzene and water – different or similar?

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Abstract: Considering the properties of water and benzene molecules, one can expect very different benzene/benzene and water/water interactions. Benzene does not have a dipole moment, while water does. Analysis of the data in the crystal structures in the Cambridge Structural Database (CSD) revealed the most frequent benzene/benzene and water/water geometries. The majority of the benzene/benzene interactions in the crystal structures in the CSD are stacking interactions with large horizontal displacements, and not geometries that are minima on benzene/benzene potential surface. A large number of the water/water contacts in the CSD are hydrogen bonds, 70% of all attractive water/water interactions. In addition, water/water contacts with two water forming antiparallel interactions are 20% of all attractive water/water contacts. In these contacts, the O-H bonds of water molecules are in antiparallel orientation. In benzene/benzene interactions at large horizontal displacements, two C-H bonds also are in the antiparallel orientation. This shows that although the two molecules are different, both of them form antiparallel interactions with a local O-H and C-H dipole moments.

Keywords: H-bond, T-shaped, stacking, noncovalent

1. Introduction

Both benzene and water are liquids at room temperature, and it is their common property. It means that intermolecular interactions are strong to keep molecules in the liquid phase, however, not strong enough to form a solid phase. It raises the interesting question of the intermolecular interactions among water molecules and among benzene molecules.

Water is a polar solvent. It has been well known, for over a hundred years, that water molecule is polar and forms hydrogen bonds, while hydrogen bonds define many properties of water as a substance. For example: melting and boiling temperatures, density of liquid water and ice, snowflakes and shapes of snowflakes. On the other hand, benzene is a non-polar solvent. Benzene boils at 80.1 °C, indicating that

interactions among benzene molecules are weaker than interactions among water molecules.

A large number of papers has been published on water hydrogen bonds and on interactions between benzene molecules. Quantum chemical calculations in the gas phase showed that the minimum on the potential surface of water/water dimer is the hydrogen bond, where the dipole moment of water plays an important role (Figure 1a). The calculations show that the minima on the potential surface for benzene/benzene are stacking (parallel displaced) geometry and T-shaped geometry (Figure 1).

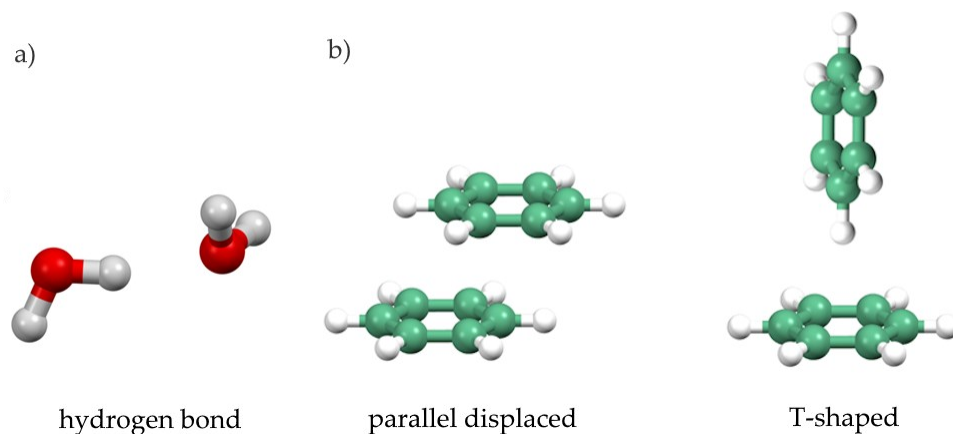


Figure 1. Minimum on potential surface for water/water dimer (hydrogen bond) and minima on potential surface for benzene/benzene dimer (parallel displaced and T-shaped geometry).

In this work, we compare the data on the water/water and benzene/benzene interactions in the crystal structures from the Cambridge Structural Database (CSD) and we show the common properties of these interactions.

2. Results and discussion

The analysis of all crystal structures in the Cambridge Structural Database (CSD) showed that the most frequent interaction between two water molecules is the hydrogen bond, in agreement with the calculated minimum on the potential surface in the gas phase (Figure 1a). However, the most frequent interaction of two benzene molecules is not in agreement with the calculated potential energy surface, it is stacking geometry (parallel displaced) with very large horizontal displacement (Figure 2b).

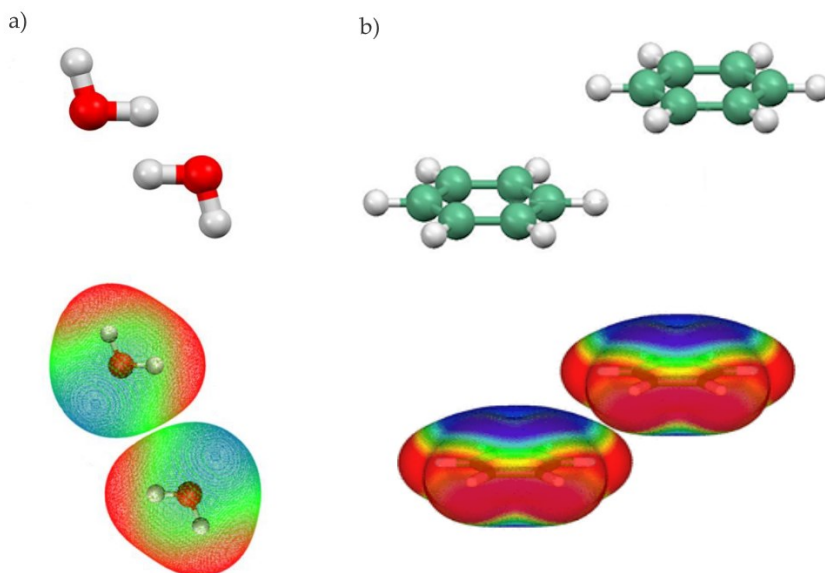


Figure 2. The water/water antiparallel interaction (a), benzene/benzene interaction at large horizontal displacement (b) and their corresponding overlaid electrostatic potentials.

The quantum chemical calculations of potential surface of water/water interactions showed that the minimum is a hydrogen bond. Analysis of the data in the crystal structures in the Cambridge Structural Database (CSD) revealed antiparallel water/water interactions, in addition to classical hydrogen bonds [1]. The geometries of all water/water contacts in the CSD were analyzed and for all contacts interaction energies were calculated at accurate CCSD(T)/CBS level. The results showed that the most frequent water/water contacts are hydrogen bonds; hydrogen bonds are 70% of all attractive water/water interactions. In addition, water/water contacts with antiparallel interactions are 20% of all attractive water/water contacts. In these contacts, O-H bonds of water molecules are in antiparallel orientation (Figure 2a).

The quantum chemical calculations of potential surface of benzene/benzene interactions showed two minima stacking (parallel displaced) geometry and T-shaped geometry. Analysis of all benzene/benzene contacts in the crystal structures in the CSD revealed the most frequent benzene/benzene geometries [2]. The majority of the benzene/benzene interactions in the CSD are stacking interactions with large horizontal displacements, and not geometries that are minima on benzene/benzene potential surface. In benzene/benzene interactions at large horizontal displacements two C-H bonds are in the antiparallel orientation (Figure 2b).

In these O-H and C-H antiparallel interactions, two dipoles are in antiparallel orientation enabling close contact of positive and negative regions of the dipoles (Figure 2). Symmetry Adapted Perturbation Theory (SAPT) analysis showed that electrostatic is the largest attractive force in antiparallel interactions. Antiparallel interactions are also possible between O-H and C-H bonds; in the crystal structures from the CSD these interactions are observed as one of the types of water benzene interactions [3].

3. Conclusions

In spite of being quite different substances, benzene and water can form similar noncovalent interactions. Analysis of the data in the crystal structures in the CSD revealed similarities in benzene/benzene and water/water interactions since both can form antiparallel interactions.

The analysis of the crystal structures from the CSD shows that the majority of the benzene/benzene interaction are stacking interactions with large horizontal displacements in which the dipole moment of the C-H bond plays an important role. A significant number of water/water interactions are antiparallel interactions, namely 20% of all attractive water/water contacts in the CSD are antiparallel interactions. These antiparallel interactions are a consequence of the interaction of two O-H bonds in which dipoles are in antiparallel orientation.

This shows that although these two molecules are very different, they can have similar interactions with respect to the local dipole moment. The deciding factor for these two important interactions is the antiparallel dipole moments of the O-H and C-H bonds.

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