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Repulsive water-water contacts from Cambridge Structural Database

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Abstract: Water is one of the most important molecules on the Earth. Since water plays a crucial role in many life processes, it is of great importance to understand every aspect of its behavior and interactions with itself and its surroundings. It is known that water molecules can interact via classical hydrogen bonds and antiparallel interactions, with interaction energies of - 5.02 kcal/mol and -4.22 kcal/mol, respectively. Besides these attractive interactions, repulsive interactions were also noticed. In this work, we analyzed repulsive water-water contacts from the Cambridge Structural Database. All interaction energies were calculated at the so- called gold standard, i.e., CCSD(T)/CBS level of theory. It was found that among all water-water contacts, ca. 20% (2035 contacts) are repulsive with interaction energies mainly up to 2 kcal/mol. Most of these repulsive contacts do not belong to two main groups of water-water contacts. Namely, 12.8% of all repulsive contacts can be classified as classical hydrogen bonds, 2.1% to the antiparallel interactions, and the rest (85.3%) as remaining contacts. This study points out that additional attention should be paid when one deals with contacts including water or, eventually, hydrogen atoms in general.

Keywords: water, repulsive interactions, CSD, quantum chemical calculations

1. Introduction

Water is the most abundant molecule. It plays important roles in life processes: transportation of protons, protein solvation, support of polar reactions and hydration of ions. Two water molecules can interact via attractive interactions as hydrogen bonds (-5.02 kcal/mol) [1]. Besides hydrogen bonds, antiparallel interactions have been recognized as a significant mode of interaction between water molecules. Surpassingly, nearly 20% of all attractive water-water contacts from the Cambridge Structural Database (CSD) form antiparallel interactions [2]. The results

show that the most stable geometry of antiparallel water-water interaction has an interaction energy of -4.22 kcal/mol. Besides attractive interactions between two water molecules, repulsive contacts were also noticed.
Here we present an analysis of repulsive water-water contacts from the CSD. Namely, it was found that more than 20% of all water-water contacts from CSD are repulsive. The results are shown in terms of the above-mentioned classical hydrogen bonds and antiparallel interactions.

2. Experimental section

2.1 CSD methodology

The statistical study was based on the data from the Cambridge Structural Database (CSD) [3]. Crystal structures taken into consideration satisfied the following criteria: (a) distance between two oxygen atoms $d_{OO} \leq 4.0$ A°; (b) a crystallographic R factor ≤ 5%; (c) error-free coordinates according to the criteria used in the CSD; (d) O—H bond lengths normalized using the CSD default O—H bond lengths (0.993 Å); (e) no ionic structures; (f) no polymer structures; (g) no powder structures; (h) no disordered structures; and (i) 3D coordinates determined. An additional restriction that could minimize structures with incorrectly introduced hydrogen atoms was achieved by taking into consideration only structures with bond angles (H—O—H) in the range 96.4–112.8° [4].

2.2 Computational methods

The interaction energies of two interacting water molecules satisfying the criteria described in the CSD methodology (9928 water dimers) were calculated at a very accurate level of theory, i.e., at CCSD(T)/CBS using the Gaussian09 program package.

3. Results and discussion

9928 water-water contacts were obtained as a result of the performed CSD search. A significant part of these contacts, i.e., 2616 contacts, are repulsive. Some repulsive contacts with short H···H or O···O contacts (581 contacts) were excluded from further consideration by applying criteria: $d_{HH} - d_{OH} < -0.6$ Å or $d_{OO} - d_{HH} < 0$. After applying geometric criteria for classical hydrogen bonds ($\alpha > 120°$, $d_{OH} \leq 3.0$ Å) and antipara llel interactions ($\beta_1 \geq 160°$, $\beta_2 \geq 160°$, $80° \leq \alpha \leq 140°$, $T_{HOHO} > 40°$) [2], it was found that the 12.8% of all repulsive water-water contacts belong to the classical hydrogen bonds, 2.1% to the antiparallel interactions, and 85.3% to remaining contacts (Figure 1). There are 4 contacts that can belong to both groups of contacts. It is important to notice that some of the water-water contacts that satisfy geometrical criteria for classical hydrogen bonds are repulsive. The CCSD(T)/CBS interaction energies of most of these repulsive contacts are up to 2 kcal/mol. Larger repulsive interaction energies

(> 2 kcal/mol) are most probably caused by short H···H contacts. The existence of short H···H contacts might be a consequence of packing of water molecules within crystal structures or poorly determined hydrogen atom positions.

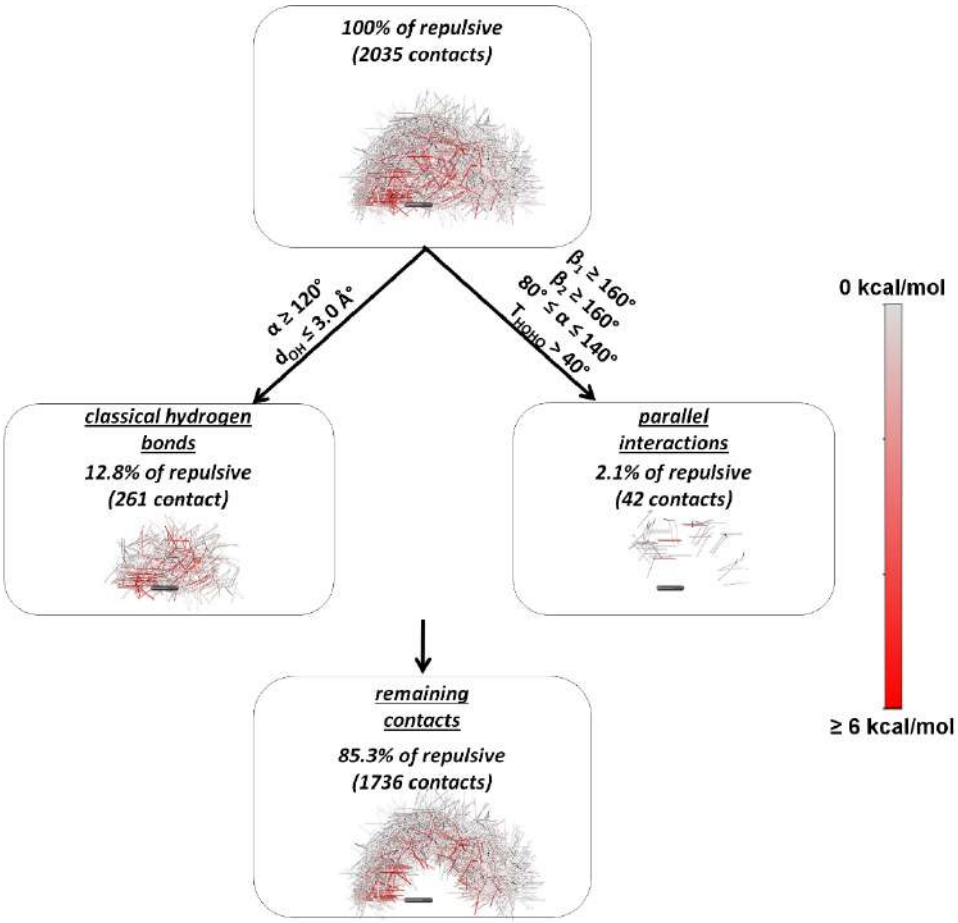

Figure 1. Sets of repulsive water–water contacts found in the CSD. In the graphical representations of water–water contacts, one water molecule was positioned in the centre (shown in dark grey). The other water molecules from every water–water contact are shown in the colour representing the CCSD(T)/CBS interaction energies, as shown in the scale.

4. Conclusions

This study aimed to point out that additional attention should be paid when contacts including hydrogen atoms are being discussed, since it was found that ca. 20% of all water-water contacts are repulsive, mostly with CCSD(T)/CBS interaction energies up to 2 kcal/mol. A cause for the overall repulsive interaction energies of these water-water contacts might be due to the existence of short H···H contacts. However, the repulsiveness of these contacts still remains unclear. On the other hand, since there is a large number of non- classified water-water contacts, one might consider that some

efforts should be dedicated to defining geometric criteria that would describe these contacts.

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References

[1] W.M. Klopper, J.G.C.M. van Duijneveldt-van de Rijdt, F.B. van Duijneveldt, *Computational determination of equilibrium geometry and dissociation energy of the water dimer*, Phys. Chem. Chem. Phys., 2 (2000) 2227-2234..

[2] M.R. Milovanović, I.M. Stanković, J.M. Živković, D.B. Ninković, M.B. Hall, S.D. Zarić, *Water: new aspect of hydrogen bonding in the solid state*, IUCrJ, 9 (2022) 639-647.

[3] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, *The Cambridge Structural Database*, Acta Cryst., B72 (2016) 171–179.

[4] M.R. Milovanović, J.M. Živković, D.B. Ninković, I.M. Stanković, S.D. Zarić, *How flexible is the water molecule structure? Analysis of crystal structures and the potential energy surface*, Phys. Chem. Chem. Phys., 22 (2020) 4138–4143.