INFLUENCE OF SUPRAMOLECULAR STRUCTURE IN THE CRYSTALS ON WATER/AROMATIC PARALLEL ALIGNMENT INTERACTIONS

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ABSTRACT. The parallel alignment interactions between water molecules and C_6-aryl groups in crystal structures and influence of supramolecular structures in crystals were studied by analyzing data in the Cambridge Structural Database (CSD). Analyses of crystal structures from the CSD reveal that the water/aromatic parallel alignment interactions, where the water molecule or one of its O-H bonds is parallel to the aromatic ring plane, are very frequent at large horizontal displacements. These orientations, observed in crystal structures, were compared with the results of *ab initio* calculations and explained by influence of supramolecular structures in crystals.

Keywords: water/aromatic parallel alignment interactions, crystal structures, influence of supramolecular structures in crystals.

INTRODUCTION

Understanding the nature of the interaction between aromatic and polar molecules, such as water, is of great importance for many areas [1] from materials to biological molecules. It is known that interactions of aromatic and water molecules have a significant role in systems such as aquaporins (water-transporting proteins) [2], nanotubes [3], and nanoporous materials [4]. Therefore, these interactions have been the subject of extensive experimental and theoretical investigations.

A substantial number of theoretical investigations have focused on characterizing the interaction between aromatic and polar molecules. The water-benzene dimer has very often been used as a prototype for aromatic–polar interactions. The OH/π [5] and CH/O [6] and parallel alignment interactions [7] between the aromatic ring and water molecules are well known in the literature. The energies of these interactions are $\Delta E_{CCSD(T)(limit)}$= -3.19 kcal/mol, [5b] $\Delta E_{CCSD(T)(limit)}$= -1.41 kcal/mol [7a] and $\Delta E_{CCSD(T)(limit)}$= -2.45 kcal/mol [7b] respectively.

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In spite of the fact that the interaction of nonpolar groups with polar solvent is somewhat weaker than a classical hydrogen bond, the experimental results showed that approximately one interaction is formed between liquid water and each dissolved benzene molecule [8].

Interestingly, by analyzing data in crystal structures from the Cambridge Structural Database (CSD) it was found that the largest number of interactions are of the CH/O type, at the expense of the OH/π interactions, even though the latter are computed to be stronger (Fig. 1). One may then conclude that packing has an important influence on the frequency of such interactions in crystal structures.
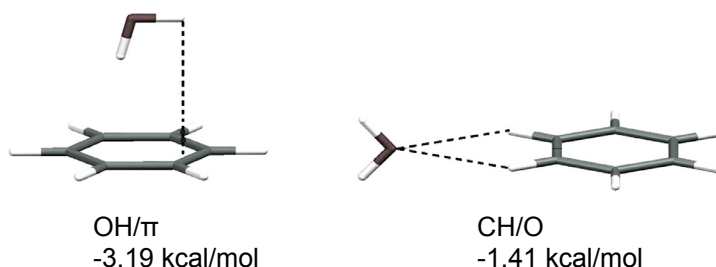

OH/π
-3.19 kcal/mol

CH/O
-1.41 kcal/mol

Figure 1. Water/benzene dimers that represent the most stable OH/π and CH/O interactions.

The earlier analysis of the CH/O interactions in the crystal structures showed that aromatic C–H donors do not have strong preference for linear contacts [6] and this is the result of the tendency of the C–H donors for additional stabilization by simultaneous interactions.

In our previous work [7], the water/benzene parallel alignment interactions with the whole water molecule (both O-H bonds) parallel to the aromatic ring plane (set A), and with one O-H bond parallel to the ring plane (set B) were analyzed. A much larger number of contacts in the set B was observed. The CSD results also showed that parallel O-H bonds are on the normal distance which are common for interactions of aromatic groups with approximately parallel molecular planes (3.3-3.8 Å) [9,10], while the normal distances for contacts at long offsets (in the C-H bond region and beyond) can be below 3.0 Å. The calculations reveal that the most stable conformation of parallel alignment interactions, with one O-H bond parallel to the plane of benzene ring, can be significantly strong ($\Delta E_{CCSD(T)(limit)}$= -2.45 kcal/mol) at large horizontal displacements, out of the aromatic ring and out of the C–H bond region (Fig. 2) [7b]. For the investigated water-benzene systems, the calculated normal distances were decreasing with increasing the horizontal displacement, and these results are in accord with the data found in crystal structures.
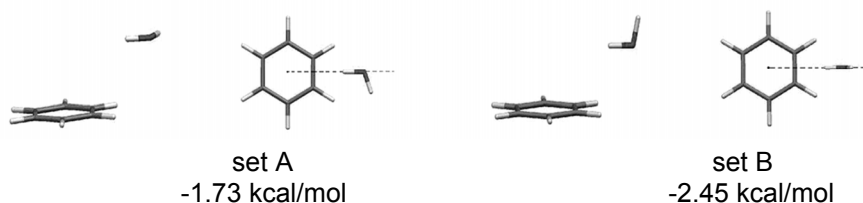
set A
-1.73 kcal/mol

set B
-2.45 kcal/mol

Figure 2. Water/benzene dimers that represent the most stable parallel alignment interactions with the whole water molecule (both O-H bonds) parallel to the aromatic ring plane (set A), and with one O-H bond parallel to the ring plane (set B).

Here, we present our new study of the parallel alignment water/aromatic interactions, based on analyses of crystal structures from the CSD. The reasons for this study are detailed examination of the geometry of these interactions in the crystal structures in order to investigate the influence of supramolecular structure on water/aromatic parallel alignment interactions. To the best of our knowledge, this is the first study that describes how the steric hindrance and conformational freedom of the system affect the frequency of interactions in the crystal structures.

RESULTS AND DISCUSSION

To study the influence of supramolecular structures in crystals on geometry of water/aromatic parallel alignment interactions, detailed statistical analysis was performed. We were interested in a number of structures satisfying the searching criteria and not in a preference for contacts to be at or near to the ring, hence, the area-corrected diagrams are not discussed.

The scattergram for the correlation between normal distance R_o and the offset r_o, for contacts in set A, reveals that most of the normal distances are in the range 3.0- 4.0 Å (Fig. 3).
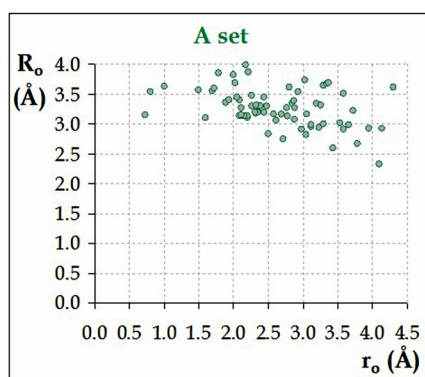

Figure 3. The correlation of the normal distance R_O with the offset r_o for intermolecular contacts of the set A.

These distances (3.3 - 3.8 Å) are common for the interactions of aromatic groups with approximately parallel molecular planes [9a]. The contacts are concentrated in the offset interval of 2.0 to 3.5 Å, suggesting that the oxygen atom may be placed above the ring but it is mostly found outside of the ring. However, while normal distances are in the range 3.0 - 4.0 Å, for the water molecule atoms above the aromatic ring, normal distances for the offsets larger of 2.5 Å can be below 3.0 Å. One should have in mind that in the aromatic ring the H atoms are at the offset ~ 2.4 Å, hence shorter normal distances are out of C-H bond region.

In order to assess mutual projections of water hydrogen and oxygen atoms onto the ring plane, Δr_1 ($\Delta r_1 = r_1 - r_O$) and Δr_2 ($\Delta r_2 = r_2 - r_O$) parameters were defined. The pattern of the results displayed in Fig. 4a shows great overall prevalence for an interaction in which the O-H_1 bond aligns itself with the H_1 atom pointing inside (Δr_1 is negative). The distribution of Δr_2 values, depicted in Fig. 4b, shows small overall prevalence for an interaction in which the O-H_2 bond points toward the ring center with the H_2 atom pointing outside (Δr_2 is positive). The typical geometry with positive Δr_1 values and negative Δr_2 value is reflected in the example shown in Fig. 5. The crystallographic evidence from the CSD search is in line with the results of *ab initio* calculations, that showed higher energy values of the complexes with water molecule outside of the ring comparing to the energies of the complexes with water directly above the ring [7].
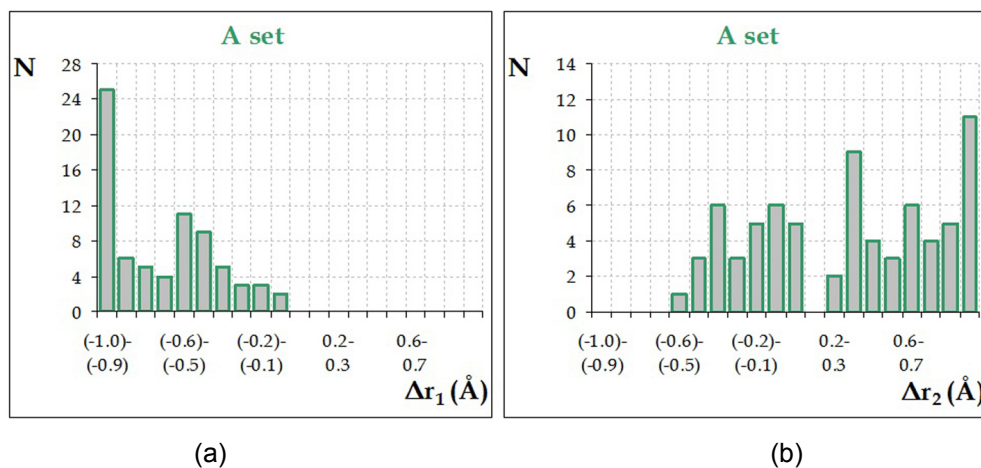

(a)

(b)

Figure 4. The histograms of the parameters Δr_1 (a) and Δr_2 (b) in retrieved crystal structures of set A.

In the set B are collected the structures where the O-H_1 bond is nearly parallel to the ring plane. Fig. 6 presents the distribution of normal distances R_o versus offsets r_o for this set of structures. Since the O-H_1 bond is almost

parallel to the ring plane, most of the observed molecular contacts are in the range 3.0 – 4.0 Å above the ring. Similar to the normal distances of the set A, normal distances for H_1 are below 3.0 Å for the offset values larger of 2.5 Å. The population distribution, presented in Fig. 6, shows that the contacts are concentrated in the offset interval of 3.0 to 4.0 Å, and indicating that most of the oxygen atom projections are outside of the ring.
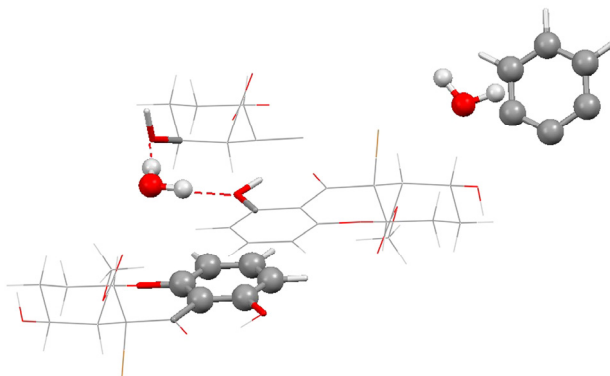

Figure 5. The fragment of crystal structure DELVIC [11]
(*8ab-bromo-5aa,5,6,7,8,8a-hexahydro-1,7a-dihydroxy-8a-methoxycarbonyl-xanthone monohydrate*) selected as an example of the typical geometry for set A
(r_O= 2.09 Å, Δr_1= -0.96 Å and Δr_2= 0.35 Å). The water molecule also builds two additional intermolecular OH/O interactions: $H_1 \cdots O_1$= 1.80 Å and O-$H_1 \cdots O_1$= 179.7°; $H_2 \cdots O_2$= 1.71 Å and O-$H_2 \cdots O_2$= 179.0°).
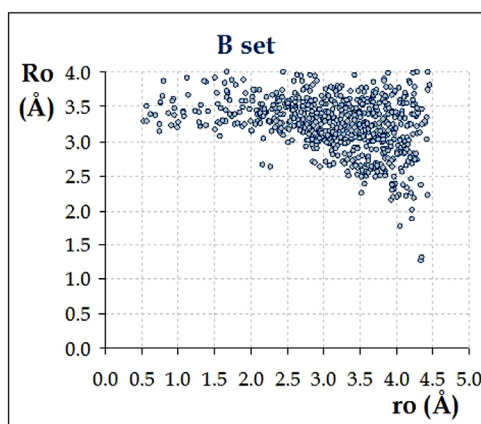

Figure 6. The correlation of the normal distance R_O with the offset r_o in intermolecular contacts of the set B.

To define the positions of hydrogen atoms, with respect to the oxygen atom and the plane of aryl group, Δr_1 ($\Delta r_1 = r_1 - r_O$) and ΔR_2 parameters ($\Delta R_2 = R_2 - R_O$) were defined. The distributions of these parameters, for set B, are shown in Fig. 7. The maximum of the Δr_1 distribution (Fig. 7a) indicates toward-center orientation of the $O-H_1$ bond with the H_1 atom pointing inside. The histogram of distribution of parameter ΔR_2 (Fig. 7b) shows two maxima, around -0.9 Å and a smaller one around +0.9 Å (O is closer to the plane of the aryl ring than H_2). In the first (densely) populated group, with $\Delta R_2 < 0$ Å, the $O-H_2$ group is directed towards to the ring plane, and is mainly involved in the interaction with the substituent of the aromatic group. However, in a second populated region, with $\Delta R_2 > 0$ Å, the $O-H_2$ group is directed upwards with respect to the ring plane. The typical geometry with negative Δr_1 and ΔR_2 values is reflected in the example shown in Fig. 8.
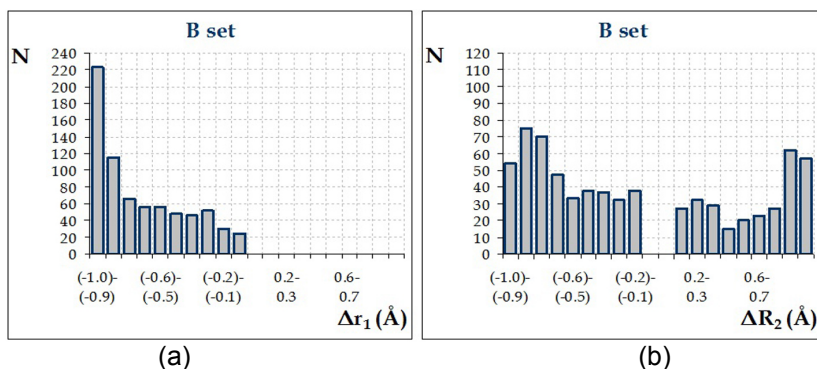

(a)   (b)

Figure 7. The histograms of the parameters Δr_1 (a) and ΔR_2 (b) in retrieved crystal structures of set B.
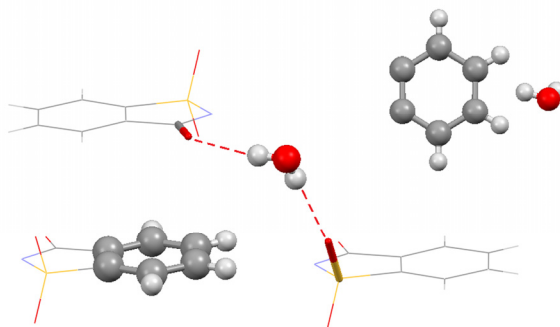

Figure 8. The fragment of crystal structure XUVHUR [12] bis(2,6-dimethanolpyridine)-nickel(II) bis(saccharinate) dihydrate) selected as an example of the typical geometry for set B (r_O= 3.84 Å, Δr_1= -0.97 Å and ΔR_2= -0.83 Å). The water molecule also builds two additional intermolecular OH/O interactions: $H_1 \cdots O_1$= 2.00 Å and $O-H_1 \cdots O_1$= 171.1°; $H_2 \cdots O_2$= 2.09 Å and $O-H_2 \cdots O_2$= 158.3°).

The results of crystallographic analysis showed that the interactions of set B (716 contacts) are ten times more numerous than the interactions of set A (71 contacts), suggesting that crystal packing has a very important influence on the geometry of water/aromatic parallel alignment interactions in the crystal structures. In order to illustrate and detail this influence, a few examples are given in the following paragraphs.

The examples given here should provide an explanation for the differences in the frequency, geometry and strength of investigated types of interactions.

Among the A complexes considered, the structures corresponding to the energy minimum have a positive Δr_2 value. However, the distribution of Δr_2 values, depicted in Fig. 4b, shows that a large number of structures (~36%) have a negative Δr_2 value, in which the O-H$_2$ bond is directed towards the ring (Fig. 6). The visual analysis of the crystal structures reveals that such orientation of water molecule and aromatic group is a consequence of the interaction between both water hydrogen atoms with the group from environment, which simultaneously interacts with the aromatic group. The typical geometry with a negative Δr_2 value is reflected in the example shown in Fig. 9. In crystal structure IVENIG [13], besides parallel interaction with phenyl group, both water hydrogen atoms build additional OH/Cl interactions with Cl atoms from the environment, that simultaneously form interactions with the phenyl group, included in parallel interaction with the water molecule.
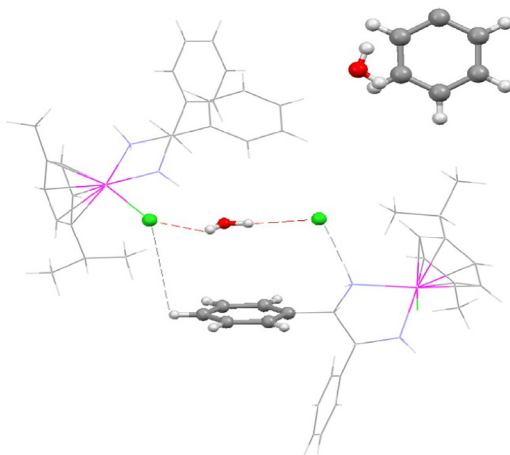

Figure 9. The fragment of crystal structure IVENIG ((η^6-1-isopropyl-4-methylbenzene)-chloro-(1,2-diphenylethylenediamine-N,N')-ruthenium(II) chloride dichloromethane solvate monohydrate) selected as an example of set A (r_O= 2.61 Å, Δr_1= -0.49 Å and Δr_2= -0.34 Å). The water molecule also builds two additional intermolecular OH/Cl contacts: H$_1$···Cl$_1$= 2.35Å and O-H$_1$···Cl$_1$= 170.3°; H$_2$···Cl$_2$= 2.50Å and O-H$_2$···Cl$_2$= 148.6°).

In the structures of set B, the water $O-H_2$ group has greater conformational freedom than the water $O-H_2$ group in the structures of set A. Namely, in the structures of set A, the water $O-H_2$ group is parallel to aryl group, in other words the $O-H_2$ group forms an angle of less than with the plane of the aryl group. The range of this angle values for structures of set B (from 10° to 90°) is much larger than the range for structures of set A, explaining the previous assertion that the water $O-H_2$ group has greater conformational freedom in the structures of set B. The higher interaction energies and greater conformational freedom of the $O-H_2$ group in the structures of set B are the reasons why the contacts of set B are about ten times more frequent than the contacts of set A in the crystal structures.

In spite of being somewhat weaker than OH/π interaction between water molecule and aryl group (-3.19 kcal/mol) [5b], we found that parallel alignment interactions occur more frequent in crystal structures. These results indicate that the influence of supramolecular structure on mutual orientation of water molecule and aromatic group is very important in the crystal structures. In the parallel alignment interaction, the additional stabilization is achieved, as all atoms of the water molecule can form additional interactions simultaneously, while one of these is eliminated by the OH/π interaction.

The number of additional supramolecular interactions, satisfying the criteria specified in Methodology section, including the parallel $O-H_1$ bonds, for contacts of set B is 913. The total number of contacts in set B is 716, what implies that in 200 contacts the parallel $O-H_1$ groups simultaneously form two additional interactions. The classical hydrogen bonds (or OH_1/X, where X=O, N, F, Cl, and S) have a majority in forming of additional supramolecular interactions (38.5%), while $OH_1/π$ interactions have a slightly smaller contribution (37.6%).

However, using the criteria for OH/π interactions, specified in Methodology section, 545 interactions of non-coordinated water and C_6-aromatic groups were found, that is less than the number of contacts with parallel alignment interactions. In these 545 contacts, water $O-H_1$ bonds build 410 additional supramolecular interactions. Hence, 135 water $O-H_1$ bonds, included in OH/π interactions, do not build additional interactions. It is obvious that the geometry of the parallel alignment orientations allows the molecules of benzene and water to form larger number of additional interactions. Therefore these interactions are more numerous than the OH/π interactions in crystal structures.

To provide further illustration for these unexpected results, the fragment of crystal structure EBAQII [14] is shown at Fig. 10.

In this structure, beside the water/aromatic parallel alignment interaction, the water $O-H_1$ group builds two classical hydrogen bonds with two O-H groups of the pyrogallol fragment from the environment. One of pyrogallol O-H groups forms an OH/π interaction with the aryl ring, that is included in water/aromatic parallel alignment interactions. However, as can be seen from Fig. 10, from

steric reasons, the pyrogallol OH group is involved in building up only one (OH/π) interaction. It means that the position of water molecule, in structures with water/aromatic parallel alignment interactions, is more stabilized by additional interactions, than in structures with OH/π interactions.
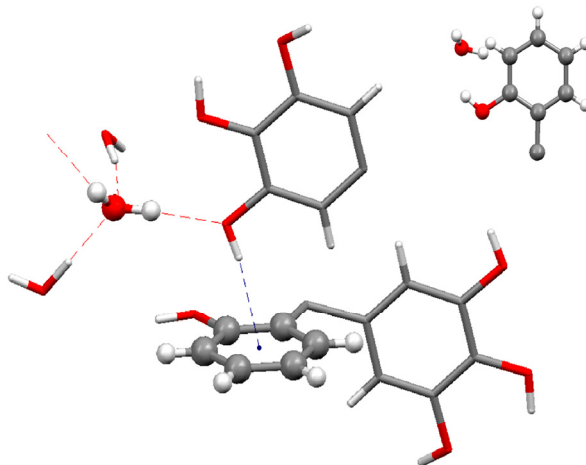

Figure 10. The fragment of crystal structure EBAQII (5-(bis(2-hydroxyphenyl)methyl)phenyl-1,3,5-triol tetrahydrate) selected as an example of B set (r_O= 3.56 Å, Δr_1= -0.92 Å and ΔR_2= 0.66 Å). The water O-H$_1$ group also builds two additional classical hydrogen bonds with two O-H groups of pyrogallol fragment (H$_1$···O$_a$= 1.87 Å and O-H$_1$···O$_a$= 165.9°, H$_1$···O$_b$= 2.61 Å and O-H$_1$···O$_b$= 118.1°). One of the pyrogallol O-H group forms OH/π interaction with aryl ring (H···Ω= 2.66 Å and O$_a$-H···Ω= 152.1°) included in water/aromatic parallel alignment interactions.

CONCLUSIONS

The data presented here show that in parallel interactions water molecules are mostly found outside of the aromatic ring. The number of interactions with one water O-H bond parallel to the plane of aromatic ring is much larger than the number of interactions with the whole water molecule parallel. The results of calculations cannot explain completely the results of CSD analysis. The reason for this disagreement can be the influence of supramolecular structure on interactions in the crystals.

METHODOLOGY SECTION

The statistical study is based on the crystal structures archived in the Cambridge Structural Database (November 2011 release, version 5.33) [15]. The crystal structures involving non coordinated water molecule and C$_6$-aromatic group were screened for intermolecular contacts. The CSD search program

ConQuest 1.14 [16] was used to retrieve structures satisfying the following criteria: a) the crystallographic R factor < 10% b) the error-free coordinates according to the criteria used in the CSD c) the H-atom positions were normalized using the CSD default X-H bond lengths (O-H = 0.983 Å; C-H = 1.083 Å) d) no polymer structures. The geometric parameters used throughout in the text and the atom labeling scheme are displayed in Fig. 11.
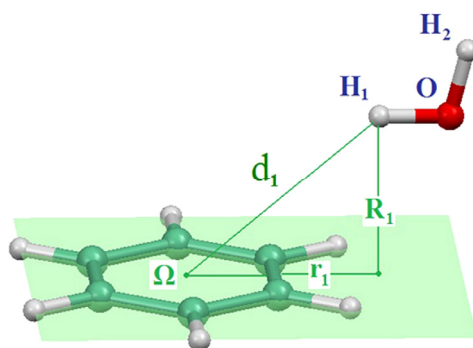

Figure 11. The geometric parameters and atoms labeling, used for the description of parallel interaction. Ω marks the centroid of the benzene ring. The hydrogen atom of the water molecule that is closer to the center of the ring, comparing to the second hydrogen atom of the water molecule, is denoted by H_1. The distances between H_1, H_2, and O, and the centroid of the ring are referred to as d_1, d_2, and d_O, respectively. The distances R_1, R_2, and R_O mark the normal distances from the ring plane to the H_1, H_2, and O atoms, respectively. The offsets r_1, r_2, and r_O are the distances from the ring centroid to the projection of the H_1, H_2, and O atom position, respectively, on the plane of the ring. In the benzene ring the distance from the ring centroid to the center of the carbon-carbon bond is about 1.2 Å and the distance between the center of the ring and the carbon atom is ~ 1.4 Å.

It is considered that parallel alignment interaction occurs if the offset value r_1 is less than 3.5 Å, the normal distance R_1 is less than 4.0 Å (**Fig. 11**), Δr_1 value is less than 0.0 Å ($\Delta r_1 = r_1 - r_O$) and the absolute value of ΔR_1 is less than 0.1 Å ($\Delta R_1 = R_1 - R_O$) [7b] The absolute value of ΔR_1 less than 0.1 Å corresponds to the parallel orientation of water O-H_1 bond and aromatic ring. A negative value of Δr parameter indicates the orientations where the projection of O-H bond points to ring with the H atom inside.

The contact was considered as a OH/π interaction if the distance between a hydrogen atom of water molecule and the center of any C_6-aromatic ring (Ω) was less than 3.5 Å, α angle (O-H_1···Ω angle) larger than 110° and β angle (the angle between the H_1···Ω line and the normal to the aromatic ring) less than 30° (**Fig. 11**).

The contacts between O-H$_1$ group and X species from environment, where O···X distance was shorter than 4.0 Å and O-H$_1$···X angle is larger than 110°, [17] were considered as "additional supramolecular interactions".

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