Parallel alignment of water and aryl rings—crystallographic and theoretical evidence for the interaction†

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Analysis of crystal structures from the Cambridge Structural Database (CSD) that involve close contact between water and aryl rings revealed the existance of conformations where the water molecule or one of its O–H bonds is parallel to the aromatic ring plane at distances typical for stacking interactions; attractive interaction energies obtained from *ab initio* calculations performed on model systems are significant (*e.g.* $\Delta E_{CCSD(T)}$ = –1.60 kcal mol^{-1}) and consistent with the observed structures.

Water plays an essential role in nature and its geometry, small size, and high polarity govern its capabilities and the complexity of its behavior. Most important is its hydrogen-bonding ability, as it forms strong hydrogen bonds to other polar molecules and builds strong networks with itself.[1]

In addition to these strong intermolecular interactions, water molecules also have important weaker interactions with less polar molecules. The so-called "OH···π" interaction, in which the water molecule interacts with aromatic rings, plays an important role by enabling interactions of nonpolar groups with polar solvent. These interactions have been observed in various molecular systems.[2] In particular, the water–benzene complex has been the subject of extensive theoretical investigation.[3] Most studies agree that the minimum energy structure of the water–benzene dimer involves the water above the ring oriented to form a single hydrogen bond with the ring, *i.e.* one H close to the center of the ring, the O atom lying close to or on the benzene six-fold axis, and the other O–H bond parallel to the benzene plane.

Here, we examine a situation in which the water/aromatic-ring interaction is modified by water having strong hydrogen bonds to other species. In this situation the strong OH···π interaction is prevented and the remaining water/aromatic-ring intermolecular interactions result in either the whole water molecule or one of its O–H bonds lying parallel to the C_6 aromatic ring. These important new geometric features were discovered by examining crystal structures from the CSD and analyzed by *ab initio* quantum mechanical calculations of the water–benzene dimer including coupled cluster electron correlation treatment (CCSD(T)) and complete basis set extrapolation. To the best of our knowledge this is the first study describing these important parallel-alignment interactions and their energies.

The statistical study is based on the crystal structures archived in the Cambridge Structural Database (November 2007 release, version 5.29).[4] Crystal structures involving non-coordinated water molecules and C_6-aromatic groups were screened for intermolecular contacts. The CSD search program ConQuest 1.10[5] was used to retrieve structures satisfying the following criteria: (a) the crystallographic *R* factor is ≤ 10%; (b) error-free coordinates according to the criteria used in the CSD; (c) H-atom positions were normalized using the CSD default bond lengths; (d) no polymer structure; (e) no powder structures; (f) not disordered structures; (g) 3D coordinates determined.

Among the CSD crystal structures we found 1598 short intermolecular contacts between a water and a C_6-aryl ring where the distance (d_1) between the H atom of the water molecule and the center of the ring is less than 4.5 Å, the normal distance (R_1) of the H atom from the plane of the ring is less than 4.0 Å and the distance (r_1) from the ring centroid to the projection of the H atom to the plane of the ring is less than 2.0 Å (Fig. 1). In these structures we found 720 parallel alignments of either the whole water molecule (79 contacts, type A set) or one of its O–H bonds.

When one O–H bond is in the parallel alignment, the other O–H bond can be in positions ranging from an upward orientation away from the aromatic ring through the totally parallel alignment (type A set mentioned above) to an

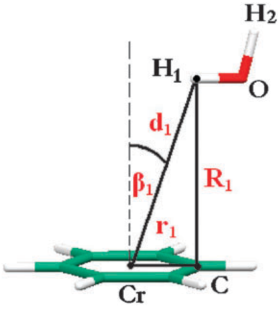

Fig. 1 The geometric parameters and atom labelling used for the description of parallel-alignment interaction. C_r-the centroid of the C_6-aromatic ring; d_1, d_2 and d_O are the distances between H_1, H_2 and O, respectively, and the centroid of the ring; R_1, R_2 and R_O are the normal distances from 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 positions, respectively, on the plane of the ring; the angles β_1, β_2 and β_O are measured between the C_r–H_1, C_r–H_2, and C_r–O lines, respectively, and the normal to the ring plane.

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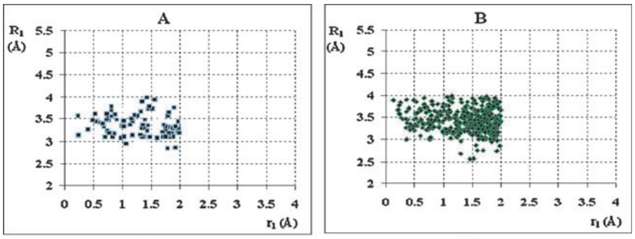

(a) (b)

Fig. 2 The scattergram for the correlation of the normal distance R_1 with the offset r_1 in intermolecular contacts of type A (a). The scattergram for the correlation of the normal distance R_1 with the offset r_1 in intermolecular contacts of the type B (b).

orientation toward the π-system of the aromatic ring. In the last case the dominant interaction is the well-known OH···π interaction, and we will not consider such structures further (250 contacts), but will focus on structures where the contribution of parallel alignment of one O–H bond is dominant (391 contacts, type B set). The analysis of the geometries of the types A and B shows that most water molecules are positioned close to the edge of the aromatic ring or just outside the ring – above the region of the C–H bonds.

The R_1 distances in these parallel alignments are between 3.0 and 4.0 Å (Fig. 2). This range is very close to the typical range for stacking (mutual slipped-parallel orientation) interactions of two aromatic rings, 3.3–3.8 Å[6,7] suggesting that this parallel-alignment interaction could be related to the stacking interaction.

Ab initio calculations were performed on model systems consisting of water–benzene dimers. The geometries of isolated molecules, the benzene and the water molecule, were optimized by gradient optimization using the cc-pVTZ basis set and the Møller–Plesset second-order perturbation method (MP2). These geometries were used for the calculation of interaction energies. The distance (R) between the benzene ring plane and the parallel OH bond (type B) or whole water molecule (type A) was systematically varied while the monomer geometries were kept rigid. These optimum intermonomer distances were computed at the MP2/cc-pVTZ level. The intermolecular interaction energies were calculated at the MP2 and CCSD(T) levels with Dunning's correlation consistent basis sets (cc-pVDZ, cc-pVTZ, cc-pVQZ, aug-cc-pVDZ and aug-cc-pVTZ). The basis set superposition error (BSSE) was calculated using the standard Boys–Bernardi counterpoise procedure.[8] The method of Helgaker *et al.*[9] for the estimation of MP2 and CCSD(T) interaction energies at the basis set limit was used. The Gaussian98 series of programs[10] were employed.

The basic arrangements chosen for the water-benzene dimers were based on the geometries observed in the crystal structures. The *ab initio* calculations were done on a number of model systems with the parallel alignment of the whole water molecule (type A structures) and with only one O–H bond parallel to the ring plane (type B structures). Typical model systems are shown in Fig. 3. The most stable structure with the parallel alignment of the whole water molecule (A_1, Fig. 3) has a calculated CCSD(T) basis set limit interaction energy ($\Delta E_{\mathrm{CCSD(T)(limit)}}$) of –1.45 kcal mol^{-1}. The model system with the water molecule above the ring (example A_2, Fig. 3) has a smaller interaction energy; $\Delta E_{\mathrm{CCSD(T)(limit)}}$ = –0.90 kcal mol^{-1}. The most stable model system of all those considered has one O–H bond parallel to the C–H bond of the benzene with the oxygen atom above the hydrogen atom of the benzene (B_1, Fig. 3), $\Delta E_{\mathrm{CCSD(T)(limit)}}$ = –1.60 kcal mol^{-1}. Like the model systems of type A, the type B structures with the water molecule above the ring, rather than above the C–H bond region, have smaller interaction energies; for example, the interaction energy of the B_2 structure (Fig. 3) is $\Delta E_{\mathrm{CCSD(T)(limit)}}$ = –0.78 kcal mol^{-1}.

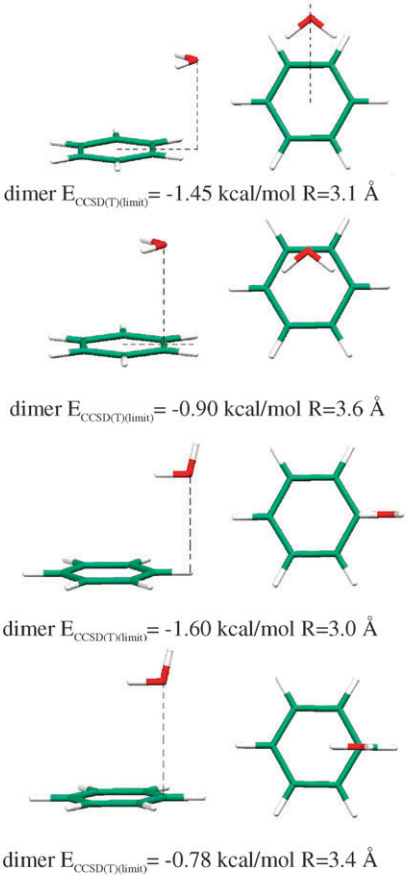

Fig. 3 The model systems of the water–benzene dimers used for the *ab initio* calculations of the normal distances and the interaction energies. The values of R are optimal distances between the benzene ring plane and the parallel OH bond (type B) or whole water molecule (type A).

In all model systems the calculated R distances are shorter for water molecules above the C–H region (3.0–3.3 Å) than above the ring (3.4–3.6 Å). The calculated distances and the calculated preferred positions above the C–H region are in agreement with the distances and the positions observed in the crystal structures.

The water and benzene also form OH···π and C–H···O interactions. In order to compare the calculated energies of the parallel-alignment interactions with the energies of these two better-known interactions, we calculated their interaction energies employing the same methodology. For the OH···π the interaction energy is $\Delta E_{\mathrm{CCSD(T)(limit)}}$ = –3.19 kcal mol^{-1}, significantly stronger than the parallel-alignment interaction. Both OH···π and parallel alignment interactions occur quite frequently in the crystal structures. In the parallel alignment interaction the

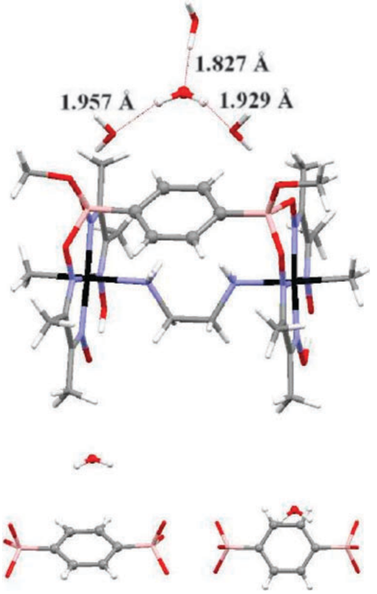

Fig. 4 An example of the crystal structure QADKEM[11] with the parallel-alignment interaction between the water and the aryl ring; side-on view (bottom left); overhead view (bottom right). The normal distances and the corresponding offset values are: $R(H_1)$ = 3.722 Å, $R(O)$ = 3.822 Å and $R(H_2)$ = 3.735 Å, and $r(H_1)$ = 1.525 Å, $r(O)$ = 1.995 Å and $r(H_2)$ = 1.760 Å, respectively. The water molecule forms additional conventional hydrogen bonds (top).

additional stabilization is achieved as all atoms of the water molecule can form classical hydrogen bonds simultaneously, while one of these is eliminated by the OH···π interaction. Such hydrogen bonds were observed in the crystal structures (Fig. 4).

The calculated interaction energy for the CH···O interaction between water and benzene is $\Delta E_{\mathrm{CCSD(T)(limit)}}$ = –1.41 kcal mol^{-1}. Some of the parallel-alignment geometries have somewhat larger interaction energies than the CH···O interactions. Thus, the parallel-alignment interactions are of comparable importance for water–aromatic contacts as the better known CH···O interactions.

The observed parallel-alignment interactions in the crystal structures and the calculations of their strengths at the CCSD(T) complete basis set limit support our conclusion that these interactions are a consequence of attractive interactions between water and the aryl ring. Our results confirm that this interaction, like other weak interactions, coexists with much stronger interactions. The results presented here elucidate these new interactions of water with aromatic rings that are important in various systems, especially biomolecules.

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