Are Water–Aromatic Complexes Always Stabilized Due to π–H Interactions? LMP2 Study

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ABSTRACT: Eight complexes of various aromatic molecules with water have been studied theoretically at the local Møller–Plesset 2nd order theory (LMP2)/aug-cc-pVTZ(-f)//LMP2/6-31+G* level of theory. Two types of complexes can be formed, depending on the electronic structure of aromatic molecules. Donor hydrocarbons form **A**-type complexes, while aromatics bearing electron-withdrawing substituents form **B**-type complexes. **A**-type complexes are stabilized due to π–H interactions with the OH bond pointing to the aromatic molecule plane, while **B**-type complexes have geometry with the oxygen atom pointing to the aromatic molecule plane stabilized by the interaction of highest occupied molecular orbital (HOMO) of water molecule with π^* orbitals of the aromatics. It has been found that a (—HOMO–lowest unoccupied molecular orbital (LUMO)/2 value of aromatic molecule, which can be called "molecular electronegativity," is useful to predict the type of complex formed by aromatic molecule and water. Aromatic hydrocarbons with "molecular electronegativity" of <0.15 tend to form **A**-type complexes, while aromatic molecules with "molecular electronegativity" of <0.15 a.u. form **B**-type complexes. The binding energy of water–aromatic complexes undergoes a minimum in the area of switching from **A**-type to **B** type complexes, which can be rationalize in terms of frontier orbital interactions.   © 2005 Wiley Periodicals, Inc. Int J Quantum Chem 104: 335–341, 2005

Key words: ab initio calculations; computer chemistry; LMP2 calculations; noncovalent interactions

Introduction

One of the major goals of chemistry in recent times has been the investigation and understanding of weak interactions [1–6]. Thus, aromatic–aromatic interactions play important roles in many chemical and biological systems. They govern base–base interactions leading to the double helical structure of DNA, the function of the special pair in photosynthetic reaction centers, packing of aromatic crystals, formation of aggregates, binding affinities in host–guest chemistry, and conformational preferences of polyaromatic macrocycles.

Local-correlation methods [7, 8] have emerged as an alternative approach to the study of intermolecular interactions [9, 10]. Although the primary goal of local-correlation methods has been to reduce the steep dependence of the computational cost on the size of the chemical system, they also introduce some conceptual advantages for studying intermolecular interactions, such as reduced basis set superposition error (BSSE) [9] and the possibility of decomposing the local-correlation energies into different excitation classes [10]. In particular, it was shown that the local Møller–Plesset 2nd order theory (LMP2) and BSSE-corrected MP2 equilibrium properties for the water dimer [9], water clusters [10], and model dimers of gold [11] are fairly close. It has been shown that the LMP2 method is superior to canonical MP2 for benzene, pyridine, and naphthalene dimers [12] and that it is also much less computationally demanding.

The LMP2 approach has been successfully applied to estimate interaction energies of C_{60} fullerene with simple donor molecules and water [13, 14]. Unlike simple aromatic molecules such as benzene, where π–H interactions are responsible for the complex formation, it has been found that C_{60} interacts with a lone pair of water molecule, acting as an electron-withdrawing unit. Actually, the understanding of the nature of the interaction of water with aromatic molecules is of importance for an ample area from biology to the oil industry. Unfortunately, because of the high computational cost, only very simple complexes such as benzene–H_2O have been studied [15–21], and no detailed reports on the electronic structure effect on the properties and geometry of water–aromatic complexes have been reported to date, except for one dealing with water/single-layer graphite interactions in which complexes between a series of acenes and water molecule have been studied at the MP2 level [22]. Judging from data obtained for C_{60} microsolvation [14], there is a possibility that the geometry and binding energy of water–aromatic complexes depends strongly on the electronic properties of the aromatic fragment of the complex. Therefore, the goal of the present study is to investigate the effect of donor–acceptor properties of aromatic molecules on the stability and geometry of their complexes with water, using the LMP2 approach.

Computational Details

All geometry optimizations were carried out without any symmetry restrictions. LMP2 geometry optimizations and single-point energy evaluations were carried out with the Jaguar 4.2 suite of programs [23], using 6-31+G* and aug-cc-pVTZ(-f) basis sets, respectively. For all binding energies, a counterpoise correction term has been computed according to Ref. [24]. In some cases (Tables I and II), counterpoise-corrected binding energies are slightly more negative compared with uncorrected ones. This is due to a numerical error originating from the grid-based implementation of LMP2 code in Jaguar 4.2. The benzene–water complex was used as a model system to test the performance of a selected model. As seen in Table I, electronic binding energy for this complex is in excellent agreement with that determined from threshold photoionization measurements [25] −2.4 (±0.1 kcal/mol), while the canonical MP2 method overestimates stabilization energy (−3.9 kcal/mol) [21] similar to that for benzene dimers [12], in which the LMP2 method was shown to be superior to canonical MP2. Two conformations were tested as initial structures for geometry optimization: one with an OH bond and oxygen pointing to the aromatic molecule plane, respectively.

Since MP2 frequencies are very computationally expensive for large systems, no systematic vibrational analysis was carried out. Nevertheless, to estimate the error introduced by zero-point energy (ZPE), the frequency jobs were run for benzene–water and triazine–water complexes. The results show that when ZPE correction is taken into account benzene–water complex reduces its stability by 0.7 kcal/mol and the triazine–water complex by 0.5 kcal/mol, which is reasonably small correction. Moreover, the relative stability of the complexes will be almost unaffected due to a similar correction in all cases.

TABLE I

LMP2/aug-cc-pVTZ(-f)/LMP2/6-31+G* energies (a.u.) and stabilization energies of water–aromatic complexes (kcal/mol).

Complex	E	Aromatic	Water	ΔE^a	ΔE_c^b	E_{corr}^c
An–H_2O	−614.409857	−538.101342	−76.30179	−4.22	−3.00	−2.44
Aza–H_2O	−1012.182899	−935.871099		−6.28	−6.21	−2.70
Cor–H_2O	−995.784271	−919.478398		−2.56	−2.63	−2.85
Naph–H_2O	−461.177124	−384.870837		−2.82	−2.93	−2.06
Tetracyano–H_2O	−829.382562	−753.075595		−3.25	−3.16	−0.95
Tetracyanoan–H_2O	−982.624975	−906.318318		−3.05	−2.97	−2.20
Triazine–H_2O	−356.031765	−279.726830		−1.97	−2.29	−2.31
Benzene–H_2O	−307.934941	−231.628740		−2.68	−2.64	−1.77

[a] LMP2 stabilization energy.
[b] BSSE-corrected LMP2 stabilization energy.
[c] Correlation stabilization [E(LMP2)–E(HF)].

Results and Discussion

To study the effect of electronic structure on the geometry and binding energy of aromatic–water complexes, a series of aromatic hydrocarbons has been selected, including benzene, naphthalene (**Naph**), anthracene (**An**), and coronene (**Cor**). The benzene–water complex is well studied both experimentally and theoretically [15–21], and it was used as a reference point. In contrast, neither experimental nor theoretical data exist on the rest of the complexes, except for the coronene–water complex studied theoretically at the MP2 level [22]. Aside from these water–aromatic complexes, others formed by triazine, 2,3,6,7-tetracyanonaphthalene (**Tetracyano**), 2,6,9,10-tetracyanoanthracene (**Tetra-**

cyanoan), and 9-azacoronene (**Aza**) were studied. The latter group is formed by hydrocarbons bearing electron-withdrawing substituents.

Table III shows HF/6-31+G*//LMP2/6-31+G* highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies of hydrocarbons, which can be considered ionization potential (IP) and electron affinity (EA) with opposite sign according to Koopmans' theorem [26]. As seen IPs increase from anthracene, coronene, naphthalene, 2,6,9,10-tetracyanoanthracene, benzene, 2,3,6,7-tetracyanonaphthalene, and 9-azacoronene to triazine, while EAs increase from benzene, naphthalene, triazine, coronene, anthracene, 2,3,6,7-tetracyanonaphthalene, and 2,6,9,10-tetracyanoanthracene to 9-azacoronene. Therefore, one could estimate the "molecular electronegativity" of

TABLE II

HF/aug-cc-pVTZ(-f)/LMP2/6-31+G* energies (a.u.) and stabilization energies of water–aromatic complexes (kcal/mol).

Complex	E	Aromatic	Water	ΔE^a	ΔE_c^a
An–H_2O	−612.194181	−536.135655	−76.05771	−0.51	−0.56
Azo–H_2O	−1008.610375	−932.546950		−3.59	−3.51
Cor–H_2O	−992.228373	−916.170990		0.2	0.22
Naph–H_2O	−459.515122	−383.456457		−0.56	−0.87
Tetracyano–H_2O	−826.490916	−750.429805		−2.13	−2.21
Tetracyanoan–H_2O	−979.175300	−903.116516		−0.67	−0.77
Triazine–H_2O	−354.833976	−278.776385		0.07	0.02
Benzene–H_2O	−306.827313	−230.768365		−0.56	−0.87

[a] HF stabilization energy.
[b] BSSE-corrected HF stabilization energy.

TABLE III

LUMO and HOMO energies for aromatic molecules and water at HF/6-31+G*/LMP2/6-31+G* level (a.u.).

Aromatic	HOMO	LUMO	(—HOMO–LUMO)/2[a]	Water	LUMO$_{H_2O}$–HOMO$_{arom}$	LUMO$_{arom}$–HOMO$_{H_2O}$
An	−0.25896	0.03540	0.11175	HOMO−0.50799	0.40507	0.54339
Aza	−0.39878	−0.10132	0.25005	LUMO 0.14611	0.54489	0.40667
Cor	−0.26394	0.05794	0.10300		0.41005	0.56593
Naph	−0.28920	0.07413	0.107535		0.43531	0.58212
Tetracyano	−0.36832	−0.01553	0.191925		0.51443	0.49246
Tetracyanoan	−0.33010	−0.04977	0.189935		0.47621	0.45822
Triazine	−0.44280	0.07080	0.18600		0.58891	0.57879
Benzene	−0.33509	0.08464	0.125225		0.4812	0.59263

[a] "Molecular electronegativity."

the molecules calculating the IP and EAs average similar to Mulliken's concept of electronegativity for atoms [27]. Then, aromatic molecules can be arranged in descending order of electronegativity as follows: 9-azacoronene, 2,3,6,7-tetracyanonaphthalene, 2,6,9,10-tetracyanoanthracene, triazine, benzene, anthracene, coronene, and naphthalene. As shown in Table III, there are two groups of molecules with close electronegativities: the first group includes donor molecules coronene, naphthalene, and anthracene; and the second group consists of acceptors 9-azacoronene, 2,3,6,7-tetracyanonaphthalene, 2,6,9,10-tetracyanoanthracene, and triazine. Benzene is closer to donor group of molecules with —HOMO–LUMO/2 value of 0.125 a.u.

Figure 1 shows the geometries of complexes obtained at LMP2/6-31+G* level. The first point to mention is that in all cases, only one type of conformation was found to be stable for each complex: either one with an OH bond (**A**-type) or the one-oxygen atom (**B**-type) pointing to the aromatic molecule plane. As can be seen from Figure 1 and Table III, aromatic molecules with high "molecular electronegativity" form **B**-type complexes, while low "molecular electronegativity" leads to the formation of **A**-type complexes.

The two complexes investigated in the present work, benzene–water and coronene–water, have been studied previously. The LMP2 method generally predicts complexes to be looser in comparison with the canonical MP2 one. It has also been shown [12] that for aromatic dimers, LMP2 produces geometries closer to those obtained with the MP4 (SDTQ) method than with the canonical MP2 approach.

In the case of coronene–water complexes, LMP2/6-31+G* geometry is qualitatively similar to

that of the MP2/aug-cc-pVDZ one [22], with the difference that C—O distance in the former is some 0.3 Å longer (Fig. 1). The benzene–water complex
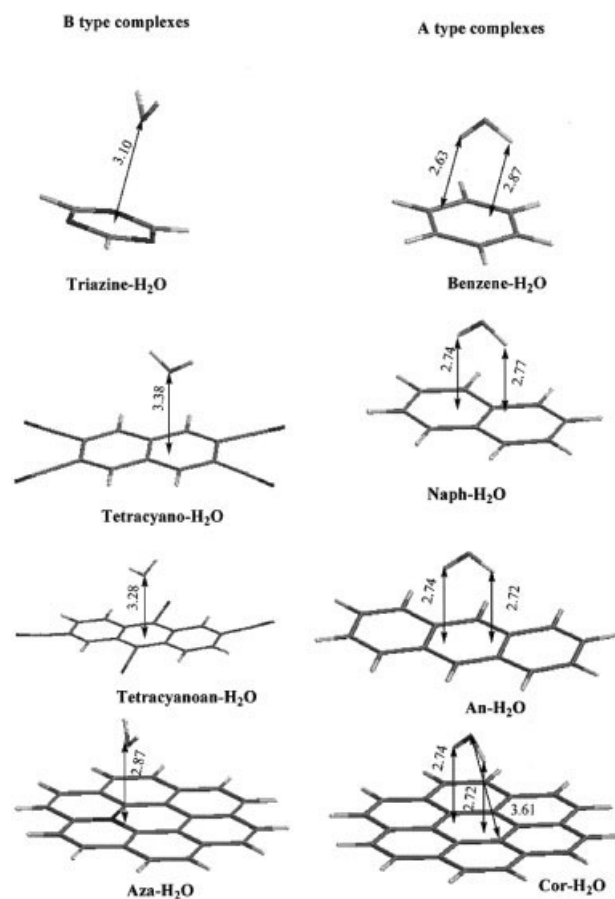

FIGURE 1. LMP2/6-31+G*-optimized geometries of molecular complexes.

follows the same trend. It is interesting to note that the distance between the center of benzene ring and the hydrogen involved in the hydrogen bond increases with basis set size when optimization is carried out at the MP2 level [21]. At MP2/aug-ccpVTZ, this distance is 2.41 Å [21], while in the case of the LMP2/6-31+G* optimized complex, this distance is 2.59 Å.

As shown in Figure 1, the distance between hydrogen atoms and the aromatic molecule plane decreases slightly with aromatic molecule size, and distances become more uniform, indicating that two hydrogens of the water molecule are involved in the formation of hydrogen bonds due to the extended π-system, allowing interactions of two hydrogens at the same time. It would be reasonable to expect the increase in binding energy for donor molecules larger than benzene. Table I shows that this is the case for naphthalene and anthracene complexes; however, in the case of coronene, the binding energies decreased slightly. One could rationalize this apparent contradiction by inspecting the Hartree–Fock binding energies (Table II). As seen from Table II at the Hartree–Fock level, all donor molecules but coronene show negative binding energies. In case of coronene–water complex BSSE-corrected binding energy is 0.2 kcal/mol. In contrast, the correlation stabilization energy (Table I) of benzene, naphthalene, anthracene, and coronene complexes is in line with the geometry evolution of the water–aromatic dimer. From our point of
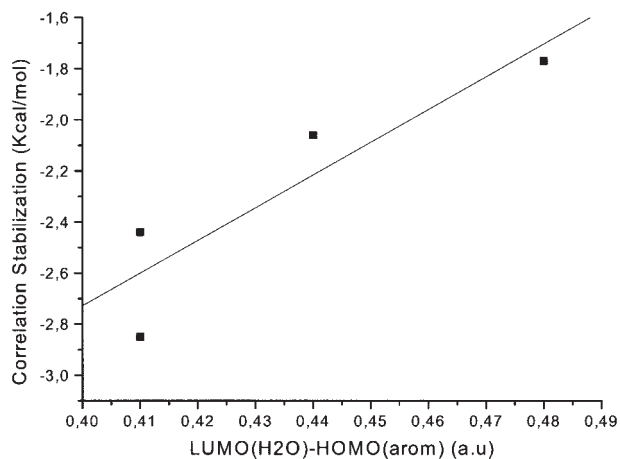

FIGURE 3. Correlation between E_{corr} of water–aromatic complexes (Table I) and "molecular electronegativity" (Table III) for donor aromatic hydrocarbons (benzene, naphthalene, anthracene and coronene).

view, the relatively low binding energy for the coronene–water complex is due to repulsion between a π-electron cloud and oxygen lone pairs.

Unfortunately, it was impossible to carry out the Kitaura–Morokuma decomposition [28] of the Hartree–Fock energy contribution to the binding energy due a technical problem for the wave function to converge; however, it seems reasonable to assume that all other terms, except for exchange repulsion, will be similar for other complexes formed by donor aromatic molecules, since the only important difference between coronene and other molecules is the molecular shape.

The importance of the π–H interaction contribution to the binding energy of donor molecules with water can be seen in Figures 2 and 3, where the correlation stabilization of complexes is plotted against the LUMO–HOMO energy difference and "molecular electronegativity", respectively, since the correlation energy represents the most important part of stabilization energies for those complexes. It is obvious that in the case of benzene, naphthalene, anthracene, and coronene, the interaction between the LUMO of water and the HOMO of aromatics contributes primarily to the stability of complexes in which the LUMO of the water molecule (σ^*-orbital of the O—H bond) interacts with the HOMO of aromatics (π-electrons). The donor–acceptor character of water–aromatic interactions for donor hydrocarbons is further confirmed by increased correlation stabilization with a decrease

FIGURE 2. Correlation between E_{corr} (Table I) of water–aromatic complexes and water LUMO aromatic–HOMO energy difference (Table III) for donor aromatic hydrocarbons (benzene, naphthalene anthracene, and coronene).
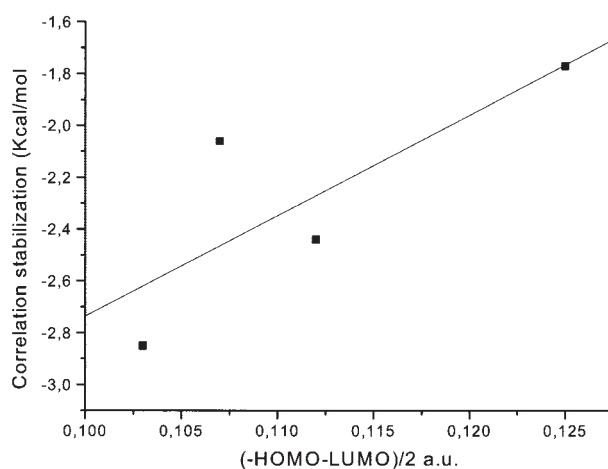
in "molecular electronegativity" for water–aromatic complexes formed by donor molecules.

As it has been stated above, the geometry of water–aromatic complexes formed by acceptor molecules is quite different from that found for benzene and other donor molecules (Fig. 1), with the oxygen atom pointing to the aromatic molecule plane (**B**-type complexes). Unlike **A**-type complexes, there is clear correlation between binding energy and O-aromatic molecule plane distance. Thus, the 9-azacoronene–water complex shows the highest binding energy of −6.21 kcal/mol and the shortest O-aromatic molecule plane distance of 2.87 Å, while the weakest triazine–water complex has an O-aromatic molecule plane distance of 3.1 Å. Unlike **A**-type complexes in which correlation stabilization dominates, in complexes formed by acceptor molecules there is a significant contribution from electrostatic interactions as follows from negative stabilization energies at the Hartree–Fock level. Thus, for 9-azacoionene- and 2,3,6,7-tetracyanonaphtalene–water complexes, the Hartree–Fock stabilization represents more than 50% of total binding energy (Tables I and II).

The difference between **A**-type complexes characteristic of donor aromatic molecules and those formed by aromatic molecules bearing electron-withdrawing groups (**B**-type) is due to the fact that the later are stabilized mostly by the interaction between the HOMO of water and the LUMO of
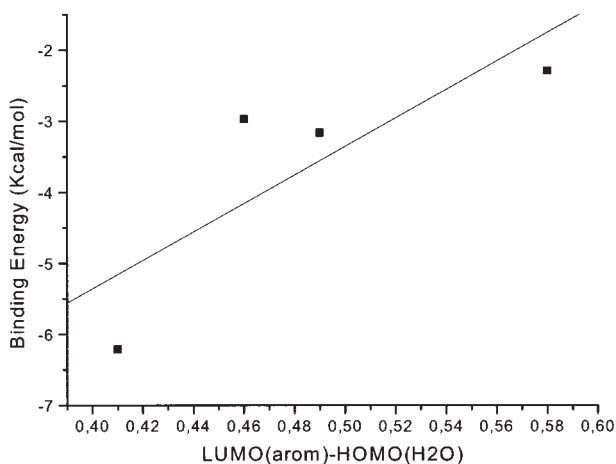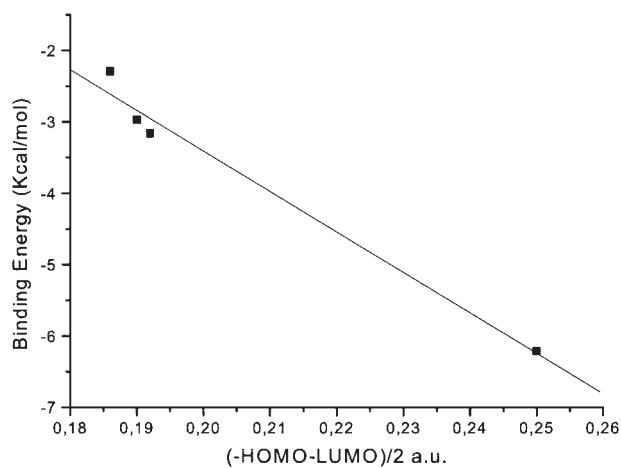
FIGURE 5. Correlation between binding energy of water–aromatic complexes (Table I) and "molecular electronegativity" (Table III) for acceptor aromatic hydrocarbons (9-azacoronene, 2,3,6,7-tetracyanonaphthalene 2,6,9,10-tetracyanoanthracene, and triazine).

aromatic molecules, and not by water LUMO–aromatic HOMO as in the former case. The HOMO of water represents the lone pair of oxygen atom, while the LUMO of aromatic molecules is a π^*-orbital. This hypothesis can be proved by inspecting Figure 4, in which the binding energy of water–aromatic complexes formed by acceptor molecules is plotted against the aromatic LUMO water–HOMO energy difference. As seen, there is a clear correlation between them proving that in this case water molecule acts as a donor. A similar correlation is observed between "molecular electronegativity" and binding energies of complexes formed by acceptor molecules (Fig. 5).

If one compares the dependence of the binding energy and correlation stabilization of water–aromatic complexes formed by acceptor and donor molecules, respectively, on "molecular electronegativity" (Figures 2–5), the difference is clearly seen. While in complexes formed by donor molecules, the stabilization decreases with "molecular electronegativity" complexes formed by acceptor aromatic molecules show the opposite trend.

A-type complexes stabilized by π-H interactions are very well studied experimentally and theoretically. In contrast, the present article reports for the first time binding energies and electronic structure of water–aromatic complexes formed by aromatic hydrocarbons bearing electron-withdrawing groups and having **B**-type geometry. To the best of our knowledge, only one system was observed in which

FIGURE 4. Correlation between binding energy (Table I) of water–aromatic complexes and aromatic LUMO water–HOMO energy difference (Table III) for acceptor aromatic hydrocarbons (9-azacoronene, 2,3,6,7-tetracyanonaphthalene 2,6,9,10-tetracyanoanthracene, and triazine).

an aromatic molecule formed **B**-type complexes with water. These are the complexes formed by the hydration of fullerene [29], which has also been confirmed by theoretical calculations [14]. The geometry of the water–aromatic complex is found to depend on the "molecular electronegativity" value (—HOMO–LUMO)/2. Thus, low values correspond to **A**-type complexes, while high "molecular electronegativity" promotes the formation of **B**-type complexes. As shown in Table III, aromatic molecules are more electropositive than benzene (0.125 a.u.)-formed **A**-type complexes, while aromatic molecules with "molecular electronegativity" of >0.186 a.u. formed **B**-type complexes with water molecules. Fullerene C_{60} also forms a **B**-type complex [29]. The calculated "molecular electronegativity" for C_{60} at HF/6-31+G* level of theory is 0.162 a.u.; therefore, switching between **A**-type and **B**-type complexes occurs at "molecular electronegativities" somewhere between 0.125 and 0.162 a.u. The binding energy should undergo a minimum near the switching area, in agreement with calculated binding energy at the LMP2/ONIOM level [14]. In this case, the binding energy was found to be as low as −0.64 kcal/mol.

Conclusions

Depending on their electronic structure, water can form two types of molecular complexes with aromatic molecules: **A** and **B** type. **A**-type complexes, which are well studied both theoretically and experimentally, are stabilized due to π–H interactions with the OH bond pointing to the aromatic molecule plane. **B**-type complexes have the geometry with oxygen atom pointing to the aromatic molecule plane and are stabilized by the interaction of the HOMO of a water molecule with π^*-orbitals of aromatics. Donor hydrocarbons form **A**-type complexes, while aromatics bearing electron-withdrawing substituents form **B**-type complexes, which can be quantified by introducing the concept of "molecular electronegativity." Aromatic hydrocarbons with a molecular electronegativity of <0.15 a.u. tend to form **A**-type complexes, while aromatic molecules with a molecular electronegativity >0.15 a.u. form **B**-type complexes. The binding energy of water–aromatic complexes undergoes a minimum in the area of switching from **A**-type to **B** type complexes, which can be rationalized in terms of frontier orbital interactions.

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