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Very Long-Range Effects: Cooperativity between Anion- π and Hydrogen-Bonding Interactions

Xavier Lucas, Carolina Estarellas, Daniel Escudero, Antonio Frontera,* David Quiñonero,* and Pere M. Deyà^[a]

The interplay between two important non-covalent interactions involving aromatic rings (namely anion- π and hydrogen bonding) is investigated. Very interesting cooperativity effects are present in complexes where anion- π and hydrogen bonding interactions coexist. These effects are found in systems where the distance between the anion and the hydrogen-bond donor/acceptor molecule is as long as ~ 11 Å. These effects are studied theoretically using the energetic and geomet-

ric features of the complexes, which were computed using ab initio calculations. We use and discuss several criteria to analyze the mutual influence of the non-covalent interactions studied herein. In addition we use Bader's theory of atoms-in-molecules to characterize the interactions and to analyze the strengthening or weakening of the interactions depending upon the variation of the charge density at the critical points.

1. Introduction

Non-covalent interactions are crucial in many areas of modern chemistry, especially in the field of supramolecular chemistry and molecular recognition.^[1] Interactions involving aromatic rings are important binding forces in both chemical and biological systems and they have been reviewed by Meyer et al.^[2] Hydrogen bonds have been widely studied in the literature, including theoretical and experimental methodologies.^[3–5] More recently, interest has been growing in another non-covalent interaction between anions, namely, the anion- π interaction.^[6–8] Following the pioneering work describing gas-phase clustering reactions between anions and hexafluorobenzene,^[9] and using theoretical methods, Mascal et al.,^[10] Alkorta et al.^[11] and our group^[12] have almost simultaneously reported the favourable π interaction of anions with electron-deficient aromatic rings. There is a great deal of experimental^[13–19] and theoretical^[20–23] work that evidence that the anion- π interactions play a prominent role in several areas of chemistry, such as molecular recognition^[24] and transmembrane anion transport.^[25–27] Anion coordination is an important and challenging aspect of contemporary supramolecular chemistry. Recent investigations have provided experimental evidence for the usefulness of pyridine, diazines and tetrazines coordinated to Ag^{I} in the design of anion receptors by demonstrating the ability of these rings to interact with anions through multiple anion- π interactions.^[28–33] The structural consistency displayed by these networks and the uniform mode of anion binding demonstrate the potential use of anion- π interactions in a structurally directing role.^[34] These interactions are also important in ADN bases like adenine.^[35] Moreover, Berryman et al. have reported structural criteria for the design of anion receptors based on the interaction of halides with electron-deficient arenes.^[20] Recent excellent reviews deal with anion-binding involving π -acidic heteroaromatic rings.^[7, 36, 37]

We have recently reported experimental^[38] and theoretical^[38, 39] evidence of interesting synergetic effects between anion- π and π - π interactions. We have demonstrated that there is a remarkable interplay between anion- π and π - π interactions in complexes where both interactions coexist. This interplay can lead to strong cooperativity effects. Herein, following our recent study on how the anion- π and the hydrogen bonding (HB) interactions influence each other in complexes where both interactions are present,^[40] we analyze whether these effects are also functional in very large systems. That is, we have selected the aromatic systems shown in Figure 1, where the distance between the atoms that participate in the H-bonding interactions and the position of the anion is progressively increased. We have selected fluoride and chloride anions to do this. We have first computed the H-

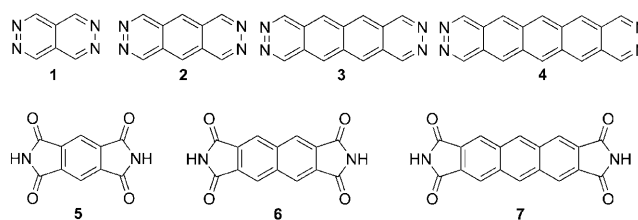


Figure 1. Aromatic compounds 1–7.

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bonding and anion- π complexes **8–32** (see Figure 2). Secondly, we have computed the anion- π -HB complexes **33–54** present in Figure 3, in order to study the interplay between the anion- π and hydrogen bonding interactions. We have used Bader's theory of atoms-in-molecules (AIM),^[41] which has been widely used to characterize a great variety of interactions and in particular ion- π interactions,^[12,42] to analyze cooperative effects in the complexes.

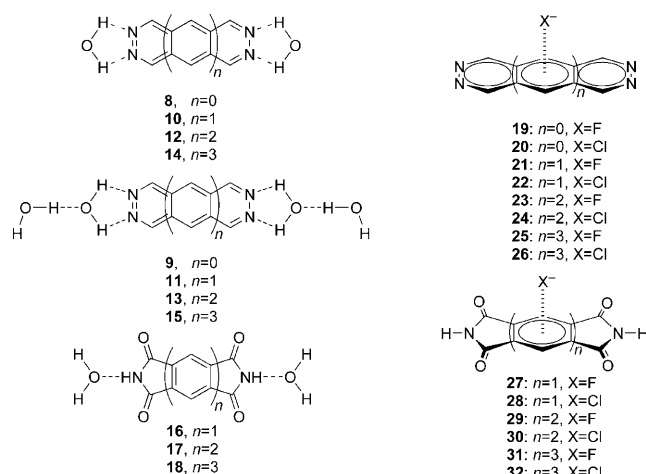


Figure 2. Hydrogen bonding and anion- π complexes **8–32**.

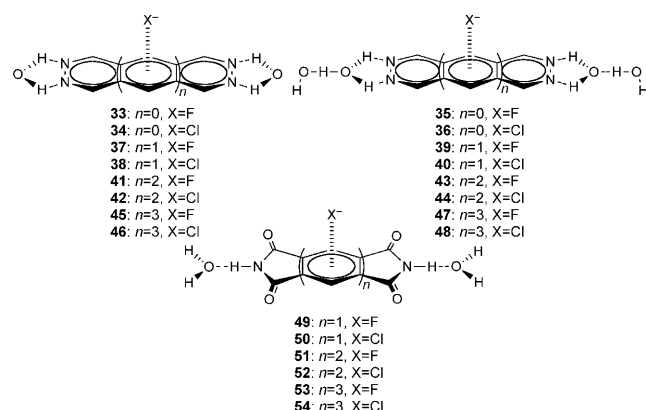


Figure 3. Multi-component complexes **33–54**.

Theoretical Methods

The geometries of all the complexes included herein were fully optimized at the RI-MP2(full)/6-31++G** level of theory within the program TURBOMOLE version 5.10.^[43] The RI-MP2 method^[44,45] applied to the study of cation- π and anion- π interactions is considerably faster than the MP2 method and the interaction energies and equilibrium distances are almost identical for both methods.^[46,47] The binding energies were calculated with correction for the basis set superposition error (BSSE) by using the Boys-Bernardi counterpoise technique.^[48] The optimization of the complexes has been performed imposing D_{2h} symmetry in complexes **1–8**, **10**, **12**, **14**, **16–18** and C_{2v} in complexes **9**, **11**, **13**, **15**, **19–54**. The AIM analysis has been performed by means of the AIM2000 version 2.0 program^[49] using the MP2/6-31++G**//RI-MP2(full)/6-31++G**

wavefunction. Charge transfer effects have been studied using the Mulliken^[50], ChelpG^[51] and NPA^[52] population analysis for deriving atomic charges.

In complexes where hydrogen bonding and anion- π interactions coexist, we have computed the genuine non-additivity energies ($E-E_A$) using Equations (1) and (2). Thus, the non-additivity energies are computed by subtracting the binding energy of the sum of all pair interaction energies (E_A) from the binding energy of the complex (E). Equation (1) was used for the complexes with two water molecules (four components), and Equation (2) for complexes with four water molecules (six components):

$$E-E_A = E_{abcd} - (E_{ab} + E_{ac} + E_{ad} + E_{bc} + E_{bd} + E_{cd}) \quad (1)$$

$$E-E_A = E_{abcdef} - (E_{ab} + E_{ac} + E_{ad} + E_{ae} + E_{af} + E_{bc} + E_{bd} + E_{be} + E_{bf} + E_{cd} + E_{ce} + E_{cf} + E_{de} + E_{df} + E_{ef}) \quad (2)$$

These equations evaluate the non-additivity energy using only two-body effects to compute the E_A energy. In some cases it has been demonstrated that the consideration of three-body effects^[53] is important to properly discuss cooperativity effects.^[54] Therefore three-body effects are also computed and discussed herein.

We have also evaluated the possible existence of cooperativity in the complexes where anion- π and HB interaction coexist, by using the expression indicated in Equation (3):

$$E_{\text{coop}} = E_{\text{BSSE}}(A\pi + \text{HB}) - E_{\text{BSSE}}(A\pi) - E_{\text{BSSE}}(\text{HB}) - E_{\text{BSSE}}(\text{Aw}) \quad (3)$$

where $E_{\text{BSSE}}(A\pi)$, $E_{\text{BSSE}}(\text{HB})$ and $E_{\text{BSSE}}(A\pi + \text{HB})$ terms correspond to the interaction energies (BSSE-corrected) of the corresponding optimized anion- π , hydrogen bonding and anion- π + HB complexes, respectively, which are gathered in Tables 1 and 2. $E_{\text{BSSE}}(\text{Aw})$ is the interaction of the water molecules with the anion as they stand in the anion- π -HB complexes. This expression has been successfully used in the study of cooperativity effects in a variety of systems^[55] where two different interactions coexist, including π -systems as simultaneous hydride and hydrogen bond acceptors^[56] and the simultaneous interaction of tetrafluoroethene with anions and hydrogen-bond donors.^[57]

The synergetic energies are computed using only the first three terms of Equation (3), as shown in Equation (4):

$$E_{\text{syn}} = E_{\text{BSSE}}(A\pi + \text{HB}) - E_{\text{BSSE}}(A\pi) - E_{\text{BSSE}}(\text{HB}) \quad (4)$$

This expression has been used in many works to study synergetic effects, such as the interplay between the ion- π interaction and π - π interaction^[38,39] and the interplay between the C-H/ π and the π - π interaction.^[58] It is easy to compute and it is a comparison between the interaction energy of a multi-component system and the sum of the interaction energies of the optimized binary systems.

2. Results and Discussion

2.1. Energetic and Geometric Results

In Table 1 we summarize the binding energies without and with the basis set superposition error (BSSE) correction (E and E_{BSSE} , respectively) and equilibrium distances (R_{HB} stands for hydrogen bonding distance and R_e stands for anion- π distance) of complexes **8–32** at the RI-MP2(full)/6-31++G** level of

Table 1. Binding energies without and with BSSE correction (E and E_{BSSE} both in kcal mol^{-1}) and equilibrium distances (R_{HB} or R_e both in \AA) at the RI-MP2(full)/6-31++G** level of theory for complexes **8–32**. R_{HB} stands for the hydrogen-bonding equilibrium distance and R_e stands for the anion– π equilibrium distance. The charge of the anion (q , e) is also summarized.

Complex	E	E_{BSSE}	R_{HB} or R_e	q (Mull)	q (ChelpG)	q (NPA)
8 (1 + 2H ₂ O)	–12.5	–9.1	2.414	–	–	–
9 (1 + 4H ₂ O)	–27.9	–20.7	2.335 (1.896) ^[a]	–	–	–
10 (2 + 2H ₂ O)	–13.8	–10.2	2.393	–	–	–
11 (2 + 4H ₂ O)	–29.8	–22.3	2.318 (1.892) ^[a]	–	–	–
12 (3 + 2H ₂ O)	–14.6	–10.9	2.381	–	–	–
13 (3 + 4H ₂ O)	–31.0	–23.4	2.292 (1.887) ^[a]	–	–	–
14 (4 + 2H ₂ O)	–15.0	–11.3	2.376	–	–	–
15 (4 + 4H ₂ O)	–31.9	–24.2	2.285 (1.886) ^[a]	–	–	–
16 (5 + 2H ₂ O)	–17.3	–12.8	1.882	–	–	–
17 (6 + 2H ₂ O)	–16.8	–12.2	1.886	–	–	–
18 (7 + 2H ₂ O)	–16.4	–11.9	1.890	–	–	–
19 (1 + F [–])	–24.9	–20.9	2.324	–0.865	–0.745	–0.920
20 (1 + Cl [–])	–19.3	–12.9	3.016	–0.903	–0.831	–0.956
21 (2 + F [–])	–24.1	–20.0	2.467	–0.909	–0.788	–0.975
22 (2 + Cl [–])	–20.7	–14.3	3.095	–0.936	–0.845	–0.974
23 (3 + F [–])	–26.6	–22.1	2.291	–0.852	–0.745	–0.903
24 (3 + Cl [–])	–23.1	–15.0	2.959	–0.922	–0.822	–0.932
25 (4 + F [–])	–25.6	–21.1	2.385	–0.890	–0.758	–0.947
26 (4 + Cl [–])	–23.5	–15.5	2.997	–0.933	–0.808	–0.934
27 (5 + F [–])	–23.8	–20.4	2.556	–0.908	–0.811	–0.992
28 (5 + Cl [–])	–21.0	–14.7	3.108	–0.898	–0.835	–0.981
29 (6 + F [–])	–25.6	–21.2	2.325	–0.860	–0.741	–0.918
30 (6 + Cl [–])	–22.2	–14.2	2.979	–0.911	–0.811	–0.950
31 (7 + F [–])	–23.7	–19.5	2.441	–0.904	–0.771	–0.970
32 (7 + Cl [–])	–21.8	–14.0	3.046	–0.937	–0.836	–0.966

^[a] Values in parenthesis correspond to the HB distance of the second water molecule.

theory. The energetic and geometric features of the H-bonded complexes **8–15** reveal that the aromatic compound increases its hydrogen bond acceptor ability as the number of fused benzene rings increases. The opposite is found in complexes **16–18**, where the arene acts as hydrogen-bond donor. The behavior of the anion– π complexes **19–32** is interesting. The variation in the binding energies of all the fluoride complexes is very small (–19.5 to –22.1 kcal mol^{-1}), taking into account the different nature of the arene systems. The same behavior is observed for chloride complexes (–12.9 to –15.5 kcal mol^{-1}). This behavior is probably due to a compensating effect between electrostatic and polarization terms, which dominate the anion– π interaction.^[59] As the number of aromatic rings increases, the electrostatic term decreases because the electron-withdrawing groups/atoms are further away from the center of the molecule. However, the polarization term increases because the π -system is more extended. The partition energy used in ref. [59] to study the physical nature of the noncovalent interactions is the molecular interaction potential with polarization (MIPp) method.^[60] MIPp is a convenient tool for predicting binding properties. It has been successfully used for rationalizing molecular interactions such as

hydrogen bonding and ion– π interactions and for predicting molecular reactivity.^[61,62] The MIPp partition scheme is an improved generalization of the MEP where three terms contribute to the interaction energy, 1) an electrostatic term identical to the MEP,^[63] 2) a classical dispersion–repulsion term,^[64] and 3) a polarization term derived from perturbational theory.^[65]

The geometric and energetic results computed for the multi-component complexes **33–54** (see Figure 3) are summarized in Table 2. Some very interesting points can be extracted from the geometrical results. The equilibrium distance (R_e) of the anion– π interactions in the anion– π -HB complexes **33–48** shortens when compared to binary complexes **19–26**, indicating that the presence of the HB interaction strengthens the anion– π interaction. In addition, the equilibrium distance of the HB interaction (R_{HB}) also shortens

with respect to complexes **9–15**, indicating that the presence of the anion– π interaction also strengthens the HB interaction. It is very important to note that this mutual reinforcement of both interactions, which was previously reported for small molecules,^[40] is maintained in systems where the HB interaction is very distant from the anion– π interaction. To exemplify this, the largest system is illustrated in Figure 4. In complex **45** the water molecules that interact with the aromatic system are located at 8.84 \AA from the anion. In spite of this long distance, a shortening of the anion– π interaction ($\Delta R_e = -0.031 \text{ \AA}$) with respect to complex **25** is observed. Moreover, the addition of a second set of water molecules (complex **47**) further strengthens the anion– π interaction. The equilibrium distance of complex **47** shortens 0.046 \AA with respect to **25** and 0.015 \AA with respect to **45**. These variations of the equi-

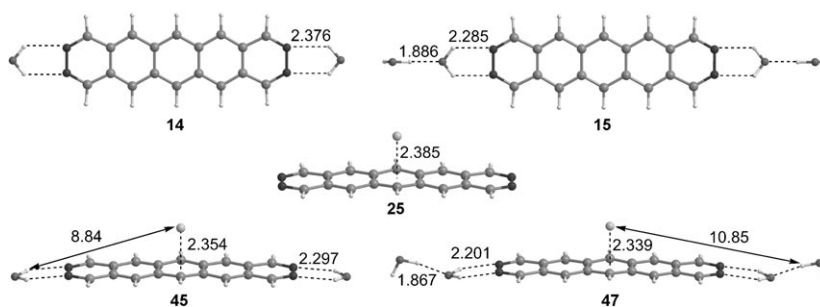


Figure 4. RI-MP2(full)/6-31++G** optimized complexes **14**, **15**, **25**, **45** and **47**. Distances in \AA .

Table 2. Binding (without and with BSSE), synergetic, cooperativity, and non-additivity energies (E , E_{BSSE} , E_{syn} , E_{coop} and $E - E_A$ kcal mol⁻¹, respectively), equilibrium distances (R_{HB} and R_e , [Å]) and their variation (ΔR_{HB} and ΔR_e , [Å]) at the RI-MP2(full)/6-31++G** level of theory for complexes **33–54**. Charge of the anion (q , e) and its variation (Δq , e) are also gathered. R_{HB} stands for the hydrogen bonding equilibrium distance and R_e stands for the anion- π equilibrium distance.

Complex	E	E_{BSSE}	E_{syn}	E_{coop}	$E - E_A$	R_e	R_{HB}	q (Mull)	q (ChelpG)	q (NPA)	ΔR_e	ΔR_{HB}	Δq (Mull)
33 (1 + 2H ₂ O + F ⁻)	-48.9	-40.6	-10.6	-2.8	-5.9	2.253	2.284	-0.841	-0.733	-0.896	-0.071	-0.130	0.024
34 (1 + 2H ₂ O + Cl ⁻)	-41.6	-30.6	-8.7	-2.1	-5.9	2.943	2.316	-0.857	-0.812	-0.940	-0.073	-0.098	0.046
35 (1 + 4H ₂ O + F ⁻)	-69.3	-56.9	-15.3	-5.0	-15.1	2.231	2.195 (1.868) ^[a]	-0.833	-0.720	-0.887	-0.093	-0.140 (-0.028) ^[a]	0.032
36 (1 + 4H ₂ O + Cl ⁻)	-61.1	-46.1	-12.5	-3.9	-14.5	2.909	2.224 (1.879) ^[a]	-0.839	-0.802	-0.932	-0.107	-0.111 (-0.017) ^[a]	0.064
37 (2 + 2H ₂ O + F ⁻)	-47.0	-38.8	-8.6	-3.2	-5.5	2.420	2.290	-0.896	-0.783	-0.970	-0.047	-0.103	0.013
38 (2 + 2H ₂ O + Cl ⁻)	-42.6	-31.8	-7.3	-2.6	-5.2	3.044	2.305	-0.917	-0.837	-0.969	-0.051	-0.088	0.020
39 (2 + 4H ₂ O + F ⁻)	-67.0	-54.6	-12.2	-5.3	-14.2	2.399	2.199 (1.868) ^[a]	-0.890	-0.777	-0.968	-0.068	-0.119 (-0.024) ^[a]	0.019
40 (2 + 4H ₂ O + Cl ⁻)	-62.1	-47.2	-10.4	-4.3	-13.2	3.022	2.215 (1.875) ^[a]	-0.908	-0.830	-0.967	-0.073	-0.103 (-0.017) ^[a]	0.028
41 (3 + 2H ₂ O + F ⁻)	-49.4	-40.6	-7.6	-3.9	-6.3	2.251	2.290	-0.839	-0.726	-0.885	-0.040	-0.091	0.013
42 (3 + 2H ₂ O + Cl ⁻)	-45.0	-32.5	-6.5	-3.1	-5.3	2.917	2.303	-0.901	-0.801	-0.922	-0.042	-0.078	0.021
43 (3 + 4H ₂ O + F ⁻)	-69.3	-56.3	-10.9	-6.1	-15.6	2.230	2.194 (1.863) ^[a]	-0.833	-0.717	-0.888	-0.061	-0.098 (-0.024) ^[a]	0.019
44 (3 + 4H ₂ O + Cl ⁻)	-64.5	-47.6	-9.2	-4.9	-13.6	2.900	2.207 (1.867) ^[a]	-0.892	-0.793	-0.917	-0.059	-0.085 (-0.020) ^[a]	0.030
45 (4 + 2H ₂ O + F ⁻)	-47.5	-38.9	-6.5	-3.8	-5.4	2.354	2.297	-0.882	-0.750	-0.941	-0.031	-0.079	0.008
46 (4 + 2H ₂ O + Cl ⁻)	-44.9	-32.6	-5.8	-3.4	-5.9	2.959	2.307	-0.919	-0.792	-0.928	-0.038	-0.069	0.014
47 (4 + 4H ₂ O + F ⁻)	-67.2	-54.3	-9.0	-5.6	-13.5	2.339	2.201 (1.867) ^[a]	-0.878	-0.743	-0.937	-0.046	-0.084 (-0.019) ^[a]	0.012
48 (4 + 4H ₂ O + Cl ⁻)	-64.2	-47.8	-8.1	-5.0	-14.8	2.945	2.210 (1.869) ^[a]	-0.913	-0.783	-0.923	-0.052	-0.075 (-0.017) ^[a]	0.021
49 (5 + 2H ₂ O + F ⁻)	-33.6	-26.2	+7.0	+3.1	-1.3	2.564	2.017	-0.916	-0.792	-0.992	+0.008	+0.135	-0.008
50 (5 + 2H ₂ O + Cl ⁻)	-31.1	-20.7	+6.8	+1.6	-1.4	3.149	1.974	-0.914	-0.822	-0.982	+0.041	+0.092	-0.016
51 (6 + 2H ₂ O + F ⁻)	-36.3	-27.7	+5.8	+2.9	-0.2	2.337	1.989	-0.863	-0.739	-0.921	+0.012	+0.103	-0.003
52 (6 + 2H ₂ O + Cl ⁻)	-33.5	-20.8	+5.6	+2.2	-0.1	2.990	1.962	-0.917	-0.806	-0.952	+0.011	+0.076	-0.006
53 (7 + 2H ₂ O + F ⁻)	-35.1	-26.4	+5.0	+2.6	+0.6	2.451	1.970	-0.907	-0.767	-0.972	+0.010	+0.080	-0.003
54 (7 + 2H ₂ O + Cl ⁻)	-33.7	-21.2	+4.8	+2.2	-0.3	3.059	1.954	-0.939	-0.817	-0.961	+0.013	+0.064	-0.002

^[a] Values in parenthesis correspond to the HB distance of the second water molecule

rium distances of the complexes are remarkable, taking into account that the second set of water molecules are located at 10.85 Å from the fluoride anion.

In complexes **49–54** the aromatic system acts as hydrogen bond donor. In these anion- π -HB complexes the equilibrium distances of both interactions increase with respect to HB complexes **16–18** and anion- π complexes **27–32**, indicating that the presence of the HB interaction weakens the anion- π interaction and vice versa. This observation was previously observed in complexes of pyromellitic imide.^[40] It is interesting to note that this interplay between both interactions is maintained even in complexes **53** and **54**, where the distances between the water molecules and the anion are 9.24 and 9.60 Å, respectively (see Figure 5).

In Table 2, we present the computed values of synergetic (E_{syn}), cooperativity (E_{coop}) and genuine non-additivity ($E - E_A$) energies which have been defined in the computational methods section. These energies are intended to provide an estimation of “extra” energetic stabilization or destabilization obtained in multi-component complexes as a consequence of the coexistence of both interactions. The simplest quantity is the synergetic energy, since it is calculated as the difference be-

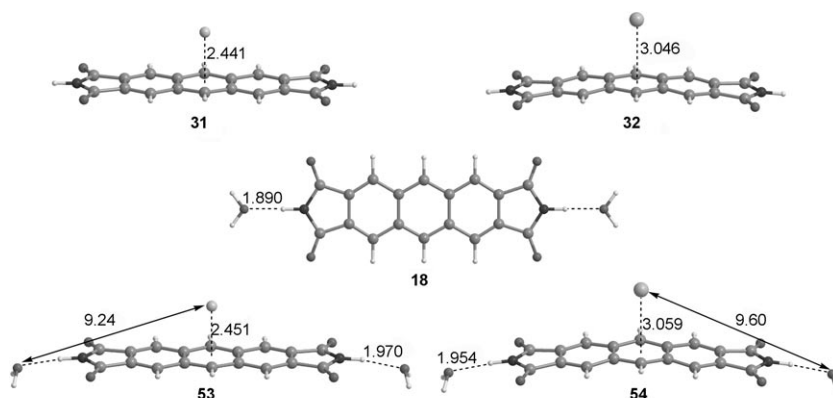


Figure 5. RI-MP2(full)/6-31++G** optimized complexes **18**, **31**, **32**, **53** and **54**. Distances in Å.

tween the binding energy of the anion- π -HB complex and the sum of the binding energies of the related HB and anion- π complexes. This quantity does not take into account the additional interaction between the water molecules and the anion. We have solved this drawback defining the cooperativity energy (E_{coop}) which is obtained similarly to the E_{syn} by adding an additional term that accounts for the water-anion interactions. Another possibility for evaluating the mutual influence of both interactions is the use of the genuine non-additivity energy, which is the difference between the binding energy of the multi-component complex and the binding energy of the sum of all pair interaction energies (denoted as E_A). This quantity has a serious problem, as has been detected before.^[66] It

should be taken into account that the sum of all pair interaction energies are performed doing single-point calculations using the geometry of the anion- π -HB complex. In cases when the geometry of this complex differs significantly from the relaxed anion- π and HB complexes, the E_A term becomes more positive than E giving rise to negative values of $E-E_A$ even in systems where the cooperativity is clearly unfavorable, as implied, among others, by the geometric features of the complex. To solve this problem, many-body effects and relaxation energies should be taken into account as is discussed herein.

From the results of E_{syn} , E_{coop} and $E-E_A$ listed in Table 2 several general conclusions can be extracted. First, the computed values of E_{syn} , E_{coop} and $E-E_A$ are negative in complexes **33–48**, where the aromatic ring acts as a hydrogen bond acceptor (anion- π_{acceptor} -HB complexes), indicating a positive synergy between both interactions in agreement with the shortening of the equilibrium distances (see ΔR values of Table 2). The difference between the E_{syn} and E_{coop} values corresponds to the interaction between the water molecules and the anion. This difference lowers on going from complex **33** to **48** because the water-anion distance increases. However, this difference is still significant in the larger systems. For instance it is 2.5 kcal mol⁻¹ in **46** and 3.1 kcal mol⁻¹ in **48**. The E_{syn} clearly overestimates the synergetic effect, especially in the complexes with four water molecules. The $E-E_A$ values computed for complexes with two water molecules are slightly more negative than the E_{coop} values. However, for complexes with four water molecules, the $E-E_A$ values are considerably more negative, indicating an overestimation of the synergetic effect. Second, the computed values of E_{syn} and E_{coop} are positive in complexes **49–54**, where the aromatic ring acts as a hydrogen bond donor (anion- π_{donor} -HB complexes), indicating a negative synergy between both interactions in agreement with the lengthening of the equilibrium distances (see ΔR values of Table 2). In contrast, the $E-E_A$ values are negative (apart from complex **53**), indicating a positive synergy between both interactions in disagreement with the lengthening of the equilibrium distances and with the E_{coop} and E_{syn} values. Third, it is interesting to note that the computed E_{coop} values for a given family of anion- π_{acceptor} -HB complexes are almost independent of the size of the π -system. For instance, all F⁻- π_{acceptor} -HB complexes with two water molecules (**33**, **37**, **41** and **45**) have E_{coop} values that range from -2.8 to -3.9 kcal mol⁻¹. This result indicates that the cooperativity effect does not depend upon the distance between the hydrogen bonding acceptor groups and the molecular center. This long through-bond effect is remarkable, since the HB interaction that involves the lone pair of the nitrogen atom is perpendicular to the π -system. Similar behavior is observed in the anion- π_{donor} -HB complexes **49–54**, where the E_{coop} values are positive. Fourth, we have included in Tables 1 and Table 2 the charge of the anion in the complex in order to investigate if the presence/absence of cooperativity effects can be related with the charge transfer from the anion to the aromatic system. We have summarized the Mulliken, ChelpG and NPA charges. The latter two methods for deriving atomic charges are expected to give better quality charges

than the former (Mulliken's method). However, as shown by the results gathered in Tables 1 and 2, the charge transfer strongly depends upon the method of choice. For instance, the ChelpG method predicts a considerable charge transfer from the anion to the aromatic ring, ranging from 0.16 to 0.28 e. In contrast, the NPA method predicts a very small charge transfer from the anion to the aromatic ring (from 0.01 to 0.11 e). Curiously, the Mulliken population analysis, which is assumed to give poor-quality charges, gives values which are between the ChelpG and NPA charge values and, remarkably, it can differentiate between anion- π_{donor} -HB and anion- π_{acceptor} -HB complexes. To demonstrate this issue, we have summarized the variation of the anion charge in the multi-component system with respect to the binary anion- π complexes **19–32**. It can be observed that in complexes with favorable cooperativity (**33–48**) Δq is positive, indicating that the anion $\rightarrow \pi$ charge-transfer is higher in these anion- π_{acceptor} -HB complexes than in the anion- π complexes **19–26**. Therefore, this can be understood as an indication of a reinforcement of the anion- π interaction. The opposite is observed in complexes **49–54**, where the variation of the anion charge (Δq) is negative. The anion $\rightarrow \pi$ charge-transfer is smaller in these anion- π_{donor} -HB complexes than in the anion- π complexes **27–32**, indicating a weakening of the anion- π interaction, in agreement with the E_{coop} , E_{syn} and ΔR_e values.

For all quaternary systems, we have performed many-body interaction analysis by computing the two- and three-body contributions to the total interaction energy.^[67,68] The two-body term can be calculated as the binding energy of each molecular pair in the quaternary complex minus the energy sum of the monomers with all of them frozen in the geometry of the complex. The three-body term is calculated as the sum of the binding energy of each molecular triad in the quaternary complex minus the energy sum of the dyads. A more comprehensive treatment can be found in the literature.^[69] The total relaxation energy (E_R) is defined as the energy sum of the isolated interacting monomers that constitute the complex, all of them frozen in the geometry of the complex, minus the energy sum of the optimized monomers. Thus, the total interaction energy of the quaternary complexes is obtained as the sum of the relaxation, two-body and three-body energies. The results are gathered in Table 3.

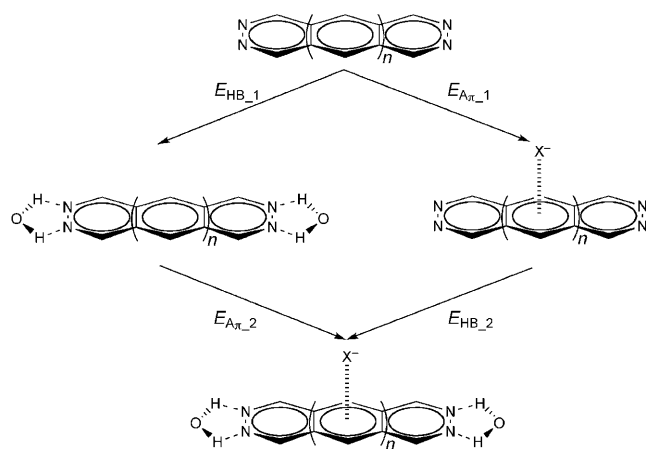
The two-body interaction energy provides the largest contribution in each complex. In some cases it reaches almost 100% of the interaction energy (complexes **49–54**). The three-body interaction energy is negative in all cases and makes a favorable contribution to the total interaction energy. Its contribution is modest in the anion- π_{donor} -HB complexes. In contrast, the contribution is much important in the anion- π_{acceptor} -HB complexes (where favorable cooperativity is present), reaching 21% of the total interaction energy in complex **34**. The relaxation energy can be used as a measure of the degree of strain that drives the distortion of the multi-component system. As seen in Table 3, the relaxation energy (E_R) is small and positive, indicating that the monomers are not very distorted in the complexes. The contribution of E_R to the total interaction energy is very small, but not negligible. In fact, if they are used

Table 3. Decomposition of the total interaction energy (E) of quaternary complexes into two-body ($\Sigma E_{\text{two-body}}$) and three-body ($\Sigma E_{\text{three-body}}$) terms, and relaxation energy (E_R). All energies are given in kcal mol⁻¹.

Complex	E	$\Sigma E_{\text{two-body}}$	$\Sigma E_{\text{three-body}}$	E_R
33 (1 + 2H ₂ O + F ⁻)	-48.9	-42.9	-7.5	1.5
34 (1 + 2H ₂ O + Cl ⁻)	-41.6	-35.7	-7.6	1.7
37 (2 + 2H ₂ O + F ⁻)	-47.0	-41.5	-6.8	1.3
38 (2 + 2H ₂ O + Cl ⁻)	-42.6	-37.4	-6.6	1.3
41 (3 + 2H ₂ O + F ⁻)	-49.4	-43.1	-7.7	1.4
42 (3 + 2H ₂ O + Cl ⁻)	-45.0	-39.7	-6.5	1.2
45 (4 + 2H ₂ O + F ⁻)	-47.5	-42.1	-6.4	1.0
46 (4 + 2H ₂ O + Cl ⁻)	-44.9	-38.9	-7.4	1.5
49 (5 + 2H ₂ O + F ⁻)	-33.6	-32.3	-2.5	1.2
50 (5 + 2H ₂ O + Cl ⁻)	-31.1	-29.6	-2.7	1.2
51 (6 + 2H ₂ O + F ⁻)	-36.3	-36.1	-1.3	1.1
52 (6 + 2H ₂ O + Cl ⁻)	-33.5	-33.4	-1.0	0.9
53 (7 + 2H ₂ O + F ⁻)	-35.1	-35.7	-0.1	0.7
54 (7 + 2H ₂ O + Cl ⁻)	-33.7	-33.4	-1.3	1.0

as a correction factor of the genuine non-additivity energies of the anion- π_{donor} -HB complexes **49–54**, the $E-E_A$ values become positive, in agreement with E_{coop} values and the geometric analysis.

In an attempt to evaluate the effect of hydrogen bonding on the anion- π interaction and vice versa we have computed the binding energy of the multi-component complexes using two different modes (see Figure 6). First, we have computed

**Figure 6.** Schematic representation of the two routes to anion- π -HB complexes.

the binding energies (with BSSE correction) of the anion- π -HB complexes **33–54**, considering that the hydrogen bonding complex has been previously formed and evaluating the interaction with the anion as a two-component system (for instance **8** + F⁻ → **33**), denoted as $E_{A\pi,2}$. Second, we have computed the binding energies (with BSSE correction) of ternary complexes **33–54** considering that the anion- π complex has been previously formed and evaluating its interaction with the water molecules (for instance **19** + 2H₂O → **33**), denoted as $E_{HB,2}$. Finally, we have compared these quantities ($E_{HB,2}$ and $E_{A\pi,2}$)

with the $E_{HB,1}$ and $E_{A\pi,1}$ binding energies, which correspond to the binding energies of complexes **8–31** (see Table 1). This comparison has been made using the following relations: $E_{HB,2}/E_{HB,1}$ and $E_{A\pi,2}/E_{A\pi,1}$. These simple relations give very interesting and useful information: 1) values of $E_{HB,2}/E_{HB,1} > 1$ mean that the hydrogen bonding is reinforced in the anion- π -HB complex and the opposite applies if $E_{HB,2}/E_{HB,1} < 1$, 2) values of $E_{A\pi,2}/E_{A\pi,1} > 1$ mean that the anion- π interaction is reinforced in the anion- π -HB complex and the opposite applies if $E_{A\pi,2}/E_{A\pi,1} < 1$. Therefore, these relations are informative regarding the mutual influence of both interactions in the anion- π -HB complexes. If both relations exceed 1, favourable synergetic effects between both interactions are present in the complex. If one relation is more than 1 and the other less than 1, would mean that one non-covalent interaction is reinforced at the expense of the other. More significantly, for a given complex, if $E_{HB,2}/E_{HB,1} > E_{A\pi,2}/E_{A\pi,1}$, it would mean that the hydrogen-bonding interaction is more reinforced than the anion- π interaction in the anion- π -HB complex, and the contrary applies if $E_{HB,2}/E_{HB,1} < E_{A\pi,2}/E_{A\pi,1}$. If both relations are equal, the reinforcement of both interactions is the same.

The values of $E_{A\pi,2}$, $E_{HB,2}$, $E_{A\pi,2}/E_{A\pi,1}$ and $E_{HB,2}/E_{HB,1}$ computed for complexes **33–54** are summarized in Table 4. It can be observed that both relations are > 1 in all anion- π_{acceptor} -HB complexes, in agreement with the previously discussed energetic and geometric results. On the contrary, both relations are < 1 in all anion- π_{donor} -HB complexes, in agreement with the E_{coop} and E_{syn} values. In all F⁻- π_{acceptor} -HB complexes $E_{HB,2}/E_{HB,1}$ is greater than $E_{A\pi,2}/E_{A\pi,1}$, indicating that the hydrogen bonding interaction is more enhanced than the anion- π interaction. The same result is observed in all Cl⁻- π_{acceptor} -HB complexes with two water molecules. In contrast, in all Cl⁻- π_{acceptor} -HB complexes with four water molecules (**36**, **40**, **44** and **48**), the $E_{A\pi,2}/E_{A\pi,1}$ values are greater than the $E_{HB,2}/E_{HB,1}$ ones, indicating that the anion- π interaction is more enhanced than the hydrogen-bonding interactions.

From the results of Table 4 we learn that the $E_{A\pi,2}/E_{A\pi,1}$ and $E_{HB,2}/E_{HB,1}$ values are useful to evaluate synergetic effects. They are easy to compute and, opposite to other criteria like $E-E_A$ and E_{syn} , they are not influenced by other factors. We have also found an interesting and strong relationship ($r=0.977$) between the $E_{A\pi,2}/E_{A\pi,1}$ values and ΔR_e (Figure 7). This relationship that correlates this energetic parameter with the geometric features of the multi-component complexes further validates the utilization of $E_{A\pi,2}/E_{A\pi,1}$ values as indicators of cooperativity. It is worth stressing the relevance of this relationship, since they cover a variation of two anions and complexes with either two or four water molecules. A similar relationship cannot be done for the $E_{HB,2}/E_{HB,1}$ values, as two different distances characterize the hydrogen-bonding interactions in the complexes with four water molecules (Figure 7). Interestingly, the $E_{A\pi,2}/E_{A\pi,1}$ values also correlate with the variation of the anion charge transfer (Δq , see Table 2 and Figure 7) from the anion to the aromatic ring. For the fluoride complexes the regression coefficient is $r=0.955$ and for chloride complexes is $r=0.923$. All these relationships validate the utilization of the $E_{A\pi,2}/E_{A\pi,1}$ values as a measure of cooperativity, since they cor-

Table 4. $E_{A\pi,2}/E_{HB,2}$, $E_{A\pi,2}/E_{A\pi,1}$, $E_{HB,2}/E_{HB,1}$ values computed for complexes **33–54** at the RI-MP2(full)/6-31++G** level of theory. The $E_{A\pi,1}$ and $E_{HB,1}$ values correspond to the binding energies of complexes **8–32** which are gathered in Table 1. Energies are given in kcal mol⁻¹.

<i>n</i>	Complex	Reaction	$E_{A\pi,2}$	$E_{A\pi,2}/E_{A\pi,1}$	Reaction	$E_{HB,2}$	$E_{HB,2}/E_{HB,1}$
0	33	8 + F ⁻	-32.0	1.53	19 + 2H ₂ O	-20.0	2.20
	34	8 + Cl ⁻	-21.9	1.70	20 + 2H ₂ O	-18.0	1.98
	35	9 + F ⁻	-36.9	1.76	19 + 4H ₂ O	-40.3	1.95
	36	9 + Cl ⁻	-25.8	2.00	20 + 4H ₂ O	-37.4	1.81
1	37	10 + F ⁻	-29.0	1.45	21 + 2H ₂ O	-19.0	1.85
	38	10 + Cl ⁻	-21.9	1.54	22 + 2H ₂ O	-17.7	1.73
	39	11 + F ⁻	-32.7	1.64	21 + 4H ₂ O	-38.8	1.73
	40	11 + Cl ⁻	-25.1	1.76	22 + 4H ₂ O	-37.0	1.65
2	41	12 + F ⁻	-30.1	1.36	23 + 2H ₂ O	-18.7	1.71
	42	12 + Cl ⁻	-21.9	1.46	24 + 2H ₂ O	-17.6	1.61
	43	13 + F ⁻	-33.5	1.52	23 + 4H ₂ O	-38.4	1.64
	44	13 + Cl ⁻	-24.7	1.65	24 + 4H ₂ O	-36.8	1.58
3	45	14 + F ⁻	-27.8	1.32	25 + 2H ₂ O	-17.9	1.58
	46	14 + Cl ⁻	-21.6	1.39	26 + 2H ₂ O	-17.2	1.52
	47	15 + F ⁻	-30.5	1.45	25 + 4H ₂ O	-37.4	1.54
	48	15 + Cl ⁻	-23.9	1.55	26 + 4H ₂ O	-36.4	1.50
1	49	16 + F ⁻	-12.8	0.62	27 + 2H ₂ O	-5.6	0.44
	50	16 + Cl ⁻	-7.7	0.52	28 + 2H ₂ O	-5.5	0.43
2	51	17 + F ⁻	-15.1	0.71	29 + 2H ₂ O	-6.4	0.52
	52	17 + Cl ⁻	-8.6	0.60	30 + 2H ₂ O	-6.6	0.54
3	53	18 + F ⁻	-14.5	0.74	31 + 2H ₂ O	-6.8	0.57
	54	18 + Cl ⁻	-9.4	0.67	32 + 2H ₂ O	-7.1	0.59

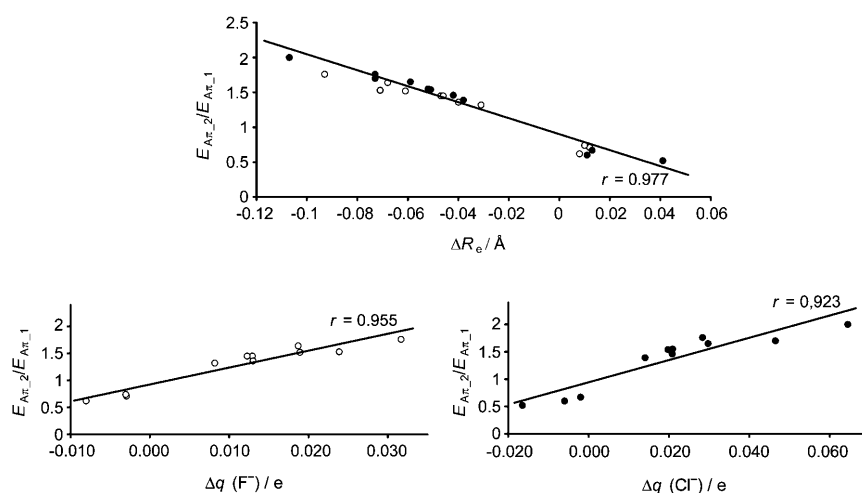


Figure 7. Top: Regression plot between the variation of the anion- π equilibrium distance (ΔR_e , Å) and the $E_{A\pi,2}/E_{A\pi,1}$ relation for complexes **33–54**. Bottom: Regression plots between the variation of the charge of the anion (Δq , e) and the $E_{A\pi,2}/E_{A\pi,1}$ relation for F⁻ (left) and Cl⁻ (right) complexes **33–54**. (○) represent the fluoride complexes and (●) the chloride complexes.

relate well with the geometric features of the complexes and with charge-transfer effects.

We have performed an AIM analysis of all compounds studied herein. It has been clearly established that the values of the charge density (ρ) at the critical points (CPs) that emerge upon complexation give helpful information regarding the strength of the non-covalent interactions involved in the complexes. As a matter of fact, they have been successfully used as a measure of the bond order in a variety of non-covalent interactions including anion- π and hydrogen-bonding interactions. Therefore, the variation in the value of ρ at the CPs in multi-

component systems with respect to the isolated anion- π and HB complexes can be used to analyze the mutual influence of both interactions. One example with positive cooperativity is illustrated in Figure 8. The anion- π -HB complex **38** has a density value of 1.3647×10^{-2} a.u. at the bond CP that characterizes the HB interaction, which is greater than the value computed at the bond CP of complex **10** (1.1269×10^{-2} a.u.). This result confirms that the hydrogen-bond interaction in **38** is reinforced with respect to complex **10**. The same behaviour is observed for the values of ρ at the cage CP that characterizes the anion- π interaction. This value varies from 0.6299×10^{-2} a.u. for complex **22** to 0.6725×10^{-2} a.u. for complex **38**, indicating a reinforcement of the anion- π interaction. Similarly, both interactions also strengthen in complex **40** (four water molecules) with respect to complexes **11** and **22**. The variations of the values of ρ at the bond and cage CPs in complex **40** are greater than in complex **38**, in agreement with the values of E_{coop} computed for them, which are -2.6 for **38** and -4.3 kcal mol⁻¹ for **40**.

Finally, in Figure 9 we represent the distribution of critical points in a set of complexes with unfavorable cooperativity as deduced by the previously used energetic and geometric criteria (apart from almost all $E-E_A$ values). It can be observed that the AIM analysis confirms

this issue. The value of ρ at the bond CP that characterizes the HB in complex **53** is 2.2473×10^{-2} a.u., which is smaller than the value obtained for **18** (2.4618×10^{-2} a.u.). The same is observed for value of ρ at the cage CP that characterizes the anion- π interaction, which is reduced from 0.8914×10^{-2} a.u. in complex **31** to 0.8802×10^{-2} a.u. in complex **53**.

3. Conclusions

The results reported herein stress the importance of non-covalent interactions involving aromatic systems and the interplay

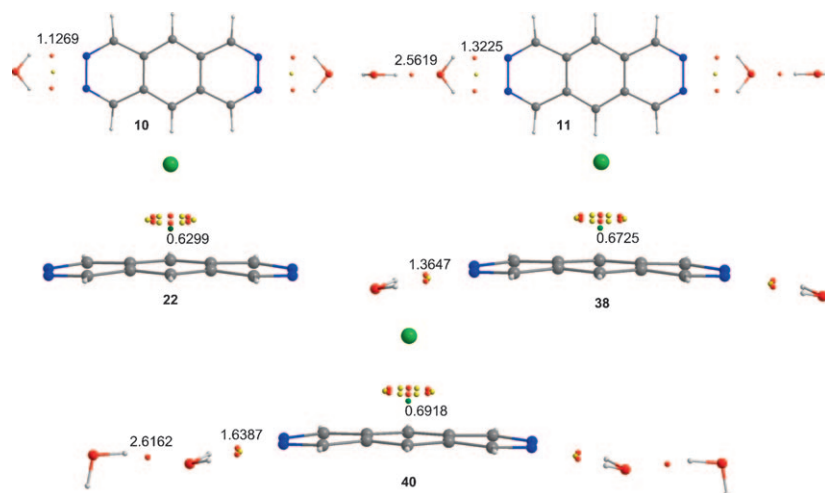


Figure 8. Representation of the bond (red), ring (yellow) and cage (green) CPs in complexes **10**, **11**, **22**, **38** and **40**. The values of the charge density ($10^2 \times \rho$) at different points are given in a.u.

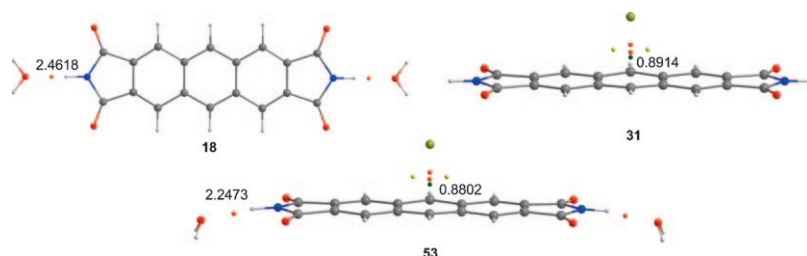


Figure 9. Representation of the bond (red), ring (yellow) and cage (green) CPs in complexes **18**, **31** and **53**. The values of the charge density ($10^2 \times \rho$) at different points are given in a.u.

among them, which can lead to synergetic effects. These effects are maintained even in systems where the distance between the hydrogen-bond donor/acceptor molecule and the anion is very large. We have estimated the synergetic effects energetically using several criteria. E_{coop} gives good results since they are in agreement with the geometric features of the complexes and the AIM analysis. An interesting point is that for a given series of complexes, E_{coop} is almost independent of the number of aromatic rings. That is to say, it is not affected by the water–anion distance. Therefore, the aromatic ring is able to transmit the synergetic effect from the anion (anion– π interaction), through the conjugated π -system, to the water molecule (HB interaction), even to the second set of water molecules, and vice versa.

The many-body partition energy reveals that the two-body term is the most important contribution to the total interaction energy. Three-body effects must be taken into account in the anion– π_{acceptor} –HB complexes, since its contribution reaches 20% in some cases. The relaxation energy is small in all complexes studied, indicating that distortion effects are not important.

We have proposed the utilization of two parameters, that is, $E_{\text{A}\pi,2}/E_{\text{A}\pi,1}$ and $E_{\text{HB},2}/E_{\text{HB},1}$ that are easy to calculate and they give useful information regarding, on one hand, the presence of cooperativity and, on the other hand, which non-covalent

interaction is more reinforced when they coexist in the same complex.

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