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Interplay between ion–π and Ar/π Van der Waals interactions

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ABSTRACT

This article analyzes the interplay between cation–π or anion–π interactions and Ar/π Van der Waals interactions. Interesting cooperativity effects are observed when cation–π/anion–π and Ar/π Van der Waals interactions coexist in the same complex. These effects are studied theoretically in terms of energetic and geometric features of the complexes, which are computed by ab initio methods. The symmetry-adapted perturbation theory (SAPT) partition scheme was utilized to analyze the different energy contributions to the binding energy and to investigate the physical nature of the interplay between the interactions. By taking advantage of all aforementioned computational methods, the present study examines how these interactions mutually influence each other. Finally, our computational results at the SCS-RI-MP2/aug-cc-pwCVTZ level of theory for the Benzene/Ar complex (D_0 = −0.90 kcal/mol and R_e = 3.595 Å) are in a very good quantitative agreement with the experimental dissociation energy (−0.90 ± 0.02 kcal/mol) and equilibrium distance (3.586 Å).

1. Introduction

The chemistry of noncovalent interactions applied to the supramolecular chemistry field crucially contributes to the intelligent utilization of interactions between molecules. Particularly, aromatic interactions play a vital role in chemistry and biology [1]. The role of aromatic interactions becomes prominent in drug receptor interactions, crystal engineering and protein folding [2]. Among these interactions we emphasize cation–π and anion–π interactions, all of them present in biomolecular systems. The cation–π interaction [3] is dominated by electrostatic [4,5] and ion-induced polarization terms [6]. The nature of the electrostatic term can be rationalized by means of the permanent quadrupole moment of the arene. The anion–π interaction [7–9] is also dominated by electrostatic and ion-induced polarization terms [8,9].

Van der Waals complexes play a major role in physics, chemistry, and biology [10]. They are characterized by an interaction dominated by dispersion, interaction that is essential in processes like the adsorption of molecules. Therefore Van der Waals complexes are used as models for the study of this type of processes [11]. Complexes formed by an aromatic molecule and noble gas atoms have been the focus of a considerable number of studies. In particular, the benzene-Ar complex has been a focus of major attention, both from the experimental and the theoretical points of view [12,13].

Manifestations of multiple, weak interactions turn up in all areas of chemistry [1,14]. They determine material properties, orchestrate chemical reactions, drive molecular recognition, and are active in the regulation of biochemical processes [15]. In these nanoscopic events, success relies on specificity and efficiency, which is accomplished by balancing intricate combinations of the intermolecular forces of attraction and repulsion. The organization of multicomponent supramolecular assemblies is often governed by multiple noncovalent interactions. In biological systems and particularly in the solid state, a host of interactions may operate simultaneously, giving rise to cooperativity effects. A recent review examined pairwise combinations of several weak interactions, including anion–π bonding, and described the synergy that operates between them [16].

We and others recently reported experimental and theoretical evidence for interesting synergistic effects between anion–π and π–π stacking [17], between anion–π and hydrogen-bonding interactions [18,19] and in anion–π and halogen–bonding [20] in complexes in which the two interactions coexist. This interplay can lead to strong cooperativity effects. In this communication, we report a theoretical study using high-level ab initio calculations (SCS-MP2 and CCSD(T)) in which we analyze the mutual influence of cation–π or anion–π interaction and the Ar/π Van der Waals interaction in several complexes. We selected three aromatic rings, namely, benzene, hexafluorobenzene and *s*-triazine, with negative, positive and negligible quadrupole moments, respectively. We first computed the geometric and energetic features of isolated argon Van der Waals complexes **1**–**3** and ion–π complexes **4**–**9** (Fig. 1). Second, we calculated cation–π/Ar complexes **10**–**12** and anion–π/Ar complexes **13**–**15** (Fig. 1), in order to study cooperativity effects between the two interactions, i.e., how the ion–π interaction influences the Ar/π interaction and vice versa. Finally the

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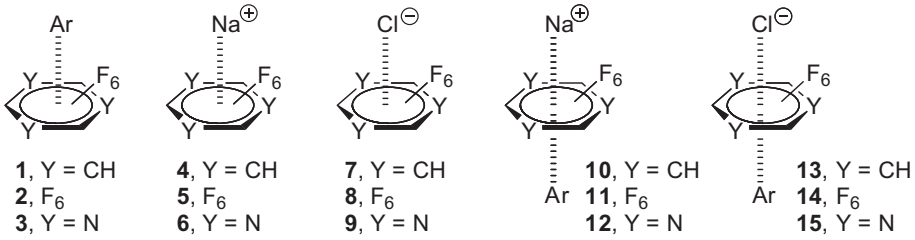

Fig. 1. Ion–π, Ar/π and ion–π/Ar complexes.

symmetry-adapted perturbation theory (SAPT) partition scheme [21] was utilized to analyze the different energy contributions to the binding energy and to investigate the physical nature of the interplay between the two interactions.

2. Theoretical methods

The geometries of all the complexes included in this study were optimized at the SCS-RI-MP2/aug-cc-pwCVTZ levels of theory within the program TURBOMOLE version 6.1 imposing the highest abelian group symmetry for each case [22]. Moreover, all complexes have been optimized with correction for the basis set superposition error (BSSE) using the Boys–Bernardi counterpoise technique [23] during the optimizations. Other possible conformations of complexes have not been considered because the ultimate aim of this study is to verify the mutual influence of the several noncovalent interactions studied herein. For the Na^+ cation the cc-pVTZ basis set was used. The RI-MP2 method [24,25] applied to study different noncovalent interactions is considerably faster than the MP2 method, and the interaction energies and equilibrium distances are almost identical for both methods [26,27]. Moreover, we have used the spin-component scaled MP2 method (SCS-RI-MP2), which is based on the scaling of the standard MP2 amplitudes for parallel- and antiparallel-spin double excitations [28]. The SCS-RI-MP2 correlation treatment yields structures that are superior to those from standard MP2, particularly in systems that are dominated by dispersive interactions [29]. Furthermore, the interaction energies were accurately computed at the coupled cluster level of theory using single and double substitutions with non-iterative triple excitations CCSD(T)/aug-cc-pCVTZ [30,31] within the program MOLPRO [32]. The binding energies were calculated at the same level with correction for the BSSE [23]. For brevity, we will often refer to the aug-cc-pwCVTZ and aug-cc-pCVTZ results by the shorthand notation AwCTZ and ACTZ, respectively. It is worth mentioning that CCSD(T) calculations were not carried out for complexes **11** and **14** due to limitations of our computer resources. For all the MP2 and CCSD(T) calculations all electrons were correlated. In complexes in which Van der Waals and an ion–π interactions coexist, we computed the cooperativity energy E_{coop} using Eq. (1)

$$E_{coop} = E_{BSSE}(Ar\pi + I\pi) - E_{BSSE}(Ar\pi) - E_{BSSE}(I\pi) - E_{BSSE}(ArI) \qquad (1)$$

where $E_{BSSE}(Ar\pi)$, $E_{BSSE}(I\pi)$ and $E_{BSSE}(Ar\pi + I\pi)$ terms correspond to the interaction energies (BSSE-corrected) of the corresponding optimized Argon/π, ion–π and Argon/π + ion–π complexes, respectively, and $E_{BSSE}(ArI)$ is the interaction between the Ar atom and the ion in the Ar/π–ion complexes. This expression has been successfully used in the study of cooperativity effects in a variety of systems in which two different interactions coexist, including π systems as simultaneous hydride- and hydrogen-bond acceptors, the simultaneous interaction of tetrafluoroethene with anions and hydrogen-bond donors [18] and anion–π and halogen-bonding interactions [20]. Zero point energies were computed by performing analytical harmonic vibrational frequency calculations using Gaussian09 package [33].

The partitioning of the interaction energies into the individual electrostatic, induction, dispersion, and exchange-repulsion components was carried out performing density functional theory (DFT) combined with the symmetry-adapted perturbation theory (DFT–SAPT) approach [21] at the DF-BP86/ACTZ//SCS-RI-MP2(full)/AwCTZ level of theory with MOLPRO progam. The DFT–SAPT intermolecular interaction is given in terms of the first-, second-, and higher-order correction interaction terms that are indicated by the superscripts in Eq. (2):

$$E_{int} = E_{el}^{(1)} + E_{exch}^{(1)} + E_{ind}^{(2)} + E_{ind\text{-}exch}^{(2)} + E_{disp}^{(2)} + E_{disp\text{-}exch}^{(2)} + \delta(HF) \qquad (2)$$

where $E_{el}^{(1)}$ and $E_{exch}^{(1)}$ are the sum of the electrostatic interaction energy and the first-order exchange energy, respectively. $E_{ind}^{(2)}$, $E_{ind\text{-}exch}^{(2)}$, $E_{disp}^{(2)}$ and $E_{disp\text{-}exch}^{(2)}$ denote the induction (with response) energy, the second order induction-exchange (with response) energy, the dispersion energy and the exchange-dispersion contribution, respectively. δ(HF) is the Hartree–Fock correction for higher-order contributions to the interaction energy and thus is not included in DFT–SAPT calculations. The aug-cc-pCVTZ basis set was used to compute this correction. Physically meaningful separation of the interaction energy may be obtained by classifying the cross terms induction-exchange $E_{ind\text{-}exch}^{(2)}$ and dispersion-exchange $E_{disp\text{-}exch}^{(2)}$ as a part of the induction and the dispersion, respectively [34]. The aug-cc-pCVTZ basis set was used for the DF–DFT–SAPT calculations. As auxiliary fitting basis set the JK-fitting basis of Weigend [35] was employed. Unless indicated otherwise the aug-cc-pVQZ JK-fitting basis was used for all atoms except for Na, for which we used the def2-AQZVPP JK-fitting basis. For the intermolecular correlation terms, i.e., the dispersion and exchange-dispersion terms, the related MP2-fitting basis of Weigend et al. [36] was employed, i.e., the aug-cc-pCVTZ MP2-fitting basis. In the DFT–SAPT calculations the BP86 functional (the B88 exchange functional [37] in combination with P86 gradient correction [38]) was employed using the SCS-RI-MP2(full)/aug-cc-pwCVTZ optimized geometries. It is recommended to use nonhybrid functional since currently only the adiabatic local density approximation exchange–correlation kernel is implemented for the case the dispersion/exchange-dispersion energy terms are requested in a DF–DFT–SAPT run. This means that a corresponding SAPT calculation would be incompatible with hybrid-DFT monomer orbitals/orbital energies.

3. Results

3.1. Energetic and geometric details of cation–π, anion–π and Ar/π complexes

Table 1 summarizes the SCS-RI-MP2(full)/AwCTZ binding energies with BSSE correction ($E_{MP2\text{-}CP}$), the CCSD(T)(full)/ACTZ binding energies without and with BSSE correction (E_{CC} and $E_{CC\text{-}CP}$), the SAPT interaction energies and equilibrium distances of complexes

Table 1
Interaction energies with BSSE correction at the SCS-MP2(full)/AwCTZ level of theory ($E_{MP2\text{-}CP}$, in kcal/mol), without and with BSSE correction at the CCSD(T)(full)/ACTZ level of theory (E_{CC} and $E_{CC\text{-}CP}$, respectively, in kcal/mol) and at the SAPT level and equilibrium distances (R_e or R_{Ar}, in Å) for complexes **1**–**9**. R_e is the cation–π (**4**–**6**) or anion–π (**7**–**9**) equilibrium distance, and R_{Ar} the Ar/π bonding (**1**–**3**) equilibrium distance. B, H and T stand for benzene, hexafluorobenzene and *s*-triazine, respectively.

Compound	$E_{MP2\text{-}CP}$[a]	E_{CC}	$E_{CC\text{-}CP}$	E_{SAPT}	R_e or R_{Ar}
1 (B + Ar)	−0.94 (−0.90)	−1.45	−1.03	−1.06	3.595
2 (H + Ar)	−1.03 (−0.94)	−1.69	−0.98	−1.16	3.533
3 (T + Ar)	−0.87 (−0.83)	−1.42	−1.00	−0.97	3.506
4 (B + Na^+)	−22.26	−25.16	−23.83	−22.49	2.419
5 (H + Na^+)	−0.59	−2.19	−0.89	−2.47	2.757
6 (T + Na^+)	−4.92	−6.08	−5.08	−4.46	2.686
7 (B + Cl^-)	0.98	0.41	0.79	0.27	3.911
8 (H + Cl^-)	−13.70	−15.18	−14.12	−13.36	3.164
9 (T + Cl^-)	−6.67	−7.84	−7.12	−7.25	3.265

[a] Values in parenthesis are with the zero-point energy correction.

1–**9** (see Fig. 2) at the SCS-RI-MP2(full)/AwCTZ level of theory. First, let us start with the Van der Waals complexes. The interaction energies of the Ar/π complexes **1**–**3** are very small (ca. −1 kcal/mol) as expected. For instance, the benzene complex has an interaction energy of −0.94 kcal/mol at the SCS-MP2 level, quite close to the CCSD(T) value of −1.03 kcal/mol. Moreover, the zero-point energy corrected SCS-MP2 value (−0.90 kcal/mol) is in strong agreement with the experimental dissociation energy of −0.90 ± 0.02 kcal/mol [39]. Previous calculations [13,40] suggest that electron correlation beyond MP2 is needed in order to obtain quantitative binding energies for the weakly interacting system **1**. However, our calculations suggest otherwise, since the MP2 level of theory in conjunction with the SCS approximation and the counterpoise technique during the optimization yields excellent quantitative results with the AwCTZ basis set. In addition, our calculated equilibrium distance (3.595 Å) is also very close to the experimental one, which is 3.586 Å [41]. Furthermore, the optimized geometry of the parent benzene molecule is almost identical to the experimentally accurately determined structure [42]; the computed bond lengths are d(CC) = 1.392 Å and d(CH) = 1.081 Å whereas their corresponding experimental values are d(CC) = 1.391 Å and d(CH) = 1.080 Å. Experimental data on complexes **2** and **3** have not been reported in the literature. According to our SCS-MP2 results, the Ar complex **3** with triazine has the smallest interaction energy (−0.87 kcal/mol) and unexpectedly the shortest equilibrium distance (0.089 Å shorter than that of **1**). This interaction energy should be a better estimate than the previously reported at the MP2/aug-cc-pVDZ level (−1.07 kcal/mol) [43], since MP2 overestimates these weak interactions. The largest binding energy is obtained for the hexafluorobenzene complex **2** (−1.03 kcal/mol) with an equilibrium distance between those of complexes **1** and **3**. As far as we are concerned this is the first time that a computational study has been carried out for complex **3**. The SAPT results are in excellent agreement with the SCS-MP2 result. However, the BSSE corrected interaction energies at the CCSD(T) level suggest that the less favorable complex is the one with hexafluorobenzene, although all complexes can be considered almost isoenergetic. However, the uncorrected CCSD(T) interaction energies give the same trend observed for the SCS-MP2 and SAPT results.

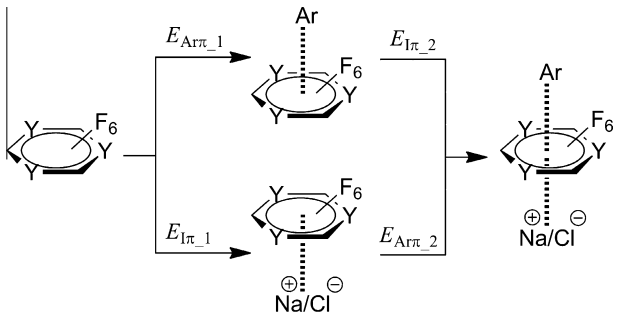

Fig. 2. Schematic representation of the two routes to form the ion–π–Ar complexes that allows computation of the $E_{Ar\pi\_2}/E_{Ar\pi\_1}$ and $E_{I\pi\_2}/E_{I\pi\_1}$ ratios.

Let us continue with the ion complexes, for which the SCS-MP2 results agree reasonably well with the CCSD(T) results (Table 1), starting with the cation–π interactions. The interaction energy of complex **6** is modest ($E_{CC\text{-}CP}$ = −5.08 kcal/mol) because the *s*-triazine ring is not electron-rich. In fact it has a very small and positive quadrupole moment and consequently the interaction with Na^+ is not electrostatically favored. However, since the quadrupole moment is very small (Q_{ZZ} = 0.8 B), the unfavorable electrostatic contribution to the interaction energy is compensated by the polarization term, as was previously demonstrated in compounds with *s*-triazine [44] and others with small quadrupole moments [45]. The same reasoning applies to the energetics of complex **5**. However, the very small interaction energy of this complex ($E_{CC\text{-}CP}$ = −0.89 kcal/mol) is due to the large and positive quadrupole moment of hexafluorobenzene (Q_{ZZ} = 8.1 B) that enhances the repulsive electrostatic contribution but without overcoming the attractive polarization term. It is worth mentioning that SAPT overestimates the binding energy for this complex with respect to SCS-MP2 and CCSD(T) results. The largest binding energy for this set of Na^+ complexes is observed for **4** ($E_{CC\text{-}CP}$ = −23.83 kcal/mol) since the benzene ring is electron-rich with a large and negative quadrupole moment (Q_{ZZ} = −8.0 B) and therefore a favorable electrostatic contribution [6,46].

The results for the anion–π complexes are collected in Table 1. As opposed to the results for complex **5**, the interaction energy for complex **8** is the largest and negative ($E_{CC\text{-}CP}$ = −14.12 kcal/mol) since the electrostatic contribution resulting from the interaction of an anion with the positive quadrupole moment of hexafluorobenzene is attractive. The interaction energy for complex **9** is modest and negative ($E_{CC\text{-}CP}$ = −7.12 kcal/mol) though larger than for **6** due to the attractive but very small electrostatic contribution. Complex **7** has a positive interaction energy of 0.79 kcal/mol as a consequence of the large and positive electrostatic contribution that overcomes the polarization term. Both SCS-MP2 and SAPT results are in good agreement with the CCSD(T) values.

3.2. Cooperativity in multicomponent cation–π, anion–π and Ar/π complexes

The geometric and energetic results computed for multicomponent complexes **10**–**15** (see Fig. 1) are summarized in Table 2. Some interesting points can be extracted from the geometrical results. The equilibrium distance R_e of the cation–π and anion–π interactions in Ar/π–Na+ complexes **10**–**12** and Ar/π–Cl^- complexes **13**–**15** is generally shorter than in their respective binary complexes **4**–**6** and **7**–**9**, respectively, i.e., the presence of the Ar/π interaction strengthens both the Na^+–π and Cl^-–π interactions. Moreover, the equilibrium distance of the Ar/π interaction R_{Ar} is also shorter compared to complexes **1**–**3**, that is, the presence of the cation–π and anion–π interactions also strengthens the Ar/π interaction. There are two exceptions, the complexes of either hexafluorobenzene or triazine with Cl^- **14** and **15** for which ΔR_{Ar} is positive and therefore the Ar/π binding is weakened.

Table 2 also lists the computed values of cooperativity energies E_{coop} (Eq. (1)), which are intended to provide an estimation of the "extra" energetic stabilization or destabilization obtained in multicomponent complexes as a consequence of the coexistence of both interactions. From the E_{coop} values listed in Table 2 several general

Table 2
Interaction energies with BSSE correction at the SCS-MP2(full)/AwCTZ level of theory ($E_{MP2\text{-}CP}$, in kcal/mol) and without and with BSSE correction at the CCSD(T)(full)/ACTZ level of theory (E_{CC} and $E_{CC\text{-}CP}$, respectively, in kcal/mol), cooperativity energies (E_{coop} in kcal/mol) and equilibrium distances (R_e and R_{Ar}, in Å) and their variation (ΔR_e and ΔR_{Ar}, in Å) for complexes **10**–**15**. R_e is the cation–π or anion–π equilibrium distance, and R_{Ar} the Ar/π bonding equilibrium distance. B, H and T stand for benzene, hexafluorobenzene and *s*-triazine, respectively.

Compound	$E_{MP2\text{-}CP}$	E_{CC}	$E_{CC\text{-}CP}$	$E_{coop\text{-}MP2}$	$E_{coop\text{-}CC}$[a]	R_{Ar}	R_e	ΔR_{Ar}	ΔR_e
10 (Ar + B + Na^+)	−24.73	−26.87	−25.05	−1.30	0.03 (−0.01)	3.525	2.418	−0.070	−0.001
11 (Ar + H + Na^+)	−2.19	–	–	−0.39	–	3.425	2.742	−0.108	−0.015
12 (Ar + T + Na^+)	−6.29	−8.12	−6.60	−0.29	−0.30 (−0.39)	3.396	2.673	−0.110	−0.013
13 (Ar + B + Cl^-)	−0.20	−1.34	−0.51	−0.15	−0.17 (−0.20)	3.591	3.871	−0.004	−0.040
14 (Ar + H + Cl^-)	−14.71	–	–	0.16	–	3.558	3.164	0.025	0.000
15 (Ar + T + Cl^-)	−7.65	−9.40	−8.25	0.04	0.02 (0.01)	3.538	3.262	0.032	−0.003

[a] Values in parenthesis are not BSSE corrected.

conclusions can be extracted. First, the computed values of $E_{coop\text{-}MP2}$ are negative in cation–π complexes, and thus indicating a positive synergy between the interactions, in agreement with the shortening of the equilibrium distances (see ΔR values of Table 2). Second, in absolute terms the computed $E_{coop\text{-}MP2}$ values are small for complexes **11** and **12** because the Na^+–π interaction is weak. Nevertheless, synergetic effects between the two interactions contribute 18% and 5%, respectively, of the total interaction energy of the complexes. The $E_{coop\text{-}MP2}$ value for complex **10** is modest due to the strong Na^+–benzene interaction, though it only contributes to a 5% of the total interaction energy. The $E_{coop\text{-}CC}$ and the $E_{coop\text{-}MP2}$ values are comparable with the exception of **10**. For this complex the $E_{coop\text{-}CC}$ value is very small but positive (0.03 kcal/mol) suggesting a weakening of the interactions, in disagreement with the shortening of the equilibrium distances. However if we do not consider the BSSE correction, the $E_{coop\text{-}CC}$ value becomes negative but very small (−0.01 kcal/mol), in agreement with the ΔR values.

For the anion–π complexes we observe different behaviors. The E_{coop} values for complex **13** are small and negative but very significant in any case since these positive synergetic effects correspond to a 75% and 33% of the MP2 and CCSD(T) total interaction energies, respectively. Therefore, there are strong cooperativity effects between the Cl^-–benzene and the Ar/benzene interactions, most likely due to a strengthening of the anion–π interaction. This fact is also reflected in the shortening of the equilibrium distances. However, Cl^-–π complexes **14** and **15** show very small (especially **15**) but positive E_{coop} values, regardless of the level of theory, thus indicating a negative synergy between the interactions, in accordance with the elongation of the equilibrium distances *R*.

3.3. Mutual influence between ion–π and Ar/π interactions

In an attempt to evaluate not only the effect of Ar/π bonding on the ion–π interaction and vice versa but also which of the two interactions is more reinforced, we computed the binding energy of the multicomponent complexes using two different approaches (see Fig. 2). First, we computed the binding energies (with BSSE correction) of the Na^+–π/Ar and Cl^-–π/Ar complexes (see Table 3), considering that the Ar/π complex has been previously formed and evaluating the interaction with the ion as a two-component system (e.g., **1** + Na^+ → **10**), denoted $E_{I\pi\_2}$. Second, we computed the binding energies (with BSSE correction) of multicomponent complexes Na^+–π/Ar and Cl^-–π/Ar (see Table 4), considering that the ion–π complex has been previously formed and evaluating its interaction with the Ar atom (e.g., **4** + Ar → **10**), denoted $E_{Ar\pi\_2}$. Finally, we compared the quantities $E_{I\pi\_2}$ and $E_{Ar\pi\_2}$ with the $E_{I\pi\_1}$ and $E_{Ar\pi\_1}$ binding energies, which correspond to the binding energies of complexes **1**–**9** (see Table 1), by using the ratios $E_{I\pi\_2}/E_{I\pi\_1}$ and $E_{Ar\pi\_2}/E_{Ar\pi\_1}$. These simple ratios give very interesting and useful information: (1) values of $E_{I\pi\_2}/E_{I\pi\_1} > 1$ mean that the ion–π interactions is reinforced in the ion–π/Ar complex, and vice versa for $E_{I\pi\_2}/E_{I\pi\_1} < 1$; (2) values of $E_{Ar\pi\_2}/E_{Ar\pi\_1} > 1$ mean that the Ar/π binding is reinforced in the ion–π/Ar complex, and vice versa if $E_{Ar\pi\_2}/E_{Ar\pi\_1} < 1$. Therefore, these ratios are informative regarding the mutual influence of the two interactions in the ion–π/Ar complexes. If both ratios are greater than unity, favorable synergetic effects between the two interactions are present in the complex. If one ratio is greater than unity and the other lesser than unity, this would mean that one noncovalent interaction is reinforced at the expense of the other. More significantly, for a given complex $E_{I\pi\_2}/E_{I\pi\_1} > E_{Ar\pi\_2}/E_{Ar\pi\_1}$ would mean that the ion–π interaction is more reinforced than the Ar/π interaction in the ion–π/Ar complex, and the contrary applies if $E_{I\pi\_2}/E_{I\pi\_1} < E_{Ar\pi\_2}/E_{Ar\pi\_1}$. If the two ratios are equal, the reinforcement of both interactions is the same.

The values of $E_{I\pi\_2}$ and $E_{I\pi\_2}/E_{I\pi\_1}$ computed for sodium and chloride multicomponent complexes are summarized in Table 3. For all levels of theory, the ratios are greater than unity in all complexes apart from **14**, in agreement with the previously discussed energetic and geometric ΔR_e results. Therefore, both the cation– and anion–π interactions are strengthened with respect to their binary counterparts when the aromatic ring is interacting with Ar on the other side of the π system. For complex **14** the ratio is one, meaning that there is neither strengthening nor weakening of the Cl^-–π interaction.

The values of $E_{Ar\pi\_2}$ and $E_{Ar\pi\_2}/E_{Ar\pi\_1}$ computed for Ar multicomponent complexes are gathered in Table 4. For all levels of theory, the computed ratios for complexes **10–13** are greater than one, in agreement with the previously discussed E_{coop} and ΔR_{Ar} results, which is indicative of a reinforcement of the Ar/π interaction

Table 3
$E_{I\pi\_2}$ and $E_{I\pi\_2}/E_{I\pi\_1}$ values computed for several complexes at the SCS-MP2(full)/AwCTZ, CCSD(T)/ACTZ and SAPT levels of theory. The $E_{I\pi\_1}$ values are taken from Table 1. Energies are given in kcal/mol.

Compound	Reaction	$E_{I\pi\_2}$			$E_{I\pi\_2}/E_{I\pi\_1}$		
		MP2	CC	SAPT	MP2	CC	SAPT
10	1 + Na^+	−23.79	−24.05	−22.67	1.07	1.01	1.01
11	2 + Na^+	−1.17	–	−3.02	2.00	–	1.22
12	3 + Na^+	−5.42	−5.64	−4.98	1.10	1.11	1.12
13	1 + Cl^-	0.74	0.51	−0.03	1.33	1.55	−0.11
14	2 + Cl^-	−13.68	–	−13.38	1.00	–	1.00
15	3 + Cl^-	−6.77	−7.23	−7.36	1.02	1.02	1.02

Table 4
$E_{Ar\pi\_2}$ and $E_{Ar\pi\_2}/E_{Ar\pi\_1}$ values computed for several complexes at the SCS-MP2(full)/AwCTZ, CCSD(T)/ACTZ and SAPT levels of theory. The $E_{Ar\pi\_1}$ values are taken from Table 1. Energies are given in kcal/mol.

Compound	Reaction	$E_{Ar\pi\_2}$			$E_{Ar\pi\_2}/E_{Ar\pi\_1}$		
		MP2	CC	SAPT	MP2	CC	SAPT
10	4 + Ar	−2.47	−1.22	−1.20	2.62	1.19	1.13
11	5 + Ar	−1.61	–	−1.66	1.57	–	1.43
12	6 + Ar	−1.38	−1.53	−1.43	1.58	1.52	1.47
13	7 + Ar	−1.18	−1.31	−1.36	1.26	1.28	1.28
14	8 + Ar	−1.01	–	−1.18	0.98	–	1.02
15	9 + Ar	−0.98	−1.12	−1.13	1.12	1.12	1.16

when the aromatic ring is ion–π interacting on the other side of the π system. The ratios for complex **15** are also greater than one, in disagreement with E_{coop} and ΔR_{Ar} values. There is some slight discrepancy between the SCS-MP2 and SAPT ratios in complex **14**. The former and latter ratios are lesser and greater than one, respectively, with the SCS-MP2 values in accordance with the E_{coop} and ΔR_{Ar} values, meaning that the Ar/π interaction is weakened in relation to complex **2**.

If we compare ratios for different interactions we notice that $E_{Ar\pi\_2}/E_{Ar\pi\_1}$ is greater than $E_{l\pi\_2}/E_{l\pi\_1}$ for complexes **10**, **12** and **15**, that is, the Ar/π interaction is more enhanced than the ion–π interaction. In contrast, for complexes **11** y **13** the $E_{l\pi\_2}/E_{l\pi\_1}$ is greater than $E_{Ar\pi\_2}/E_{Ar\pi\_1}$, implying that the ion–π interaction is more reinforced than the Ar/π interaction. For the remaining complex **14**, the ratios are more or less equivalent, with equal strengthening of both interactions. These interesting results allow us to learn which interaction in the multicomponent system is more reinforced. This information cannot be obtained from the cooperativity energies E_{coop}.

3.4. SAPT energetic partition scheme

The SAPT partition energy scheme has been used to analyze the physical nature of the Van der Waals and ion–π interactions in complexes **1**–**3** and **4**–**9**, respectively, and to understand the bonding mechanism and the cooperativity effects in the ternary complexes **10**–**15**. The SAPT results are summarized in Table 5. As expected the dispersion term is the main contribution in the Ar/π complexes **1**–**3**. For the cation–π complexes **4**–**6**, the main contribution comes from the induction term and in the case of benzene, with a large and negative quadrupole moment, the electrostatic contribution is also very important. For the anion–π complexes **7**–**9**, depending on the aromatic system, the most important contribution comes from induction (complex **7**) or electrostatic (complexes **8** and **9**) effects.

In an attempt to analyze the nature of the synergistic effects in complexes **10**–**15**, we computed the SAPT of these multicomponent complexes using the approaches described in Section 3.3 (see Fig. 2). First, we computed the SAPT of **10**–**15** considering that the ion–π complex has been previously formed and analyzing the interaction with Ar as a two-component system (e.g., **4** + Ar → **10**). Second, we computed the SAPT of **10**–**15** considering that the Ar/π complex has been previously formed and analyzing its interaction with the ion (e.g., **1** + Na^+ → **10**).

Let us first analyze the Ar/π interaction. For complexes **10**–**15** the major contribution to the Ar/π binding is the dispersion. However, the observed synergistic effects of the ionic complexes have their origin in a remarkable enhancement of the induction term. For instance, for complex **3** the induction contribution amounts −0.03 kcal/mol whereas the induction term is −0.52 kcal/mol for complex **12**. The only exception for which synergistic effects are observed is complex **15**, that come from an enhancement of the electrostatic term that varies from −0.40 kcal/mol in **3** to −0.54 kcal/mol in **15**.

Let us continue with the analysis of the ion–π interaction. The induction term is the main contribution for the cation–π interaction in complexes **10**–**12**. Moreover, the synergistic effects found by analyzing the energetic and geometric criteria (Tables 2 and 3) are due to an enhancement of the induction component. For instance this contribution varies from −9.78 kcal/mol in **6** to −10.27 kcal/mol in **12**. For the anionic complexes a different behavior is obtained. Thus, the major contribution to the anion–π interaction in the benzene complex **13** is induction whereas electrostatics is the most important contribution for the hexafluorobenzene and triazine complexes **14** and **15**, respectively. However, the cooperativity effects observed for complexes **13** and **15** originate from an enhancement of the induction component.

Table 5
SAPT interaction energies and their partitioning into the electrostatic, induction, dispersion and exchange contributions (E_{SAPT}, E_{ee}, E_{ind}, E_{disp}, E_{exch}, respectively, in kcal/mol) and the Hartree–Fock correction for higher-order contributions δ(HF) for complexes **1**–**15** at the RI-BP86/ACTZ level of theory using the DF–DFT–SAPT approach.

Compound	E_{SAPT}	E_{ee}	E_{ind}	E_{disp}	E_{exch}	δ(HF)
1	−1.06	−0.48	−0.03	−1.89	1.42	−0.08
2	−1.16	−0.51	−0.04	−2.04	1.50	−0.07
3	−0.97	−0.40	−0.03	−1.80	1.31	−0.05
4	−22.49	−13.86	−15.64	−1.58	8.16	0.43
5	−2.47	7.32	−11.29	−0.85	2.60	−0.25
6	−4.46	−4.06	−9.78	−0.83	2.22	−0.14
7	0.27	3.05	−3.19	−2.69	2.97	0.12
8	−13.36	−17.01	−5.73	−7.14	16.81	−0.29
9	−7.25	−9.36	−4.21	−5.42	11.92	−0.18
10 (4 + Ar)	−1.20	−0.43	−0.21	−1.95	1.45	−0.07
10 (1 + Na^+)	−22.67	−13.69	−16.01	−1.59	8.20	0.43
11 (5 + Ar)	−1.66	−0.56	−0.55	−2.30	1.84	−0.09
11 (2 + Na^+)	−3.02	7.13	−11.78	−0.88	2.75	−0.24
12 (6 + Ar)	−1.43	−0.46	−0.55	−2.05	1.69	−0.06
12 (3 + Na^+)	−4.98	3.93	−10.27	−0.85	2.34	−0.14
13 (7 + Ar)	−1.36	−0.65	−0.30	−2.03	1.72	−0.10
13 (1 + Cl^-)	−0.03	2.86	−3.42	−2.85	3.25	0.13
14 (8 + Ar)	−1.18	−0.70	−0.07	−2.04	1.71	−0.08
14 (2 + Cl^-)	−13.38	−16.86	−5.91	−7.17	16.86	−0.30
15 (9 + Ar)	−1.13	−0.53	−0.12	−1.86	1.45	−0.06
15 (3 + Cl^-)	−7.36	−9.32	−4.42	−5.46	12.02	−0.19

4. Conclusions

The results reported stress the importance of the mutual effects between noncovalent interactions involving aromatic systems, namely, cation–π, anion–π and Ar/π bonding, which can lead to strong cooperativity effects. These effects are maintained even when the electrostatic nature of the aromatic system is changed. We estimated the cooperativity effects energetically (E_{coop} values), obtaining results that are in agreement with the geometric features of the complexes. Consequently, the aromatic ring is able to transmit the synergetic effect from the ion (ion–π interaction) through the conjugated π–system to the Ar atom (Van der Waals interactions) and vice versa. We have proposed utilization of two parameters, that is, $E_{l\pi\_2}/E_{l\pi\_1}$ and $E_{Ar\pi\_2}/E_{Ar\pi\_1}$, which are easy to calculate and give useful information regarding, on one hand, the presence of cooperativity and, on the other hand, which noncovalent interaction is more reinforced when they coexist in the same complex. In addition, by means of SAPT calculations we have studied the physical nature of the synergetic effect, which is mainly due to an enhancement of the induction term for the ion–π/Ar complexes. An exception is the Van der Waals interaction with Cl^-–triazine where the synergetic effects come from enhancing the electrostatic term. Finally our computational results at the SCS-RI-MP2/aug-cc-pwCVTZ level of theory for the benzene/Ar complex (D_0 = −0.90 kcal/mol and R_e = 3.595 Å) are in an excellent quantitative agreement with the experimental dissociation energy (−0.90 ± 0.02 kcal/mol) and equilibrium distance (3.586 Å).

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