MP2 study of cooperative effects between cation–π, anion–π and π–π interactions†

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Received (in Montpellier, France) 5th September 2006, Accepted 24th January 2007
First published as an Advance Article on the web 26th February 2007
DOI: 10.1039/b612848c

In this manuscript we report high level *ab initio* calculations (RI-MP2(full)/6-31++G**) and experimental evidence that demonstrate that important non-additivity effects between three noteworthy non-covalent interactions that involve aromatic rings (benzene and hexafluorobenzene), *i.e.* cation–π, anion–π and π–π interactions, occur when the interactions coexist in the same complex. In some cases we have observed very high non-additivity energies (up to -20.3 kcal mol^{-1}) that indicate that the cation–π and/or the anion–π have a strong influence on the π–π interaction and *vice versa*.

Introduction

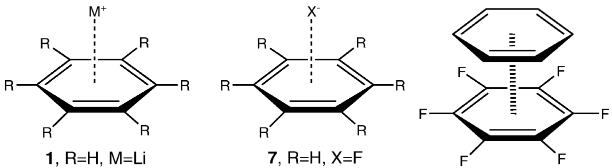
Non-covalent interactions play a key role in many areas of modern chemistry, especially in the field of supramolecular chemistry and molecular recognition.[1] In particular, interactions involving aromatic rings are key processes in both chemical and biological recognition and they have been recently reviewed by Meyer *et al.*[2] For instance, cation–π interactions[3] are supposed to be an important factor in ion selectivity in potassium channels,[4] they are also important for the binding of acetylcholine to the active site of the enzyme acetylcholine esterase,[5] and, recently, their importance has been demonstrated in neurotransmitter receptors.[6] In addition, attractive interactions between π systems are very important forces that govern molecular recognition and influence structures of proteins, DNA and solid materials. Anion–π interactions[7] are also important non-covalent forces that have attracted considerable attention in the last three years. Recently, anion–π complexes have been observed experimentally, supporting the theoretical predictions and the promising proposal for the use of anion receptors based on anion–π interactions in molecular recognition.[8] Lastly, π–π interactions[9] are weak non-covalent forces that play an essential role in the folding of proteins,[10] and in the structure of DNA as well as in its interactions with small molecules.[11] They are widely used in supramolecular chemistry and are very important binding forces that determine the packing of organic molecules in crystals. They are also used in crystal engineering for the design of functional materials.[12]

The cation–π and anion–π interactions are dominated by electrostatic and ion-induced polarization terms.[13] The nature of the electrostatic term can be rationalized by means of the permanent quadrupole moment of the arene. The favorable face-to-face interaction of the benzene–hexafluorobenzene complex has been explained emphasizing the important role of the large and opposite permanent quadrupole moments of the two molecules.[14] The π–π interaction in the benzene dimer is governed by dispersion effects.[15]

In this manuscript, we study how the π–π interaction influences the cation–π and anion–π interactions. We have optimized the complexes present in Fig. 1–3 and computed their interaction energies. We have first computed the 1 : 1 complexes present in Fig. 1 and, subsequently, we have computed the ternary 1 : 1 : 1 cation–π–π and anion–π–π complexes present in Fig. 2, in order to study the interplay between the π–π and both the cation–π and anion–π interactions separately, and how they influence each other. Finally, we have computed the quaternary 1 : 1 : 1 : 1 cation–π–π–anion complexes where we study the interplay between all interactions. We have found that both the cation–π and the anion–π interactions have a strong influence upon the π–π interaction and *vice versa*.

Theoretical methods

The geometries of all complexes studied in this work were fully optimized using the resolution of the identity MP2 (RI-MP2) level and the 6-31++G** basis set. The RI-MP2 calculations were done using the program TURBOMOLE version 5.7.[16] The RI-MP2 method[17] applied to the study of cation–π,



1, R=H, M=Li
2, R=H, M=Na
3, R=H, M=K
4, R=F, M=Li
5, R=F, M=Na
6, R=F, M=K

7, R=H, X=F
8, R=H, X=Cl
9, R=H, X=Br
10, R=F, X=F
11, R=F, X=Cl
12, R=F, X=Br

13

Fig. 1 Cation–π, anion–π and π–π complexes **1–13**.

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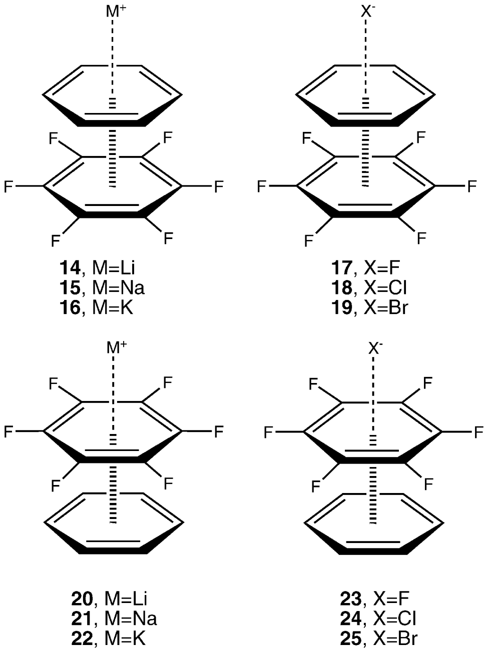
† The HTML version of this article has been enhanced with colour images.



14, M=Li
15, M=Na
16, M=K

17, X=F
18, X=Cl
19, X=Br

20, M=Li
21, M=Na
22, M=K

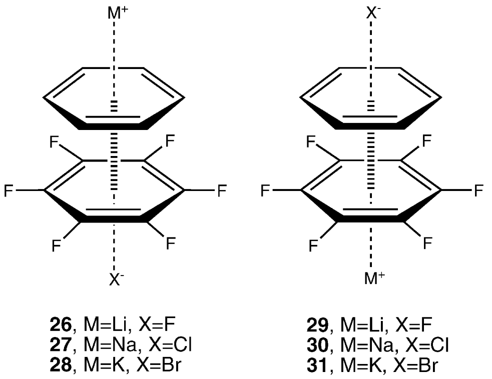
23, X=F
24, X=Cl
25, X=Br

Fig. 2 Ternary cation–π–π and anion–π–π complexes **14–25**.

anion–π and π–π interactions is considerably faster than the MP2 and the interaction energies and equilibrium distances are almost identical for both methods.[18] The binding energies were calculated with correction for the basis set superposition error (BSSE) by using the counterpoise technique.[19] The optimization of the complexes has been performed imposing C_{6v} symmetry. As discussed below, some representative ternary and quaternary complexes have been optimized without symmetry constraints.

Results and discussion

In Table 1, we summarize the binding energies and equilibrium distances obtained for complexes **1–13**. As expected, the cation–π complexes of benzene (BEN) **1–3** give large and negative binding energies and the cation–π complexes of hexafluorobenzene (HFB) **4–6** give small binding energies. Similarly, the anion–π complexes of HFB have favorable binding energies and the anion–π complexes of BEN have small and positive binding energies. This is due to a compensating effect between the electrostatic and polarization terms which are similar in magnitude but of opposite sign in complexes **4–9**.



26, M=Li, X=F
27, M=Na, X=Cl
28, M=K, X=Br

29, M=Li, X=F
30, M=Na, X=Cl
31, M=K, X=Br

Fig. 3 Quaternary cation–π–π–anion complexes **26–31**.

In order to analyze the influence of the anion–π and cation–π interactions on the π–π interaction we have computed complexes **14–25** (see Fig. 2) and the energetic and geometric results are present in Table 2. From the inspection of the results, several interesting issues arise. First, for all complexes the binding energies are negative, regardless of whether the cation is interacting with the electron poor or the electron rich aromatic ring. Second, we have included in the table what we entitle genuine non-additivity energies ($E - E_A$), which is the difference between the binding energy of the ternary 1 : 1 : 1 complex and the binding energy of the sum of all pair interaction energies (denoted as E_A). For instance, in complex **14** (HFB···BEN···Li$^+$) we have computed the non-additivity energy by subtracting the sum of three pair interaction energies: (i) BEN···Li$^+$, (ii) HFB···Li$^+$ and (iii) HFB···BEN from the binding energy of **14**. This value gives valuable information regarding the interplay between all the non-covalent interactions present in the ternary complexes. It is worth mentioning that this term is negative in the complexes where either the cation interacts with HFB or the anion with BEN (complexes **17–22**). In these cases, the HFB···BEN distance shortens indicating that the π–π interaction strengthens; and the same effect is observed in the ion to ring centroid distances, compared to the respective 1 : 1 complexes, indicating that the ion–π interaction is also reinforced. In contrast, in the complexes where the cation interacts with BEN and the anion with HFB the genuine non-additivity term is slightly positive or negligible. These results indicate that either the ion–π interaction has an important influence upon the π–π interaction or *vice versa* in the complexes where either the cation interacts with HFB or the anion with BEN. In these cases the interplay between the interactions contributes to the global stabilization of the system of 2.5–4.5 kcal mol^{-1} (complexes **17–22**).

In Fig. 3 we depict the quaternary cation–π–π–anion complexes **26–31**. These complexes allow us to study the interplay between the three non-covalent interactions simultaneously. The energetic and geometric results are summarized in

Table 1 Interaction energies without (E) and with (E_{CP}) the BSSE correction and equilibrium distances (R_e) computed at the RI-MP2/6-31++G** level of theory for **1–13**

Compound	E/kcal mol^{-1}	E_{CP}/kcal mol^{-1}	R_e/Å
1 (BEN···Li$^+$)	−38.5	−33.7	1.91
2 (BEN···Na$^+$)	−26.1	−21.4	2.39
3 (BEN···K$^+$)	−18.0	−14.9	2.90
4 (HFB···Li$^+$)	−5.0	−1.3	2.19
5 (HFB ···Na$^+$)	0.1	3.5	2.65
6 (HFB ···K$^+$)	1.1	3.4	3.40
7 (BEN···F$^-$)	0.8	2.8	3.16
8 (BEN···Cl$^-$)	0.0	2.4	3.73
9 (BEN···Br$^-$)	−0.6	1.9	3.84
10 (HFB··· F$^-$)	−21.9	−18.8	2.57
11 (HFB ···Cl$^-$)	−18.4	−13.1	3.15
12 (HFB ···Br$^-$)	−17.7	−12.7	3.28
13 (BEN···HFB)	−11.1	−5.2	3.39

Table 2 Interaction (E_{CP}) energies with the BSSE correction, non-additivity energies ($E - E_A$) and equilibrium distances (R_e and R_s) computed at the RI-MP2/6-31++G** level of theory for complexes **14–25**

Compound	E_{CP}/kcal mol^{-1}	$E - E_A$/kcal mol^{-1}	R_s^{a}/Å	R_e/Å
14	−35.5	0.3	3.37	1.90
15	−23.0	0.0	3.39	2.39
16	−17.6	−0.3	3.38	2.91
17	−6.5	−2.6	3.35	3.00
18	−6.0	−2.6	3.36	3.59
19	−6.2	−2.5	3.36	3.59
20	−12.2	−4.5	3.25	2.10
21	−6.1	−3.9	3.27	2.57
22	−4.9	−2.9	3.31	3.16
23	−21.8	0.5	3.48	2.59
24	−16.3	0.2	3.46	3.16
25	−16.1	0.4	3.44	3.31

[a] R_s stands for the BEN$\cdots$HFB distance.

Table 3. In all cases the binding energy is large and negative indicating that the formation of these complexes is highly favoured. In addition the genuine non-additivity energies, computed similarly to the ones present in Table 2, indicate important cooperativity effects between the interactions. For instance, in the quaternary complex **26** (F$^-\cdots$HFB$\cdots$BEN$\cdots$Li$^+$) the additivity energy (E_A) has been calculated as the sum of six pair interaction energies: (i) BEN$\cdots$Li$^+$, (ii) HFB$\cdots$Li$^+$, (iii) HFB$\cdots$F$^-$, (iv) BEN$\cdots$F$^-$, (v) HFB$\cdots$BEN and (vi) F$^-\cdots$Li$^+$ at the geometry of the complex. Complex **26** has a non-additivity term ($E - E_A$) of −10.9 kcal mol^{-1}, indicating that the simultaneous formation of cation–π, π–π and anion–π contacts implies significant cooperativity effects between the three non-covalent interactions. The equilibrium distances that characterize the non-covalent interactions are considerably shorter than the ones of the related binary complexes. In complex **26**, the distance of the π–π interaction shortens from 3.39 to 3.21 Å, the cation–π from 1.91 to 1.83 Å and the anion–π from 2.57 to 2.44 Å, in agreement with the non-additivity term. The most important cooperativity effect is found in complex **29** (Li$^+\cdots$HFB$\cdots$BEN$\cdots$F$^-$) where the shortest distance for the π–π interaction is observed, that is 3.12 Å, and the Li$^+\cdots$HFB distance in **29** is similar to the observed for the 1 : 1 complex **1** (BEN$\cdots$Li$^+$), indicating that the cation–π interaction between the lithium cation and the electron deficient HFB ring in **29** is comparable to that in **1** between Li$^+$ and BEN. These results demonstrate that both the cation–π and the anion–π interactions have a strong influence on the π–π interaction and these cooperativity effects can be important in supramolecular and biological systems where the effect of the counterion is often forgotten. On the other hand, it is well known that ion-induced polarization effects[13] are very important in ion–π interactions and they are likely playing an important function in the quaternary complexes. In Scheme 1 we represent the dipole moments that the ions induce by means of polarizing the π-cloud of the aromatic rings. In the quaternary complexes a favourable dipole–dipole interaction is generated that strengthens the π–π interaction (the representation is only qualitative; obviously the magnitude of the ion-induced dipole is lower in HFB than in BEN).

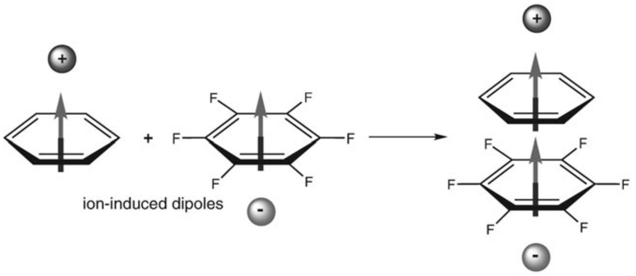
As mentioned above, the optimization of the complexes has been performed imposing C_{6v} symmetry to minimize the computational cost. Since the aim of this study is to verify the synergic behaviour between cation–π, anion–π and π–π non-covalent interactions rather than locate the genuine minimum energy structures, the use of symmetry is justified. However, in three representative complexes, we have performed the optimization without symmetry constraints in order to locate the minimum energy structures and compare them with the ones computed imposing the C_{6v} symmetry constraint. The fully optimized structures of **18**, **21** and **27** as examples of anion–π–π, cation–π–π and cation–π–π–anion complexes, respectively, are shown in Fig. 4. Geometrically, the results indicate that the BEN$\cdots$HFB stacking interaction in the ternary complexes **18** and **21** changes with respect to the symmetric complexes. The parallel face-to-face stacking is, to a minor extent, lost and the distance between the ring planes shortens. In contrast, the geometry of the quaternary complex **27** is maintained, the face-to-face stacking is preserved and the equilibrium distances are almost identical with and without the symmetry constraint (see Fig. 4, the values in parentheses correspond to the C_{6v} symmetric complexes). Energetically, the results of the interaction energies give reliability to the calculations imposing C_{6v} symmetry, since the values of E_{CP} are very similar for the symmetric and non-symmetric complexes.

The theoretical results reported in this manuscript can be used to explain an unexpected experimental finding regarding the face-to-face stacking of pentafluorophenyl groups in substituted ferrocenes. In Fig. 5 we show the three ferrocene derivatives studied by Blanchard *et al.*[20] in the conformation observed in their crystal structures. The conformation adopted in the crystal of the substituted ferrocenes **A** and **B** can be explained intuitively, while the conformation of **C** is counter-intuitive, as stated by the authors. We also show in Fig. 5 a fragment of the crystal structure of **C** where the unexpected face-to-face π-stacking of two pentafluorophenyl groups is observed. As noticed by the authors, the cyclopentadienyl ring of a neighbour molecule is forming an intermolecular stacking with the pentafluorophenyl ring. The distance between the ring planes of both molecules is 3.35 Å and between the cyclopentadienyl ring centroid and the pentafluorophenyl centroid is 3.61 Å. In order to give an explanation to this unexpected face-to-face stacking of the pentafluorophenyl groups we have performed additional computations on anion–π–π and

Table 3 Interaction (E_{CP}) energies with the BSSE correction, non-additivity energies ($E - E_A$) and equilibrium distances (R_e and R_s) computed at the RI-MP2/6-31++G** level of theory for complexes **26–31**

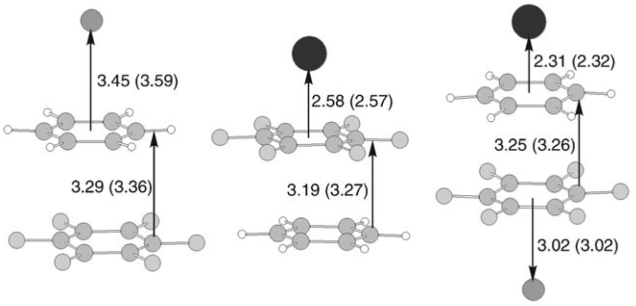
Compound	E_{CP}/ kcal mol^{-1}	$E - E_A$/ kcal mol^{-1}	R_s/Å	R_e (M$^+$/X$^-$)^a/Å
26	−102.7	−10.9	3.21	1.83/2.44
27	−78.3	−8.6	3.26	2.32/3.02
28	−68.4	−7.3	3.27	2.81/3.27
29	−63.1	−20.3	3.12	1.99/2.59
30	−48.3	−16.9	3.15	2.45/3.16
31	−43.5	−13.1	3.18	2.94/3.36

[a] The cation/anion-ring centroid distances are given.



Scheme 1 Schematic representation of the ion-induced dipoles and their favorable interaction in the quaternary complex.

anion–π–π-cation complexes where both π-systems are HFB rings (see Fig. 6). The binding energies are summarized in Table 4, where the binding energy of the hexafluorobenzene dimer has been also included. The computed binding and non-additivity energies of the ternary complexes **32–34** are negative and the equilibrium distances are shorter than in the related 1 : 1 complexes indicating that cooperativity effects are also found between anion–π and π–π interactions when both π-systems are HFB. The highest non-additivity energies correspond to the quaternary complexes **35–37**, where the π–π interaction is clearly reinforced as deduced by its very short equilibrium distance. These results are useful to explain the behaviour of structure **C** of Fig. 5. The presence of the cyclopentadienyl anion interacting with a pentafluorophenyl group induces the face-to-face stacking interaction with the other pentafluorophenyl unit. Similar behaviour is observed in related ferrocene compounds which have been extensively studied by Deck *et al.*[21] Although it was either not discussed or not noticed by the authors, an important number of structures with face-to-face stacking interactions between pentafluorophenyl groups are present, and in all cases a cyclopentadienyl anion interacts with the pentafluorophenyl group. Lastly, a very elegant work recently reported by Dunbar *et al.*[22] has given experimental evidence of the interplay between anion–π and π–π interactions in π-acidic rings, in particular between *s*-tetrazine rings and anions. This interplay may influence self-assembly reactions.



18 E_{CP}=-5.8 (-6.0)

21 E_{CP}=-6.5 (-6.1)

27 E_{CP}=-78.5 (-78.3)

Fig. 4 RI-MP2/6-31++G** optimized structures of complexes **18**, **21** and **27**. Energies are in kcal mol^{-1} and distances are in Å. The results imposing C_{6v} symmetry are shown in parentheses.

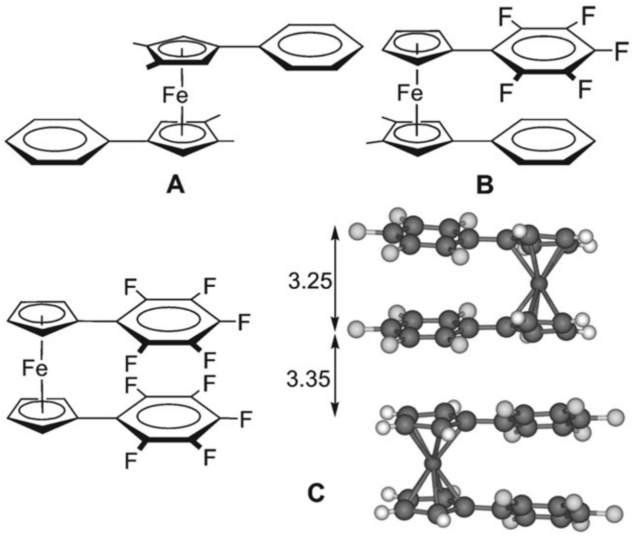
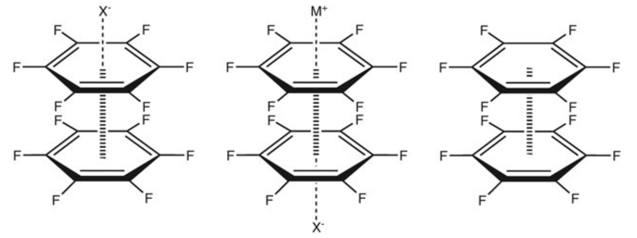


Fig. 5 Substituted ferrocene compounds **A**–**C** and the X-ray packing of **C**, distances in Å.



32, X=F
33, X=Cl
34, X=Br

35, M=Li, X=F
36, M=Na, X=Cl
37, M=K, X=Br

38

Fig. 6 Ternary anion–π–π and quaternary cation–π–π–anion complexes **32–37**, and HFB dimer.

Table 4 Interaction (E_{CP}) energies with the BSSE correction, non-additivity energies ($E - E_A$) and equilibrium distances (R_e and R_s) computed at the RI-MP2/6-31++G** level of theory for complexes **32–38**

Compound	E_{CP}/ kcal mol^{-1}	$E - E_A$/ kcal mol^{-1}	R_s/Å	R_e $(M^+/X^-)^a$/Å
32	−24.4	−0.8	3.40	2.53
33	−17.4	−1.5	3.38	3.08
34	−17.1	−1.0	3.39	3.24
35	−73.0	−14.5	3.19	2.00/2.39
36	−54.7	−12.2	3.22	2.47/2.96
37	−50.4	−9.1	3.25	2.99/3.13
38	−1.7	—	3.41	—

[a] The cation- and anion-ring centroid distances are given.

Conclusions

In summary, the results reported in this manuscript stress the importance of non-covalent interactions involving aromatic systems and the interplay among them, which can lead to strong cooperativity effects. Taking into account that a great deal of medicinal agents contain aromatic groups and their recognition by proteins is likely dominated by aromatic–aromatic interactions, these synergic effects might be of pivotal importance in many areas of biological chemistry.

Acknowledgements

We thank the DGICYT of Spain (projects CTQ2005-08989-01 and CTQ2005-08989-02) for financial support. We thank the Centre de Supercomputació de Catalunya (CESCA) for computational facilities. A. F. and D. Q. thank the MEC for "Ramón y Cajal" and "Juan de la Cierva" contracts, respectively.

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